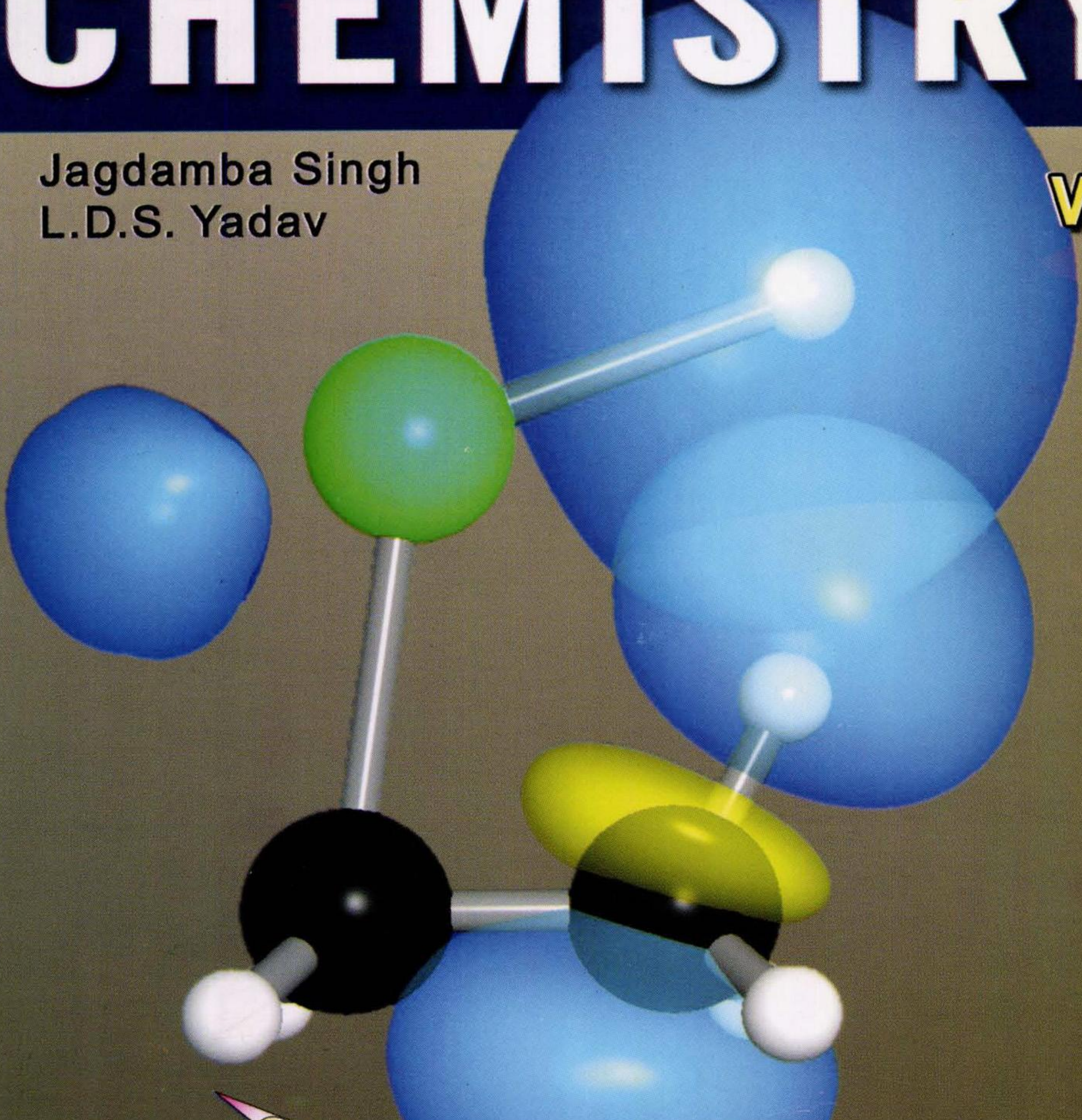
UNDERGRADUATE

ORGANIC CHEMISTRY

Jagdamba Singh
L.D.S. Yadav

VOL - I



A Pragati Edition

Pragati's

UNDER GRADUATE

ORGANIC CHEMISTRY

Vol. I

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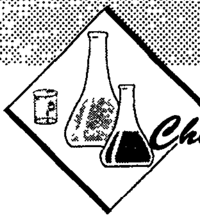


Chapter 1

STRUCTURE AND BONDING

Organic chemistry is the chemistry of carbon compounds. This definition includes compounds like CO, CO_2, CS_2, carbonates, cyanates, cyanides, etc. but they are usually described in textbooks of inorganic chemistry due to their greater resemblance with inorganic compounds. Organic chemistry is a very systematic subject which is based on the structures of molecules and their reactivity. The presence of covalent bonds is the characteristic of organic (carbon) compounds. This implies that most of the organic compounds are covalent compounds. Thus, the covalent bond is of chief importance in the study of organic chemistry.

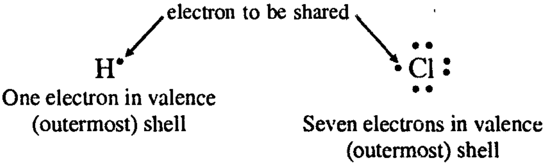
1.1 LOCALIZED CHEMICAL BONDING

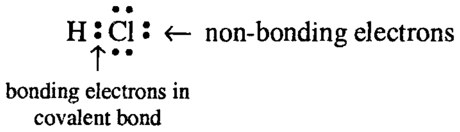
Localized chemical bonding may be defined as bonding in which the electrons are shared by two and only two nuclei.

1.1.1 Covalent Bonding

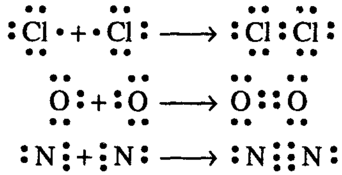
The Electronic Theory : It was based on the electronic structure of atoms. In 1916, G.N. Lewis (of the University of California) was the first to suggest that chemical combination of atoms can take place through covalent bond formation. A covalent bond is formed by sharing of electrons, each atom contributing one or more electrons to form the shared pair or pairs. In this way, each of the bonded atoms attains the stable electronic configuration of the nearest noble gas. The two bonded atoms are held together by shared pair or pairs of electrons, *i.e.*, *covalent bond(s)*. The covalent bond formed by sharing of one electron pair is called a single bond (as in hydrogen and chlorine molecules), whereas that formed by sharing of two electron pairs (as in oxygen molecule) and three electron pairs (as in nitrogen molecule) are called double and triple bonds, respectively. Double and triple bonds are collectively called multiple bonds.

The structures in which the shared electron pair(s) as well as all the unshared valency electrons (non-bonding electrons) of bonded atoms are shown by dots were first used by Lewis and they are known as Lewis structures. In Lewis structures, the symbol of the atom represents **kernel** (nucleus + electrons except valency electrons) but not only nucleus. The electrons of the outermost shell of an atom are called valency (valence) electrons.





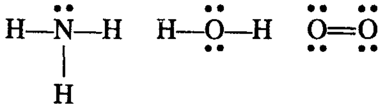
(In HCl, hydrogen has two electrons in its valence shell and chlorine has eight electrons in its valence shell)



When a dash (—) is used in place of dots corresponding to each shared pair of electrons and the dots corresponding to all the non-bonding electrons are omitted, the structures of molecules are known as **Couper structures** (structural formulae) because he proposed such structures. For example, the Couper structures of covalent compounds like H_2, O_2 and N_2 are depicted as follows :

$H—H$ (single bond) $O=O$ (double bond) $N \equiv N$ (triple bond)

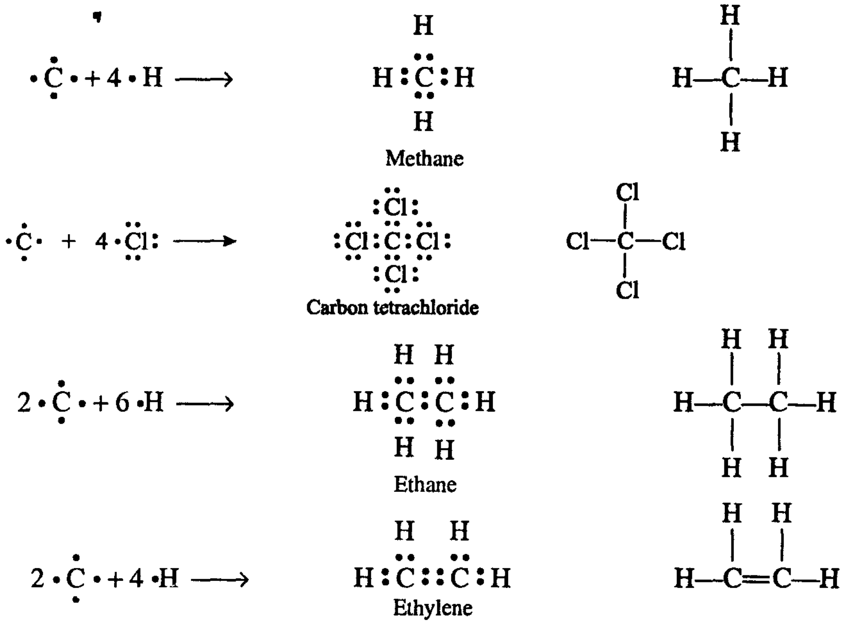
The omission of the unshared valency electrons is the limitation of Couper structures. A widely used scheme for representing structure of molecules uses Couper structures indicating all the unshared valency electrons by dots, such structures are also called as Lewis structures, for example :

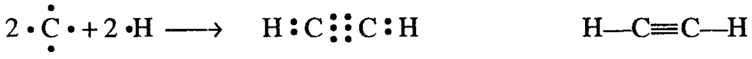


1.1.2 Covalency of Carbon

Carbon has four valency electrons and usually it acquires the stable electronic configuration of the nearest noble gas neon by sharing its electrons with other atoms. Thus, carbon is tetracovalent (quadricovalent). Lewis and Couper structures of some covalent carbon compounds are given below :

Combining atoms **Lewis Structure** **Couper structure**





$2\cdot\underset{\cdot}{\dot{C}}\cdot + 2\cdot H \longrightarrow H:C\vdots\vdots C:H \qquad H—C\equiv C—H$

Acetylene

Carbon atoms have unique ability to join together to form very long chains and large rings, which can have branches and cross-links. This unique property of carbon is known as **catenation**, which is responsible for the wide variety and large number of carbon compounds. Since **catenation** is not possible to such an extent for atoms of any other element, inorganic compounds are far less in number.

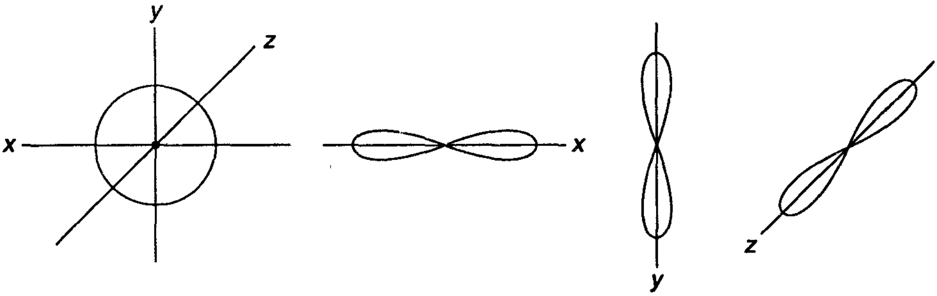
1.1.3 Orbital (Wave Mechanical) Concept of Bonding

The electronic theory of bonding could not answer fundamental questions concerning, *e.g.*, the bond energy, and geometry and shapes of molecules. The emergence of quantum (wave) mechanics ultimately led to the development of two theories of bonding, *viz.*, the valence bond (VB) theory and the molecular orbital (MO) theory to explain the nature of covalent bonds. Both of these theories involve atomic orbitals (AO's), thus before intelligently discussing them, we must consider the shapes and orientations of atomic orbitals.

1.1.4 Atomic Orbitals

An atomic orbital is defined as the definite region in three-dimensional space around a nucleus where there is high probability of finding an electron of specific energy. In organic chemistry, we are mainly concerned with *s* and *p*-orbitals, hence the shapes and orientations of these orbitals are described below :

An *s* orbital has spherical shape. The atomic nucleus in the centre of *s* orbital and the orbital is spherically symmetrical about the nucleus.



s orbital p_x orbital p_y orbital p_z orbital

Fig. 1.1. Shapes of *s* and *p* orbitals.

A *p* atomic orbital consists of two equal lobes forming a dumb-bell shape. The two lobes do not touch each other at the nucleus, thus the probability of finding electrons in this region is zero and it is called the nodal plane. There are three *p* orbitals of equal energy. They are directed perpendicular to each other just as Cartesian co-ordinates and are designated as p_x, p_y and p_z corresponding to their axes of orientation.

1.1.5 Valence Bond Theory

The valence bond (VB) theory of bonding is mainly based on the work of Heitler, London, Pauling and Slater. According to this theory, a covalent bond is formed by overlapping of two half-filled atomic orbitals containing electrons of opposite spins. For example, let us consider the formation of a hydrogen molecule (H_2) from two hydrogen atoms. When two hydrogen atoms come enough close to each other, a covalent bond is formed between them by overlapping of their half-filled 1*s* orbitals containing electrons of opposite spins. The greater the overlapping, the stronger is the resulting bond. However, total overlapping is prevented by repulsion between the nuclei.

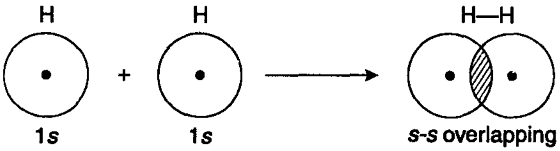


Fig. 1.2. Formation of H—H covalent bond according to the valence bond theory.

After this overlapping, each of the two electrons can be found in the atomic orbital of one or the other atom and they can exchange their positions. Further, the probability of finding the two electrons of the two overlapped orbitals is much greater in the space between the two atomic nuclei than that in other places. Consequently both the electrons are attracted by either nucleus and the internuclear repulsion is also shielded by them. Thus, there is decrease in the potential energy of the system which causes the overlapping of atomic orbitals to form a covalent bond. Thus, the resulting hydrogen molecule has 104 kcal/mole less energy than the constituent hydrogen atoms. This is called the bond strength of H—H bond.

If the atoms come too close to each other, there are internuclear and interelectronic repulsions which increase the energy of the system. Thus, there is a critical internuclear distance, called bond length or bond distance, for overlapping of atomic orbitals to form a covalent bond. This is 0.74 Å for the formation of hydrogen molecule. When this distance is less or more than 0.74 Å, the formation of H—H covalent bond cannot take place.

Similar to that described above for the formation of a covalent bond in hydrogen molecule, one can apply the VB theory to the covalent bond formation in other molecules also. Non-spherical orbitals (*e.g.*, *p* and *d* orbitals) show directional preference and tend to form bonds in the direction of maximum electron density within the orbital, hence a covalent bond is generally directional. The direction of the electron density in the bonds determines the bond angles.

The principles of overlap can be summarized as :

(i) Only those orbitals overlap which participate in the bond formation. Orbitals of the bonded atoms retain their individual identity.

(ii) The greater overlapping of the atomic orbitals leads to a lowering of energy due to the attractive forces between electrons and the nuclei between atomic orbitals. Thus the greater the overlap between atomic orbitals, the stronger is the covalent bond (This is known as principle of maximum overlap).

(iii) The direction of the electron density in the bonds determines the bond angle.

Limitations of Valence Bond Theory : The following are chief drawbacks of VB theory :

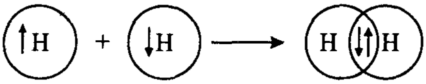
(i) It has to introduce hypothetical concepts of hybridisation, resonance and hyperconjugation to explain the formation and structures of various molecules.

(ii) It does no explain why atomic orbitals of bonded atoms should retain their identity, whereas the nuclei of approaching atoms are bound to affect nearly all atomic orbitals of each other.

(iii) It does not explain the paramagnetic behaviour of oxygen molecule.

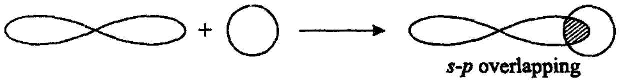
Types of Overlapping :

(i) *s-s* overlapping : Overlapping between *s-s* orbitals of two similar or dissimilar atoms is known as *s-s* overlapping. This forms a single covalent bond as shown below :

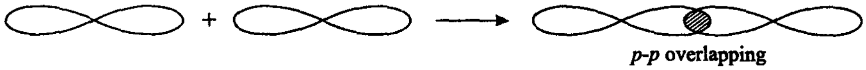


s-s overlapping

(ii) *s-p*-overlapping : Overlapping between *s* and *p*-orbitals is known as *s-p* overlapping.



(iii) *p-p* overlapping : *p-p* overlapping is produced by the end to end overlapping of two *p*-orbitals.

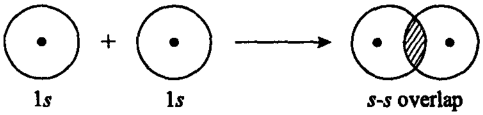


1.1.6 Multiple Bonds

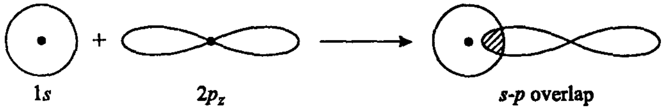
If two atoms are joined by more than one bond then the bond is called a multiple bond. In multiple bonds there are two types of bonds known as *sigma* and *pi* bonds.

Sigma (σ) ***Bond*** **:** A bond formed by coaxial overlapping of two atomic orbitals is known as σ bond. Since two atomic orbitals overlap along their axes, maximum overlap is possible. Hence, the bond thus formed is a strong bond. σ bonds are formed as a result of maximum overlapping of various atomic orbitals as outlined below* :

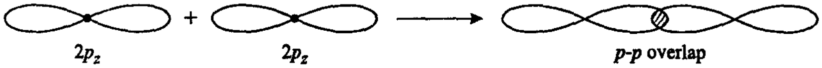
(i) By *s-s* overlapping as in the case of H_2 :



(ii) By *s-p* overlapping as in the case of HF :

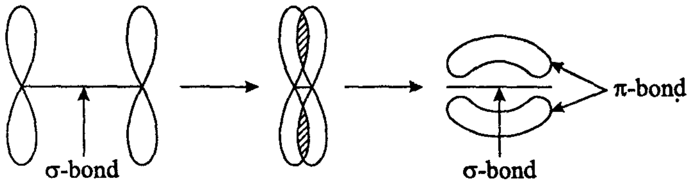


(iii) By *p-p* overlapping as in the case of F_2 :



(iv) σ-bonds are also formed by mutual overlapping of hybrid orbitals (sp^3, sp^2 and *sp*) and also by overlapping of hybrid orbitals and *s* or *p* orbitals (see hybridisation section).

Pi (π) ***Bond*** **:** A bond formed by parallel to axes overlapping of two *p* orbitals is known as π-bond.



1.1.7 Molecular Orbital Theory

The molecular orbital (MO) theory of bonding is mainly based on the work of Hund, Lennard-Jones, Hückel and Mulliken. According to this theory the molecule is regarded as being formed by the overlap of all atomic orbitals (*n*) of the bonded atoms. When two atoms are brought closer to one another, their all atomic orbitals combine to give a set of new **molecular orbitals** (wave functions) in equivalent number (*n*) that encompass the entire molecule. Thus, every molecule is

---

* The atomic orbitals other than those overlapped are not shown for the sake of convenience of representation.

Table 1.1 ***Difference between σ and π-bonds***

σ-Bond	π-Bond
1. It is formed by coaxial overlapping of atomic orbitals.	1. It is formed by parallel to axes overlapping of two *p*-orbitals.
2. It has maximum electron density along the bond axis.	2. It has a nodal plane along the bond axis.
3. It has cylindrical charge symmetry about the bond axis.	3. It has two electron clouds above and below the nodal plane.
4. There is free rotation about a σ-bond.	4. Rotation is restricted (frozen) about a π-bond.
5. Area of overlapping is greater, hence σ-bond is stronger.	5. Area of overlapping is smaller, hence π-bond is weaker.
6. It can have independent existence.	6. It always exists along with a σ-bond, and π-bond is formed after the formation of σ-bond
7. Only one σ-bond can exist between two atoms.	7. One or two π-bonds can exist between two atoms.
8. σ-bonds are directional, hence the geometry of the molecule depends on them.	8. π-bonds are not directional, hence the geometry of the molecule does not depend on them.

supposed to have orbitals associated with it in much the same way as a single isolated atom has. The Pauli's exclusion principle is applied to the MO's in the same way as it is applied to the atomic orbitals. MO's also follow Aufbau principle and Hund's rule.

According to molecular orbital theory, the atomic orbitals combine (overlap) and form a resultant orbital known as the molecular orbital in which the identity of both atomic orbitals is lost. All the electrons pertaining to, both the atoms are considered to be moving along the entire molecule under the influence of all the nuclei.

Basic Principles of Molecular Orbital Theory

(1) When nuclei of two atoms come close to each other, their atomic orbitals interact resulting in the formation of molecular orbitals (MO). In molecule atomic orbitals of atoms lose their identity after the formation of molecular orbitals.

(2) Each molecular orbital may be described by the wave function ψ, which is known as MO, wave function, ψ^2 represents the electron density.

(3) Each MO wave function (ψ) is associated with a set of quantum numbers which represent energy and shape of the occupied MO.

(4) Each MO wave function (ψ) is associated with a definite energy value. The total energy of the molecule is the sum of the energies of the occupied MO.

(5) Molecular orbitals follow Pauli's exclusion principle, Hund's rule and Aufbau principle.

(6) Each electron in a molecular orbital belongs to all the nuclei present in the molecule.

(7) Each electron moving in the molecular orbital is having clockwise or counter-clock wise $\left(i.e., +\frac{1}{2} \text{ or } -\frac{1}{2}\right)$ spin.

(8) Number of molecular orbitals are always equal to the number of atomic orbitals.

The molecular orbitals can be obtained by the method of **Linear combination of atomic orbitals (LCAO)**. Let two atoms A and B form AB molecule which is hetero diatomic molecule. Their atomic orbitals are represented by ψ_A and ψ_B, respectively. There are following two ways of their combination :

(i) Additive Overlap : Additive overlap is also known as positive overlap or ++ overlap. In this type of linear combination the positive lobe (*i.e.*, the lobe having positive sign) of ψ_A overlaps with the positive lobe of ψ_B, thus a molecular orbital is formed. This molecular orbital has lower energy than that of atomic orbitals of atom A and B due to attraction between the nuclei of A and B. Such type of molecular orbitals are known as **bonding molecular orbitals** (BMO) and represented as ψ_b.

(ii) Subtractive Overlap : Subtractive overlap is also known as negative overlap or +− overlap. In this type of the linear combination the positive lobe of ψ_A overlaps with the negative lobe of ψ_B, thus a molecular orbital is formed. This molecular orbital has higher energy than that of atomic orbitals of atom A and B due to repulsion between nuclei of A and B. Such type of molecular orbitals are known as **anti-bonding molecular** orbitals (ABMO) and represented as ψ_a or ψ^*.

On the basis of above discussion, the formation of BMO and ABMO by the LCAO of ψ_A and ψ_B may be represented as :

$$\psi_b = \psi_A + \psi_B \text{ (++ overlap)} \qquad \text{...(1)}$$

$$\psi_a = \psi_A - \psi_B \text{ (+− overlap)} \qquad \text{...(2)}$$

When we show the contribution made by ψ_A and ψ_B in ψ^a and ψ^b molecular orbitals, the above equations may be written as :

$$\psi_b = \frac{1}{\sqrt{2}}(\psi_A + \psi_B) \qquad \text{...(3)}$$

$$\psi_a = \frac{1}{2}(\psi_A - \psi_B) \qquad \text{...(4)}$$

The relative order of the energy of ψ_A, ψ_B, ψ_b and ψ_a is shown in Fig. 1.3.

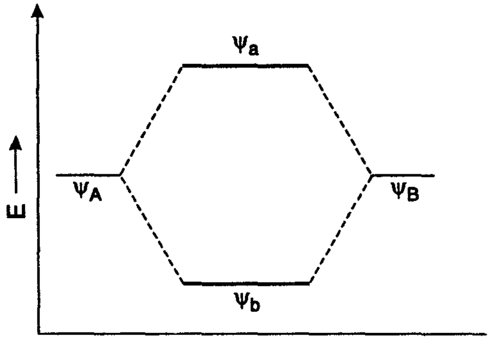


Fig. 1.3. Relative order of energies ψ_A, ψ_B, ψ_b and ψ_a

It is to be noted that in the case of a bonding molecular orbital electron density is concentrated between two nuclei of the two atoms (Fig. 1.4), while in the case of an anti-bonding molecular orbital nuclei of the two atoms come close to each other due to same charge and absence of the electron density, the nuclei repel each other (Fig. 1.5). We know that the square of the wave function (ψ^2) is known as probability of finding the electrons hence :

$$\psi_b^2 = \psi_A^2 + \psi_B^2 + 2\psi_A \psi_B \qquad \text{...(5)}$$

$$\psi_a^2 = \psi_A^2 + \psi_B^2 - 2\psi_A \psi_B \qquad \text{...(6)}$$

It is clear from the equation (5) that the value of ψ_b^2 is greater than the sum of ψ_A^2 and ψ_B^2. It means that the probability of finding the electrons in the molecular orbitals obtained by the LCAO in accordance with equation 1 is greater than that in either of the AO's ψ_A and ψ_B. In other words, the energy of ψ_b is lower than either of ψ_A and ψ_B. Hence this orbital forms stable chemical bond and named as **bonding molecular orbital.**

In the same way we can say that from equation (6) that the value of ψ_a^2 is lesser than $\psi_A^2 + \psi_B^2$. It means that the probability of finding the electron in the MO's obtained by the LCAO in accordance with equation (2) is lesser than that in either of the AO's ψ_A and ψ_B. In other words, the energy of ψ_a is higher than either of ψ_A and ψ_B. Hence, this orbital cannot form a stable chemical bond and is named as **anti-bonding molecular orbital.**

Combination of Atomic Orbitals to Form Molecular Orbitals

(i) Combination of *s*-orbitals :

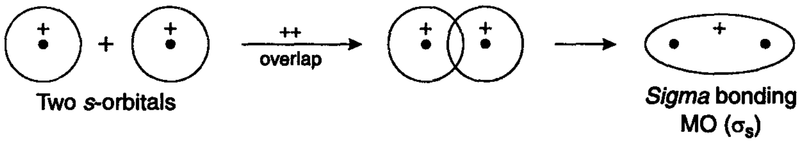


Fig. 1.4.

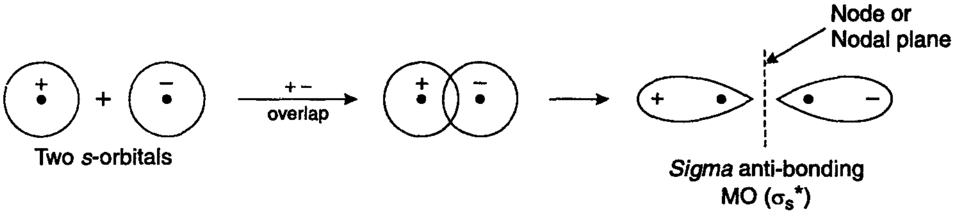
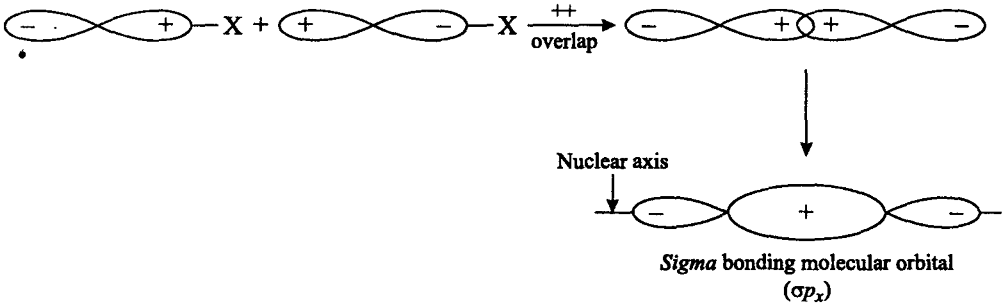
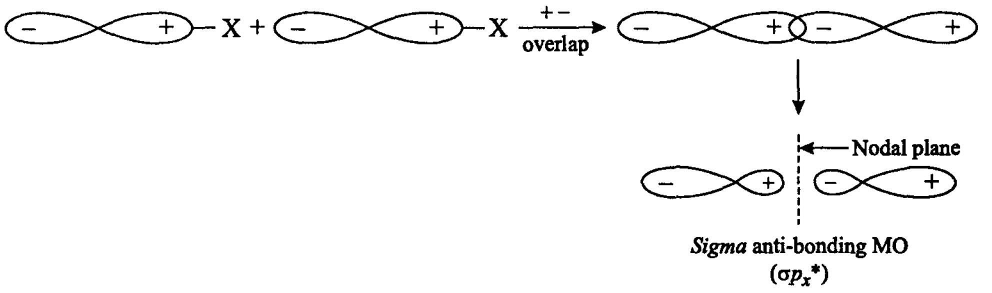


Fig. 1.5.

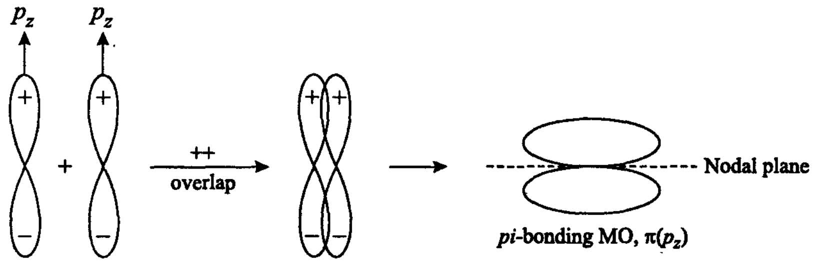
Combination of *p*-orbitals :

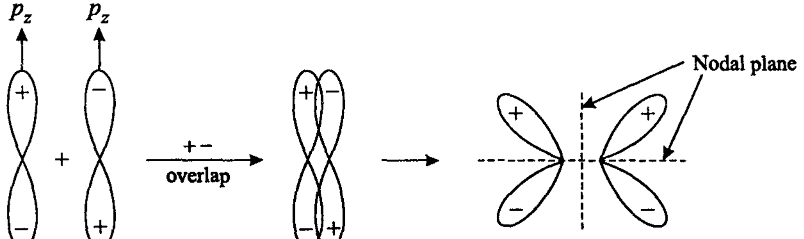
(i) Combination of two p-orbitals





(ii) Combination of two p_z-atomic orbitals





pi-antibonding MO, $\pi^*(p_z)$

1.1.8 Comparison between VB and MO theories

(A) Similarities between VB and MO theories :

(i) They account for the directional nature of the bond.
(ii) Bond results by the overlapping of two orbitals of minimum energy.
(iii) Electronic charge persists in between two atomic nuclei in bond formation.
(iv) Atomic orbitals should be of same energy, should overlap and should have same symmetry.

(B) Dissimilarities between VB and MO theories :

VB Theory	MO Theory
(i) Inter-atomic orbitals are produced by multiplying, exchanging and combination of wave functions of two **unpaired electrons**.	(i) Molecular orbitals are formed by LCAO of all atomic orbitals from the valency shell of two atoms.
(ii) Orbitals of the bonded atoms retain their individual identity.	(ii) Orbitals of bonded atoms lose their individual identity.
(iii) Molecular orbitals are monocentric.	(iii) Molecular orbitals are polycentric.

Characteristics of Covalent Bonds

The following important charactersitic properties of covalent bonds give us valuable information specially when we compare them in different molecules.

1.1.9 Bond Lengths

The critical distance between the nuclei of two bonded atoms is known as the **bond length** or **bond distance**. This distance ensures maximum stability of the covalent bond because at this distance the internuclear and interelectronic repulsions are completely balanced by the stabilizing effect of overlapping atomic orbitals. The unit which is usually used to express bond lengths is angstrom (Å is the symbol for angstrom, 1 Å = 10^{-8} cm). The most important method for measuring bond lengths are X-ray diffraction (only for crystals), electron diffraction (only for gases) and spectroscopic methods. Since molecules are always vibrating the distance between atoms of a bond is not constant. Therefore, the measurements obtained are average values and different methods give different values. Bond lengths of some important covalent bonds are given in Table 1.2.

Table 1.2. ***Bond lengths***

Bond	Bond Length (Å)	Bond	Bond length (Å)
H—H	0.74	N—H	1.03
C—C	1.54	O—H	0.97
C=C	1.34	C—F	1.42
C≡C	1.20	C—Cl	1.77
C—H	1.10	C—Br	1.91
C—O	1.41	C—I	2.13
C—N	1.47	C=O	1.20
C=N	1.28	C—S	1.82

1.1.10 Bond Strengths (Bond Energies)

There are two measures of bond strengths :

(i) Bond dissociation energy (*D*) and

(ii) Average bond energy (*E*)

(i) Bond dissociation energy (*D*) : The energy required to break a particular bond (in the gaseous phase) to give free radicals (in the gaseous phase) is called the dissociation energy, *D*. For example, *D* for $H_2O(g) \rightarrow {}^{\bullet}OH(g) + {}^{\bullet}H(g)$ is 118 kcal/mole. It should be noted that the same amount of energy is released during the formation of the particular bond. It is characteristic of a particular bond. The greater the bond dissociation energy, the stronger is the bond.

(ii) Average bond energy (*E*) : It is often simply called as bond energy (*E*). In polyatomic molecules, bond dissociation energies (*D*) are not identical even where apparently equivalent bonds dissociate. For example, when the four equivalent C—H bonds in methane dissociate successively, they have different values of *D*, *viz*., 102 kcal/mole for CH_3—H, 105 for CH_2—H, 108 for CH—H and 83 kcal/mole for C—H. Thus, the average value of the C—H bond energy in methane would be $\frac{1}{4}(102 + 105 + 108 + 83) = 99.5$ kcal/mole. The dissociation of a bond also depends on various factors like resonance, hyperconjugation, hybridisation, angle strain, steric effects, etc. Usually average of all the *D* values of equivalent bonds is taken, and this average value is called the bond energy (*E*). Bond energy (*E*) may be measured from heat of atomization, but the more usual practice is to calculate it from the heat of combustion. Bond energies (*E*) for some important bonds are given in Table 1.3.

Table 1.3. ***Bond energy (E) values at 25°C***

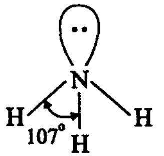
Bond	Bond Energy *E* (kcal/mole)	Bond	Bond energy, *E* (kcal/mole)
H—H	104	C=O	173–181
C—H	96–99	C—F	116
N—H	93	C—Cl	79
O—H	110–111	C—Br	66
S—H	82	C—I	52
C—C	83–85	H—F	135
C=C	146–151	H—Cl	103
C≡C	199–200	H—Br	87
C—N	69–75	H—I	71
C=N	143	F—F	36
C≡N	204	Cl—Cl	58
C—O	85–91	Br—Br	45
C—S	61	I—I	36
C=S	132		

Bond energies are measures of bond strengths. Shorter bonds are stronger bonds (*cf.* Table 1.3) due to stronger attraction between nuclei and electrons. Double bonds are both shorter and stronger than σ bonds, but not twice strong, because π overlapping is lesser than σ overlapping.

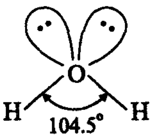
1.1.11 Bond Angles

All atomic orbitals (except *s* orbital) have directional preferences, hence covalent bonds formed by their overlapping are also directional and have an angle between them. *The angle between the directions of two covalent bonds is known as the bond angle.* Since *s*-orbital is spherical, it has no directional preference, but the three *p*-orbitals have different directions. They are directed at right angles to each other. Similarly, different hybrid orbitals, *e.g.*, *sp*, sp^2 and sp^3 also have directional preference. The most important methods for determining bond angles are X-ray diffraction (only for crystals), electron diffraction (only for gases) and spectroscopic methods. Due to continuous atomic vibrations in molecules, the measured bond angles are average bond angles.

Bond angles give an idea of the geometries and shapes of molecules, as they depend on bond angles. As we shall see while dealing with hybridisation (Section 1.1.12), the methane molecule has HCH bond angle of 109° 28′ (the tetrahedral angle), hence it has tetrahedral shape. Similarly, ammonia and water molecules have bond angles of 107° and 104.5°, respectively, showing that they have distorted tetrahedral shapes being pyramidal in ammonia and "V" shaped in water. This suggests that nitrogen and oxygen in these compounds are in the sp^3 hybrid state. Since the four pairs of electrons in ammonia and water are not equivalent, the bond angles are slightly deviated from the ideal value of 109.5°.



Ammonia



Water

These deviations are understandable in the light of the following order of repulsions between electron pairs in the valence shell :

lone pair–lone pair > lone pair–bond pair > bond pair–bond pair.

This order can be explained on the basis that the lone pair is under the influence of only one nucleus, hence its electron cloud will spread out in space to a greater extent than that of a bond pair, which is under the influence of two nuclei. This greater spread over of electron cloud in space results in a greater repulsion between a lone pair and another lone pair than that between a lone pair and a bond pair, and there is least repulsion between a bond pair and another bond pair of electrons.

In methane there are four bond pairs with equal repulsive forces which completely balance each other, thus tetrahedral valency angle HCH of 109.5° is maintained.

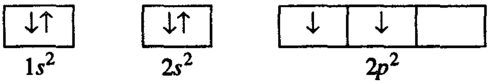
In ammonia, there are three bond pairs and one lone pair, and since the latter has a greater repulsive force, the bond pairs are forced closer together resulting in the HNH bond angle of 107°.

Similarly, in water molecule, because of two lone pairs there is greater repulsion than that in ammonia molecule, and thus forcing the bond pairs still closer together resulting in the HOH bond angle of 104.5°.

1.1.12 Hybridisation

The chemical properties of an element depend on the electronic configuration of the outermost shell. Carbon has four electrons in its outermost shell.

${}_6C = 1s^2 2s^2 2p^2$



The valency of an element is usually defined as the number of half-filled orbitals present in the outermost shell of its atom. Thus, according to the ground state electronic configuration of carbon, it should be divalent, but actually it is tetracovalent in most of its compounds.

Carbon's tetravalency is explained by promoting one, 2*s*, electron to a 2*pz* orbital. Some energy must be supplied to the system in order to effect this promotion. This promotion requires energy about 96 kcal/mole, but this energy is more than regained by the concurrent formation of chemical bonds.

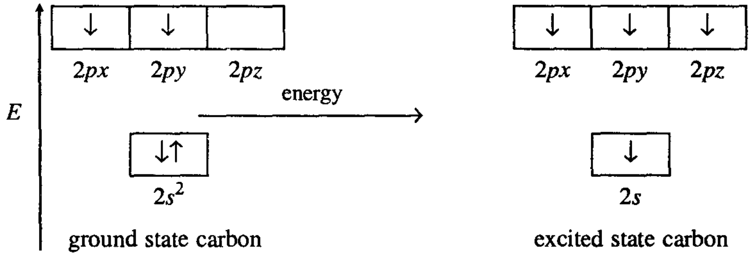


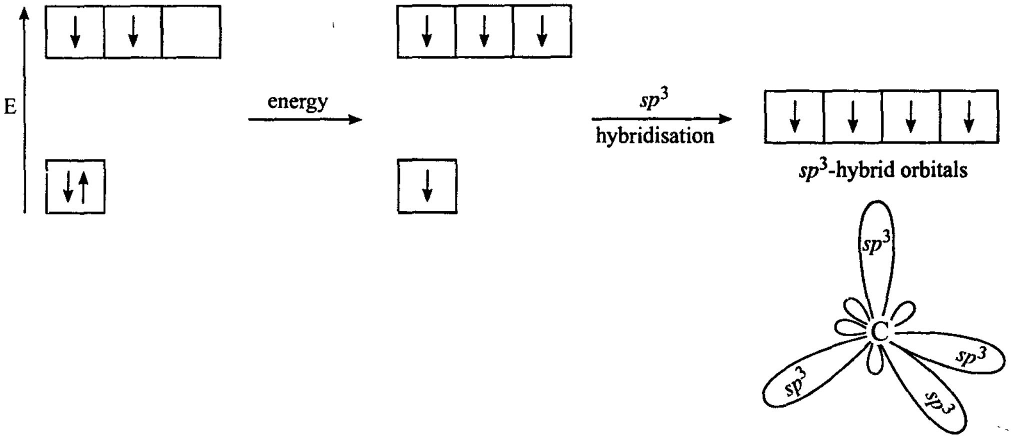
Fig. 1.6. Promotion of an electron in carbon allowing formation of four covalent bonds

The promotion of an electron from 2*s* orbital to one of the vacant 2*p* orbitals explains the observed valencies of this element. But there is one difficulty that three of the electrons have *p*-orbitals and the fourth one has *s*-orbital. It means we would expect to obtain three bonds of one kind and the fourth bond of a different kind; as well as the mutual angles as calculated for *p*-*p* bonds and *s*-*p* bonds are 90° and 125.4°, respectively. But the bond angle is equal to 109.5° in methane and all four bonds are equivalent. In order to explain these results, the **valence bond theory** has been supplemented by the concept of **hybridisation.** This is a hypothetical concept and has been introduced by **Pauling** and **Slater.**

According to this concept all the four orbitals of carbon (one *s* and three *p*) are mixed together and their energies redistributed in order to get the resultant orbitals having greatest directional character, because such an orbital will form strongest covalent bonds. The result of this mixing and energy redistribution is that one gets four new orbitals each having equal energy, and each being directed towards the corner of a regular tetrahedron because in this geometry, the orbitals each having one electron, are farthest apart.

This mixing and redistribution of energy is called **hybridisation** and the resultant orbitals are called **hybrid orbitals.** Because in this hybridisation there are one *s*-orbital and three *p*-orbitals, hence it is called as sp^3-hybridisation and hybrid orbitals are known as sp^3-hybrid orbitals.

A schematic representation of sp^3-hybridisation is shown below :



1.1.13 Hybridisation Rules

(1) The orbitals of similar energies take part in hybridisation.

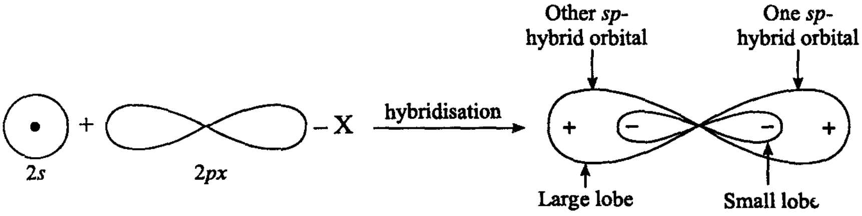
(2) Number of hybrid orbitals formed is always equal to the number of atomic orbitals which have taken part in the hybridisation.

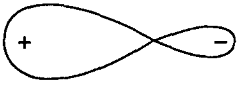
(3) Generally, all the hybrid orbitals are similar but they are not necessarily identical in shape. They may differ from one another mainly in shape.

(4) Hybrid orbitals form only *sigma* bonds.

Examples of sp, sp^2 and sp^3 Hybridisation :

(1) *sp* or Digonal Hybridisation : In this type of hybridisation one *s* and one *p*-orbital of the valence shell of central atom of the given molecule combine to form two *sp* hybrid orbitals as follows :





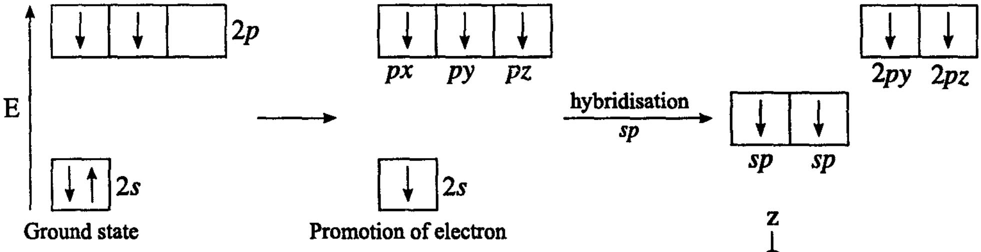
One *sp*-hybrid orbital

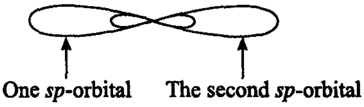
Characteristic of *sp*-Hybrid Orbitals :

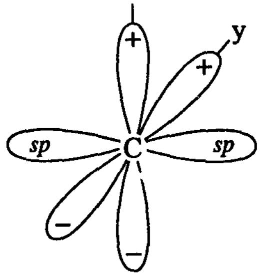
(i) Both *sp*-hybrid orbitals are completely equivalent and symmetrical.
(ii) Energy of *sp*-hybrid orbital is more than *s*-orbital but less than the *p*-orbital.
(iii) These two *sp*-hybrid orbitals are collinear, *i.e.*, angle between the hybrid orbitals is 180°.
(iv) Shape of *sp*-hybrid orbital is oval.
(v) Its relative power of overlapping is 1.93 with respect to *s* orbital.

In *sp*-hybrid orbital one lobe is bigger while other lobe is small. The bigger lobe is very large with respect to *p*-orbital, hence it has higher degree of overlaping. Thus it forms stronger bond.

Let us take the formation of acetylene. In acetylene hybridisation of carbon is *sp*. One 2*s* orbital blends with only one 2*p* orbital to form two *sp*-hybrid orbitals. In this case two unhybridised orbitals remain, each with one electron.

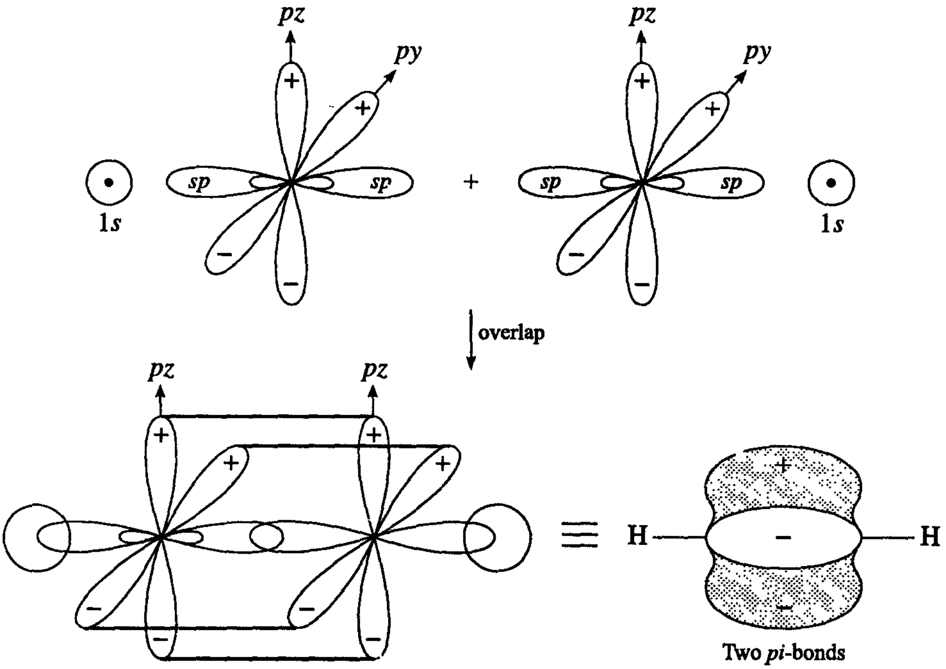




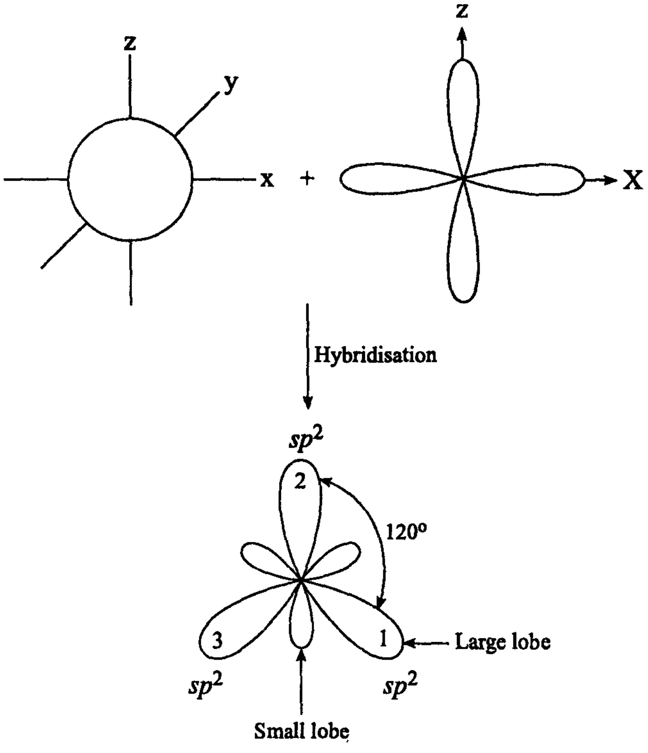


py and *pz* atomic orbitals are perpendicular to each other and to the linear *sp*-orbitals

In $CH\equiv CH$, the two carbon atoms are joined by an *sp-sp sigma* bond. Each carbon atom is also bonded to a hydrogen atom by an *sp-s sigma* bond. The two *p*-orbitals of one carbon then overlap with the two *p*-orbitals of the other carbon to form two *pi* bonds. One *pi* bond is above and below the line of the *sigma* bond; the other *pi* bond is located in front and back.



(2) ***sp*²- or Trigonal Hybridisation :** In this type of hybridisation one *s* and 2*p* orbitals of the valence shell of central atom of the given molecule combine to form three sp^2-hybrid orbitals as shown below :

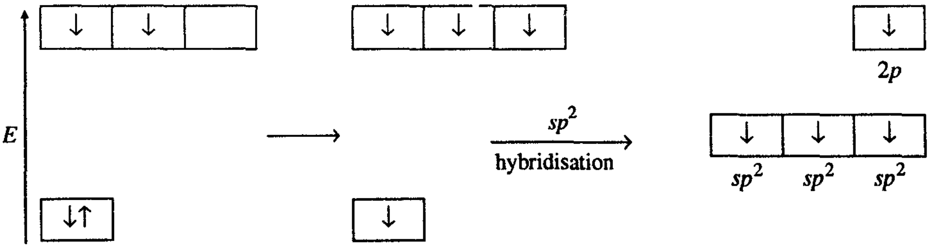


Characteristics :

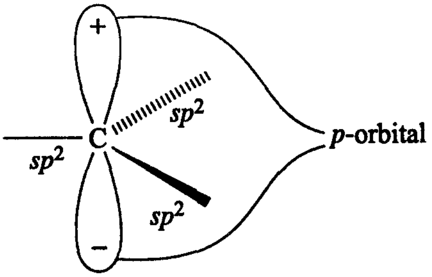
(1) These sp^2-hybrid orbitals are completely equivalent and symmetrical.
(2) These hybrid orbitals are planar with bond angle 120°.
(3) Since in this hybridisation contribution of p-orbitals is more hence it is less oval than sp-hybrid orbitals. In this case one lobe is bigger and one lobe is smaller and it forms stronger bond.
(4) These are stronger than s and p orbitals. Its relative power of overlapping is 1.99 with respect to s-orbital.

When carbon is bonded to another atom by a double bond, the carbon atom is in the sp^2-hybrid state. Example is ethylene.

To form sp^2 bonding orbitals, carbon hybridises its $2s$ orbital with only two of its $2p$-orbitals. One p-orbital remains unhybridised on the carbon atom.

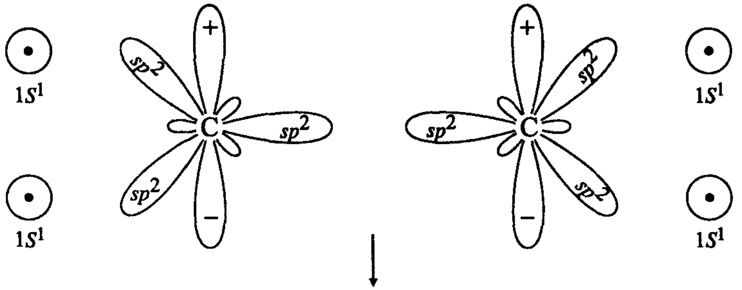


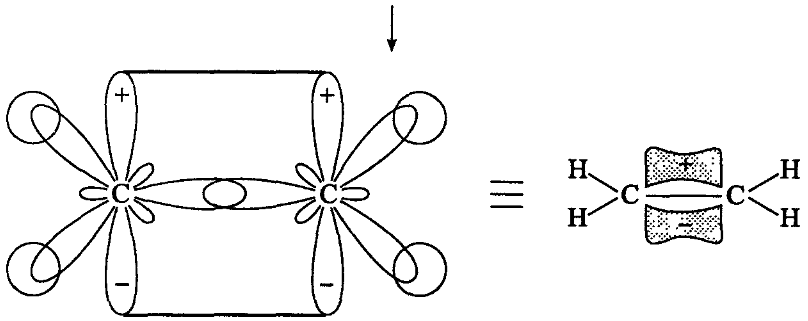
An sp^2-hybridised carbon atom is said to be a trigonal carbon. Figure given below shows a carbon atom with three sp^2 orbitals and the one unhybridised p orbital which is perpendicular to the sp^2 plane.



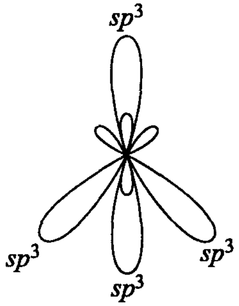
In ethylene two sp^2 carbons are joined by a *sigma* bond formed by the overlap of one sp^2 orbital from each carbon atom (This σ-bond is one of the bonds of the double bond).

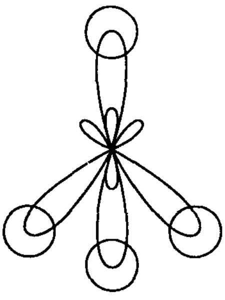
Both carbon atoms have also unhybridised p-orbitals, which can be oriented parallel to each other and thereby overlap. Both lobes of the p-orbitals merge above and below the *sigma* bond forming a π MO. Thus double bond is composed of a σ bond and a π bond. The ethylene molecule is completed when σ bonds are formed between the overlapping sp^2 orbitals of carbons and the s-orbitals of the hydrogens.





(3) **sp^3- or Tetrahedral Hybridisation :** In this hybridisation one *s* and three *p*-orbitals of the valence shell of central atom of the given molecule combine to form four sp^3-nybrid orbitals.





Methane

Characteristics :

1. All the four sp^3 hybrid orbitals are completely equivalent and symmetrical.
2. These orbitals are directed towards the four corners of a regular tetrahedron and the angle between each pair of them is 109° 28′ or 109.5°.
3. Their relative power of overlapping is 2.00 with respect to *s*-orbital. This shows that sp^3-orbitals are stronger than sp^2 which is stronger than *sp*-orbitals.
4. Since in sp^3-hybridisation the contribution of *p*-orbitals is 75%, its shape is almost same as that of the parent *p*-orbitals except that the bigger lobe in sp^3-orbital is somewhat more spread and shorter in length than the pure *p*-orbitals.

1.1.14 Hybridisation in Organic Species

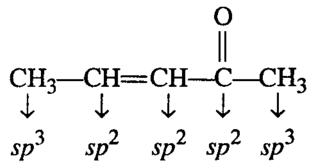
Hybridisation in organic species can be known by two methods :

First Method : In this method hybridisation can be known by the number of pi bonds present on that particular atom.

Number of pi bond(s)	Type of hybridisation
Zero	sp^3
One	sp^2
Two	sp

Examples :

(i)



$$\underset{sp^3}{CH_3}—\underset{sp^2}{CH}=\underset{sp^2}{CH}—\underset{sp^2}{\overset{\overset{\displaystyle O}{\|}}{C}}—\underset{sp^3}{CH_3}$$

(ii) $\underset{sp^2}{CH_2}=\underset{sp}{C}=\underset{sp^2}{CH_2}$

(iii) $$\begin{array}{cccccc} CH_3— & CH= & CH— & CH_2— & C\equiv & N \\ \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ sp^3 & sp^2 & sp^2 & sp^3 & sp & sp \end{array}$$

This method cannot be used for those atoms of the molecule which have positive charge, negative charge or odd electron.

Second method : Electron pair method

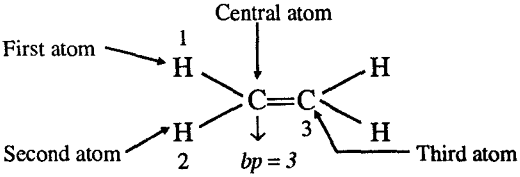
$ep = bp + lp$

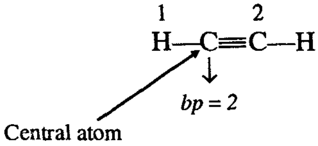
where ep = electrons pair present in hybrid orbitals

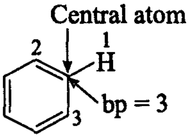
bp = bond pair present in hybrid orbitals

Determination of bond pairs :

Number of bp = Number of atoms present on central atom of the species







Determination of lone pair of electrons : Number of lp's can be determined as follows :

(i) If carbon has *pi* bond/(s) or positive charge or odd electron, then lp on carbon will be zero.

(ii) If carbon has negative charge, then lp will be equal to one.

Number of electron pairs tells us the type of hybridisation as follows :

ep	hybridisation
2	sp
3	sp^2
4	sp^3
5	sp^3d
6	sp^3d^2

Examples :

(i) $CH_3—\overset{\oplus}{C}H_2$

$\downarrow$

$bp = 3$

$lp = 0$

$ep = 3,\ sp^2$

(ii) $CH_2=\overset{\oplus}{C}H$

$\downarrow$

$bp = 2$

$lp = 0$

$ep = 2,\ sp$

(iii) $CH_3—\overset{\ominus}{C}H—CH_3$

$\downarrow$

$bp = 3$

$lp = 1$

$ep = 4,\ sp^3$

(iv) $CH_2=\overset{\ominus}{C}H$

$\downarrow$

$bp = 2$

$lp = 1$

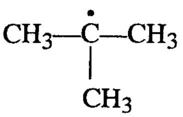
$ep = 3,\ sp^2$

(v) $CH\equiv\overset{\ominus}{C}$

$\downarrow$

$$\frac{\begin{array}{c} bp = 1 \\ lp = 1 \end{array}}{ep = 2,\ sp}$$

(vi)



$$CH_3-\overset{\bullet}{\underset{CH_3}{\underset{|}{C}}}-CH_3$$

$$\frac{\begin{array}{c} bp = 3 \\ lp = 0 \end{array}}{ep = 3,\ sp^2}$$

(vii)

$$\underset{\overset{\downarrow}{sp^3}}{CH_3}-\underset{\overset{\downarrow}{sp^3}}{CH_2}-\underset{\overset{\downarrow}{sp^2}}{CH}=\underset{\overset{\downarrow}{sp}}{C}=\underset{\overset{\downarrow}{sp^2}}{CH}-\underset{\overset{\downarrow}{sp^2}}{\overset{\oplus}{CH_2}}$$

1.1.15 Hybridisation and Bond Properties

Bond properties like bond angles, geometry of molecules, electronegativity, dipole moments, bond lengths, bond strengths, bond energies and acidity of hydrocarbons are greatly influenced by the hybrid states of bonded atoms. Here, we shall discuss correlations of hybridisation with these properties.

(A) Bond Angles and Geometry of the Molecule : The carbon valency angles follow the following order :

$$sp^3\ (109.5°) < sp^2\ (120°) < sp\ (180°)$$

Thus, the bond angle increases with increasing s character, or decreasing p character. This is because of the particular orientation (or geometry) assumed by hybrid orbitals in a given hybridisation. Thus, bond angles and geometry of the molecule can be known by hybridisation :

	Type of hybridisation	Number of orbitals used	Number of unused *p*-orbitals	Bond angle	Geometry	% of *s*-character
(i)	sp	One s and one p	Two	180°	Linear	50
(ii)	sp^2	One s and two p	One	120°	Trigonal planar	33.33
(iii)	sp^3	One s and three $3p$	Nil	109.5°	Tetrahedral	25

(B) Bond Lengths : An s-orbital is nearer to the nucleus than a p-orbital of the same shell. Hence, a hybrid orbital with more s-character is also nearer to the nucleus and it has smaller size than a hybrid orbital with more p-character. The sizes of different hybrid orbitals follow the following order :

$$sp^3 > sp^2 > sp$$

Obviously, the smaller the effective size of overlapping orbitals, the shorter is the bond formed. Thus :

Bond length and bond strength of C—C and C—H bonds in hydrocarbons depend on % s-character :

(i) Size of orbital $\propto \dfrac{1}{s\text{-character}}$

(ii) Bond length $\propto \dfrac{1}{\%\ s\text{-character}}$

Thus bond length in hydrocarbons is as follows :

	Alkane C—C	Alkane C=C	Alkyne C≡C
% s-character	25	33.33	50
Bond length	1.54 Å	1.34 Å	1.20 Å

Bond length of C—H bonds in hydrocarbons :

	sp^3 C—H	sp^2 C—H	sp C—H
% *s*-character	25	33.33	50
Bond length	1.10 Å	1.09 Å	1.06 Å

(C) Bond Strengths (Bond Energies) : We know that shorter bonds are stronger bonds. Thus, bond energies (and bond strengths) of bonds in different hybrid states follow the following order :

$$sp^3 < sp^2 < sp$$

Thus :

(i) Bond strength $\propto \dfrac{1}{\text{Bond length}} \propto$ % *s*-character $\propto$ Electronegativity.

(ii) Bond energy $\propto$ Bond strength

(iii) Bond energy $\propto$ % *s*-character

Bond energies of some bonds are given below in the table :

Bond type		% *s*-character	Bond energy (k cal/mole)
(C—H)			
$sp^3 - s$	(in alkane)	25	104
$sp^2 - s$	(in alkene)	33.33	106
$sp - s$	(in alkyne)	50	121
C—C			
$sp^3 - sp^3$	(in alkane)		83–85
$sp^2 - sp^2$	(in alkene)		146–151
$sp - sp$	(in alkyne)		199–200

(D) Electronegativity : Bond properties like dipole moments and inductive effect depend on the electronegativity of bonded atoms, thus, one should learn about correlation of hybridisation with the electronegativity. The power of an atom to attract electrons of a bond is called electronegativity. We have seen above that bonds formed by overlapping of orbitals with more *s*-character have a shorter bond length, consequently their electrons are nearer to the nucleus and will be attracted towards the nucleus with a greater force. This means, the greater is the *s*-character in a hybrid orbital, the greater will be the electronegativity of the atom in that hybrid state. The order of electronegativities of carbon in different hybrid states is :

$$sp > sp^2 > sp^3$$

Thus, electronegativity of hybrid orbital $\propto$ % *s*-character in hybrid orbitals :

Orbital	sp	sp^2	sp^3
% *s* Character	50	33.33	25

$$\xrightarrow{\hspace{12em}}$$

s-character in decreasing order; electronegativity in decreasing order

(E) Acidity of Hydrocarbons : (1) Hydrogen present on electronegative carbon is acidic in character.

(2) Acidity of hydrogen is directly proportional to the electronegativity of atom on which hydrogen is present. Thus :

$$\text{H—O—H},\ NH_3,\ CH{\equiv}CH$$

$$\xrightarrow{\hspace{10em}}$$

(i) Electronegativity of atom in decreasing order

(ii) Acidity of compounds in decreasing order

(3) Acidity of hydrocarbon ∝ % *s*-character

	$CH{\equiv}CH$	$CH_2{=}CH_2$	$CH_3{-}CH_3$
% *s*-character	50	33.33	25
pKa	25	44	50

→ *s*-character in decreasing order; acidity in decreasing order.

Note : $\text{Acidity} \propto Ka$

and $\text{Acidity} \propto \dfrac{1}{pKa}\ (pKa = -\log Ka)$

1.2 DELOCALIZED CHEMICAL BONDING

***Delocalized chemical bonding* may be defined as bonding in which the electrons are shared by more than two nuclei.** Molecules having conjugated systems exhibit delocalization of electrons, *i.e.*, they have delocalized bonds. For example, resonance, hyperconjugation and aromaticity involve delocalized chemical bonding.

1.2.1 Resonance

A concept that makes valence bond theory useful for the structural description of complex molecules is resonance theory. Resonance theory is an extension of valence bond theory which recognises that more than one Lewis structure can be written for many molecules. Resonance is hypothetical state of a chemical species in which its electronic structure can be hypothetically represented by two or more resonating structures, each differing only in the distribution of electrons but not of the constituent atoms. The properties of the species will not be those to be expected of any of the resonating structures, but they will be those to be expected from a combination (or hybridisation) called a resonance hybrid of them. The resonance hybrid is the real structure of the chemical species. Thus the chemical species has a single structure (*i.e.*, resonance hybrid) of its own by the conventional Lewis method. So we take the help of other possible though non-existent, structures (*i.e.*, canonical structures) which could be represented by Lewis method. Generally, the resonance hybrid is projected on the paper by writing down all the resonating structures and placing a double-headed arrow between each pair. Its usefulness in organic chemistry lies in its being a convenient way of depicting electron delocalisation. Resonance theory is particularly useful in describing conjugated species.

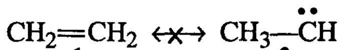
Arguments based on resonance theory are usually made in a qualitative way.

The elements of resonance theory that are necessary for qualitative applications are as follows :

(1) All the canonical structures must be written according to the Lewis method showing bonds, lone pair of electrons and formal charges where required.

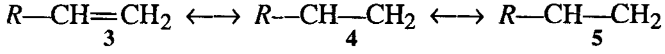
(2) The positions of the atomic nuclei of the chemical species must remain unchanged in all the resonating structures.

Thus (**1**) and (**2**) are not canonical structures.



$$\underset{\mathbf{1}}{CH_2{=}CH_2} \not\leftrightarrow \underset{\mathbf{2}}{CH_3{-}\ddot{C}H}$$

(3) To write resonating structures, only the π-bonds can be converted to a lone-pair of electrons and *vice-versa*. Thus the resonance hybrid of alkene may be written as :



$$\underset{\mathbf{3}}{R{-}CH{=}CH_2} \longleftrightarrow \underset{\mathbf{4}}{R{-}\overset{\oplus}{C}H{-}\overset{\ominus}{C}H_2} \longleftrightarrow \underset{\mathbf{5}}{R{-}\overset{\ominus}{C}H{-}\overset{\oplus}{C}H_2}$$

(4) The number of unpaired electrons in each resonating structure must be the same. Thus structure **6** cannot be a resonating structure of alkene.

$$\underset{\mathbf{3}}{R\text{—}CH{=}CH_2} \longleftrightarrow \underset{\mathbf{4}}{R\text{—}\overset{\oplus}{C}H\text{—}\overset{\ominus}{C}H_2} \longleftrightarrow \underset{\mathbf{5}}{R\text{—}\overset{\ominus}{C}H\text{—}\overset{\oplus}{C}H_2} \not\longleftrightarrow \underset{\mathbf{6}}{R\text{—}\dot{C}H\text{—}\dot{C}H_2}$$

(5) The several resonating structures must be of comparable energies. Thus for alkenes, structures **4** and **5** have such a high energy in comparison to **3** that they do not at all contribute to the hybrid.

(6) All atoms involved in the resonance must lie in the same plane or nearly in the same plane; any change in structure which prevents planarity will diminish resonance simply because maximum overlap of *p*-orbitals cannot be possible to form *pi*-bond.

1.2.2 Contribution of Resonating Structures to Resonance Hybrid

The most stable resonating structure contributes most and the least stable structure contributes least to the resonance hybrid.

Stability of resonating (or contributing) structures can be known by the following emperical rules :

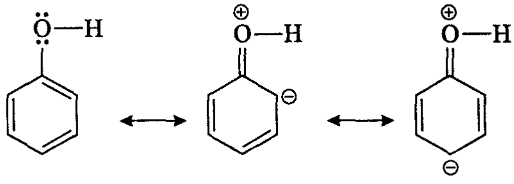
(1) Resonating structures with more covalent bonds are normally more stable than those with fever covalent bonds. Thus the structure **7** of 1, 3-butadiene has major contribution in its resonance hybrid and the structures **8** and **9** have minor contributions.

$$\underset{\mathbf{7}}{CH_2{=}CH\text{—}CH{=}CH_2} \longleftrightarrow \underset{\mathbf{8}}{\overset{\oplus}{C}H_2\text{—}\overset{\ominus}{C}H\text{—}CH{=}CH_2} \longleftrightarrow \underset{\mathbf{9}}{\overset{\oplus}{C}H_2\text{—}CH{=}CH\text{—}\overset{\ominus}{C}H_2}$$

(2) If the different resonating structures have the same number of covalent bonds, then uncharged structures have major contribution to the resonance hybrid. Thus structure **10** has much greater contribution than structure **11** of vinylamine in its resonance hybrid.

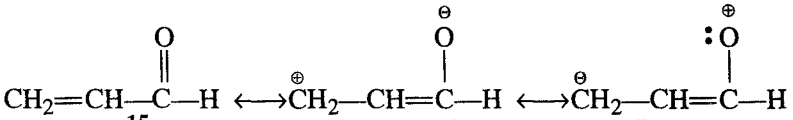
$$\underset{\mathbf{10}}{CH_2{=}CH\text{—}\ddot{N}H_2} \longleftrightarrow \underset{\mathbf{11}}{\overset{\ominus}{C}H_2\text{—}CH{=}\overset{\oplus}{N}H_2}$$

(3) Structures with isolated unlike charges have less contribution than those in which they are close to each other. Thus structure **13** of phenol has more contribution than structure **14** to its resonance hybrid.



12 **13** **14**

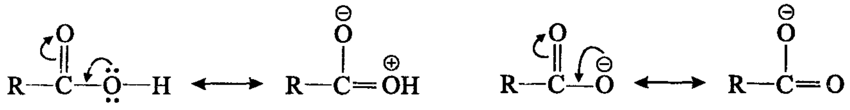
(4) Structures with negative formal charge on the most electronegative atom and positive charge on the least electronegative atom have significant contribution, structures with negative formal charge on the electropositive atom and positive charge on the electronegative atom have least contribution to the resonance hybrid.



$$\underset{\mathbf{15}}{CH_2{=}CH\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}H} \longleftrightarrow \underset{\mathbf{16}}{\overset{\oplus}{C}H_2\text{—}CH{=}\overset{\overset{\displaystyle \overset{\ominus}{O}}{|}}{C}\text{—}H} \longleftrightarrow \underset{\mathbf{17}}{\overset{\ominus}{C}H_2\text{—}CH{=}\overset{\overset{\displaystyle :\overset{\oplus}{O}}{|}}{C}\text{—}H}$$

Thus structure **16** is more contributing than structure **17** to the resonance hybrid of α, β-unsaturated aldehyde **15**.

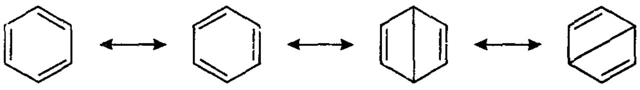
(5) Equivalent resonating structures are more important than non-equivalent resonating structures, because in the former case the equivalent structures have equal energy but in the latter case non-equivalent structures do not have identical amount of energy. Thus resonance in the the carboxylate ion is more important than that in the carboxylic acid.



18 **19** **20** **21**

Non-equivalent resonating structures   Equivalent resonating structures

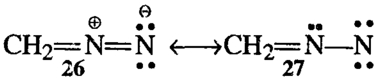
(6) Isovalent resonating structures, *i.e.*, having the same number of covalent bonds are more significant than heterovalent resonating structures.



22 **23** **24** **25**

Structures **22** and **23** are isovalent resonating structures of benzene. These resonating structures are very important. Structures **22** (or **23**) and **24** (or **25**) are not isovalent resonating structures.

(7) Structures with electron deficient atom, *i.e.*, possessing less than eight electrons in its outermost shell, have high energy, *i.e.*, low stability, hence they contribute less than those structures in which octet rule is not violated.



$$\underset{\mathbf{26}}{CH_2{=}\overset{\oplus}{N}{=}\overset{\ominus}{\underset{\cdot\cdot}{\ddot{N}}}} \longleftrightarrow \underset{\mathbf{27}}{CH_2{=}\ddot{N}{-}\underset{\cdot\cdot}{\ddot{N}}}$$

Thus, structure **26** contributes more than structure **27** to the resonance hybrid of diazomethane.

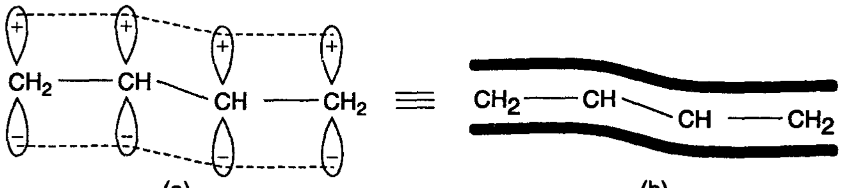
(8) Resonating structures are more important in a conjugated system than those in an isolated system.

(9) Greater number of significant structures in a resonance hybrid means greater importance of the resonance in comparison to another hybrid possessing fewer number of resonating structures. Thus greater number of significant resonating structures means greater stability of the hybrid structure.

In conjugated systems electrons are distributed over whole of the molecule embracing all the carbon atoms and do not remain localised; this phenomenon is called **delocalisation of electrons.** In an isolated system delocalisation also occurs between two adjacent atoms only, but such a wide range of delocalisation of electrons involving large number of atoms cannot take place as in a conjugated system. So we can conclude that more the delocalisation of the electrons or positive charge, more is the stability of species and lower is its energy.

1.2.3 Delocalisation in 1, 3-Butadiene and Benzene

Both of the adjacent doubly bonded carbons in the 1, 3-butadiene (conjugated system) have a



(a) (b)

Fig. 1.7. Delocalisation of π electrons in 1,3-butadiene.

p atomic orbital in the same plane and overlap side-by-side to engender an extended *pi* system involving all four carbons (Fig. 1.7 a, b).

Delocalisation of electrons in benzene makes the molecule stable. Each of the six carbon atoms are sp^2 hybridised and each of them possesses one (say *pz*) orbital with an unpaired electron. Three sp^2 hybrid orbitals of a carbon are utilised to form one *sigma* C—H bond and two *sigma* C—C bonds. In this way six carbon atoms of the benzene form a planar hexagonal ring structure and six hydrogens also lie in this plane.

Therefore, six *pz* orbitals of six carbon atoms are now parallel to each other. By side on overlaping of two *pz* orbitals of two adjacent carbon atoms a *pi* bond is formed. In this way three *pi* bonds are formed in five different ways in a molecule of benzene (Fig. 1.8).

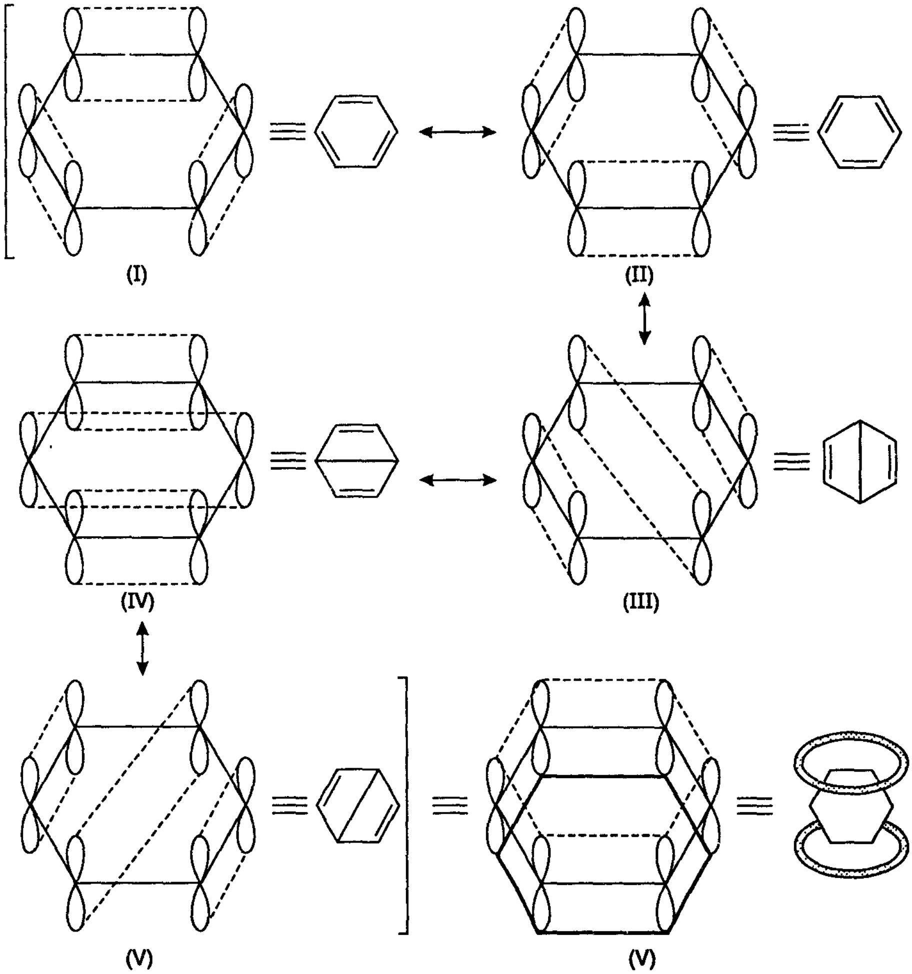
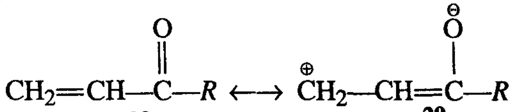


Fig. 1.8. Delocalisation of π electrons in benzene.

Delocalisation of electrons does not only take place in alternate single and multiple bonds involving carbon atoms (as in the case of 1, 3-butadiene and benzene), but it may also occur in a conjugated system involving carbon atom and atom other than the carbon, *e.g.*



$$\underset{\mathbf{28}}{CH_2{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R} \longleftrightarrow \underset{\mathbf{29}}{\overset{\oplus}{C}H_2{-}CH{=}\overset{\overset{\displaystyle \overset{\ominus}{O}}{|}}{C}{-}R}$$

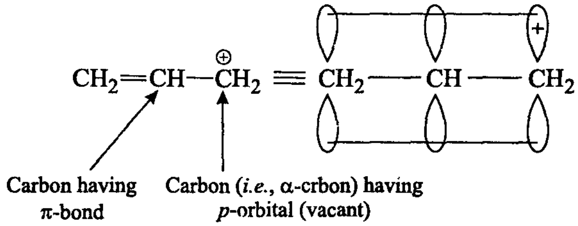
$$\underset{30}{CH_2=CH-C\equiv N} \longleftrightarrow \underset{31}{\overset{\oplus}{C}H_2-CH=C=\overset{\ominus}{N}}$$

There are also examples in which *pi* orbital and *p*-orbital (vacant or half-filled or filled) overlap or with each other to develop delocalisation.

Thus delocalisation are of the following types :

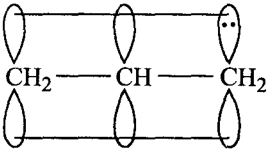
(i) **Delocalisation by π, π overlap :** This type of delocalisation takes place in those systems where single and multiple bonds are alternate.

(ii) **Delocalisation by π–p orbital overlap :** This type of delocalisation takes place in those systems where π-bond and *p*-orbital are present on adjacent atoms. For example :

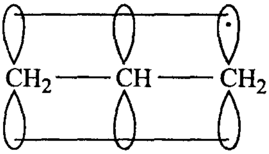


In this case π bond and *p* orbital is present on adjacent atoms. In other words, we can say that *p*-orbital should be present on α-carbon (or atom) with respect to multiple bond.

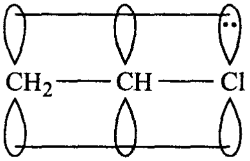
$CH_2=CH-\overset{\ominus}{C}H_2$ ≡
Allyl carbanion



$CH_2=CH-\dot{C}H_2$ ≡
Allyl free radical



$CH_2=CH-\ddot{\underset{\cdot\cdot}{Cl}}:$ ≡
Vinyl chloride

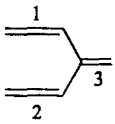


(iii) **Delocalisation by σ–π overlap** and

(iv) **Delocalisation by σ–p overlap**

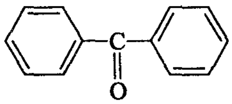
1.2.4 Cross-conjugation

In cross conjugated compound, three groups are present, two of which are not conjugated with each other, although each is conjugated with the third. Examples are :



1

In this example (**1**) 1 and 2 are not conjugated but third one is conjugated with 1 as well as (**2**). Cross conjugated triene is known as **dendralenes**.



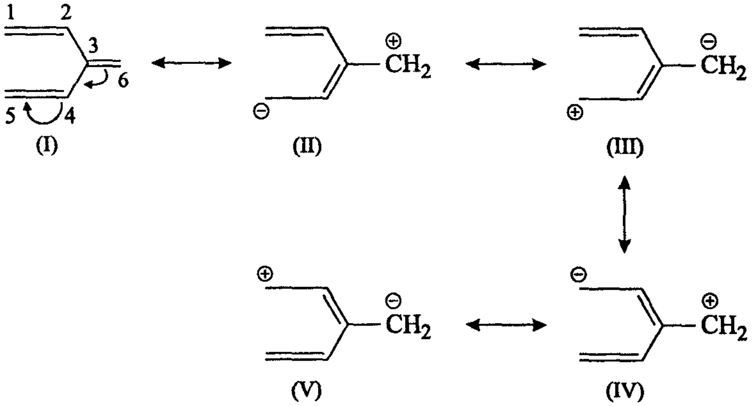
2

In this example carbonyl group is in conjugation to both the rings, but both rings are not in conjugation to each other.

$$\underset{\mathbf{3}}{CH_2{=}CH{-}\ddot{N}H{-}CH{=}CH_2}$$

In example (**3**) lone pair present on nitrogen is in conjugation to both double bonds but both double bonds are not in conjugation to each other.

Let us consider the example (**1**) :



C_1—C_2 (or C_4—C_5) bond is double in three (I, II and III) out of the five resonating structures while the C_3—C_6 bond is double only in one resonating structure. Thus bond order for C_1—C_2 should be maximum and bond order for C_2—C_3 should be minimum. The bond-order calculated for different bonds are as follows :

C_1—C_2 bond 1.930
C_3—C_6 bond 1.859
C_2—C_3 bond 1.363

1.2.5 Resonance Energy or Delocalisation Energy

The resonance hybrid of a species is a more stable structure than any one of the resonating structures contributing to it. The resonance energy is a measure of the **extra stability** of the resonance hybrid. It is defined as the difference in energy between the actual structure of the species and the most stable of the hypothetical structures (*i.e.*, canonical structures). The resonance energy of a molecule may be calculated by any one of the following methods :

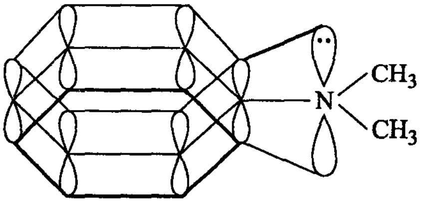
(i) Resonance energy = (Observed heat of formation) − (Calculated heat of formation of the stablest resonating structure)

(ii) Resonance energy = (Observed heat of combustion) − (Calculated heat of combustion of the stablest resonating structure)

(iii) Resonance energy = (Observed heat of hydrogenation) − (Calculated heat of hydrogenation of the stablest resonating structure)

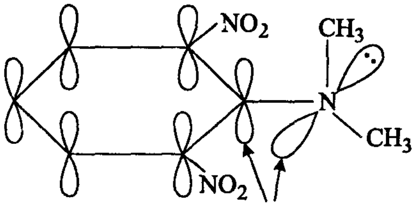
1.2.6 Steric Inhibition of Resonance

The most important condition for resonance to occur is that the involved atoms in resonating structures must be coplanar or nearly coplanar for maximum resonance energy (or maximum stability). If this condition does not fulfil, the involved orbitals cannot be parallel to each other and as a consequence delocalisation of electrons or positive charge cannot occur. There are many examples in which resonance is inhibited or reduced because the involved atoms and orbitals are sterically forced out of planarity and the phenomenon is called steric inhibition of resonance. There are many examples in which planarity of orbitals are inhibited by the bulky groups present at the proper position of the molecule. For example, in dimethylaniline (I) the orbital having lone pair of electrons present on nitrogen atom is in the plane of the benzene ring hence lone pair takes part in the delocalisation.



(I)

On the other hand, in N, N-dimethyl-2, 6-dinitroaniline (II), the NMe_2 group is out of the plane of benzene ring owing to the presence of two bulky nitro groups in the vicinity of $\ddot{N}Me_2$ group and consequently the lone pair of electrons on the nitrogen atom of $\ddot{N}Me_2$ group cannot get delocalised through lone pair-π conjugation (π–p conjugation).



(II) These two orbitals are not in the same plane due to the steric hindrance by the two bulky groups at *ortho* positions·

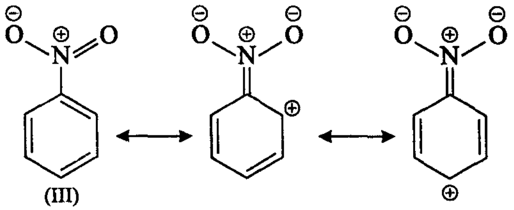
The steric inhibition of resonance has profound effect on :

(i) Physical properties
(ii) Acidity and basicity, and
(iii) Reactivity of organic compounds

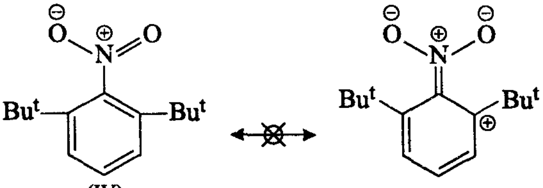
Physical Properties and Steric Inhibition of Resonance

(1) Bond Length and Bond Strength : Owing to the involvement of resonance, a single bond assumes a partial double bond character while a double bond assumes a partial single bond character. Thus resonance increases bond length of the double bond and decreases bond length of the single bond of conjugated compounds. If steric effect inhibits resonance the shortening of single bond or lengthening of double bond does not occur.

For example, in nitrobenzene (III) bond length between C and N is in between single and double bond due to the resonance, but in compound (IV) bond length between carbon and nitrogen is only of single bond due to the inhibition of resonance.



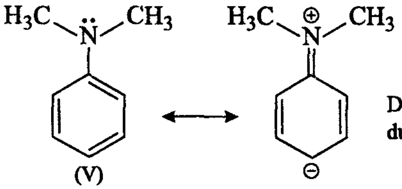
(III)



(IV)

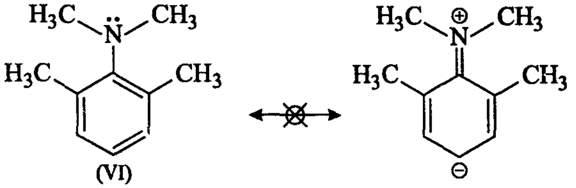
From the above structures one can very easily explain why C—N bond strength in (III) will be more than the C—N bond strength in (IV).

Dipole moment : Steric inhibition of resonance in an aromatic compound lowers its dipole moment since the distance between the two poles of such a compound is less than that in a similar compound without steric inhibition of resonance. For example :

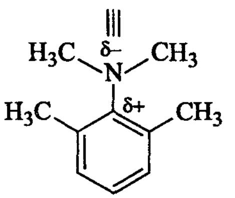


(V)

Distance between two poles is large due to the resonance; μ = 1·61 D



(VI)

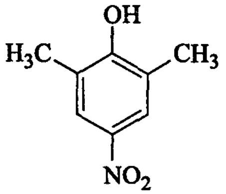


Distance between two poles is less due to the steric inhibition of resonance; μ = 0·95 D

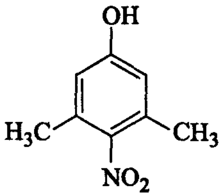
Acidity and Basicity

Acidity : Since steric hindrance reduces or prevents delocalisation of electrons through resonance, steric inhibition of resonance has appreciable effect on acidity of compounds.

Let us consider the acidity of two isomeric phenols (VII) and (VIII).

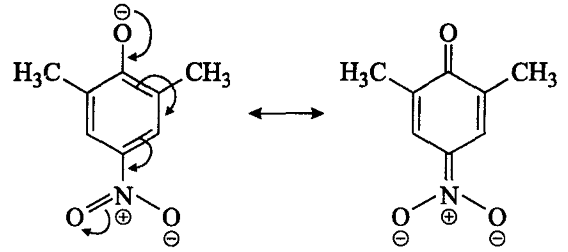


(VII)
pKa = 7·22

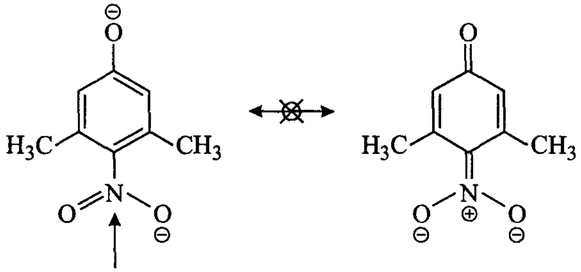


(VIII)
pKa = 8·25

Phenol (VII) is more acidic than phenol (VIII). In (VII) nitro group takes part in the delocalisation of negative charge of the phenoxide ion. Thus anion of phenol is stabilised due to the delocalisation which increases acidity.



In (VIII) nitro group does not take part in delocalisation due to the steric inhibition of resonance.

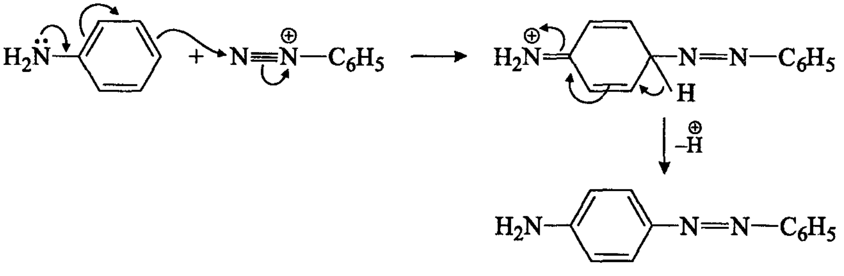


Nitro group is not in the plane of the benzene ring due to steric hindrance by two CH_3 groups

Basicity : Since steric hindrance reduces or prevents delocalisation of electrons through resonance, steric inhibition of resonance has appreciable effect on basicity of compounds.

On the basis of steric inhibition of resonance one can easily explain that N, N-dimethylaniline is less basic than 2, 6-dimethyl-N, N-dimethylaniline (structures V and VI).

Reactivity : Coupling reaction takes place between aniline and benzenediazonium salt. In this reaction benzenediazonium salt behaves as electrophile. It is very weak electrophile, hence it couples with strong nucleophile, *i.e.*, aniline.



Although aniline gives coupling reaction, N, N- 2, 6-tetramethylaniline does not because of steric inhibition of resonance. Four methyl groups being very closely placed, there is a good deal of steric congestion. In order to avoid steric congestion, the NMe_2 group rotates round C—N bond axis; because of this rotation the *p* atomic orbital containing the lone pair of electrons on the nitrogen atom is not parallel to *p*-orbitals of the benzene ring. Thus owing to the steric inhibition of resonance, N, N- 2, 6-tetramethylaniline becomes a weak nucleophile. Being a weak nucleophile it does not couple with the weak electrophile, benzenediazonium cation.

1.2.7 Hyperconjugation—Interaction between σ-π or σ-*p* Systems

Chemical and structural evidence indicate that alkyl substituents (having hydrogen on *alpha* carbon) on a carbon-carbon double bond act as electron donors to the *pi* system. In valence bond language this electronic interaction is known as no-bond resonance or hyperconjugation.

We know that *pi-pi* or π-*p* (vacant or filled) type of orbital overlap gives rise to conjugation. But σ-π or σ-*p* (incomplete or vacant) type of orbital overlap gives rise to hyperconjugation. The prefix hyper means excessive. The excessive, *i.e.*, extended conjugation involves σ-orbitals, generally of C—H or C—X (X=F or Cl) bond.

The delocalisation of σ-electrons through conjugation with π-electrons (or with vacant or half-filled *p* orbital) is known as hyperconjugation (or Baker-Nathan effect or no-bond resonance). The hyperconjugative effect was first of all observed by Baker and Nathan (1935).

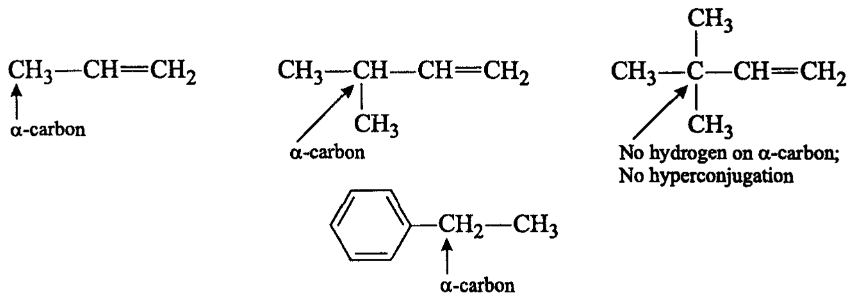
Structural requirement of hyperconjugation : Any organic species can show hyperconjugation phenomenon if it will fulfil the following conditions :

(1) Compound should have at least one sp^2 hybrid carbon of alkane, arene carbocation or free radical

(2) *Alpha* carbon with respect to sp^2 hybrid carbon should have at least one hydrogen

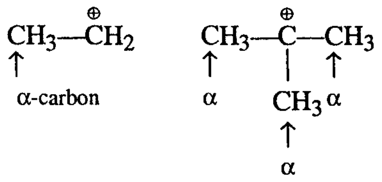
Thus hyperconjugation is of three types :

(1) σ (C—H), π conjugation : This type of conjugation occurs in alkenes and alkyl substituted aromatic compounds.



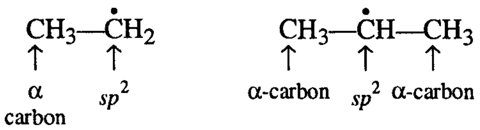
$CH_3—CH=CH_2$ $\quad$ $CH_3—CH(CH_3)—CH=CH_2$ $\quad$ $CH_3—C(CH_3)_2—CH=CH_2$ $\quad$ $C_6H_5—CH_2—CH_3$

(ii) σ (C—H), positive charge (vacant *p*-orbital) conjugation : This type of conjugation occurs in alkyl carbocations.



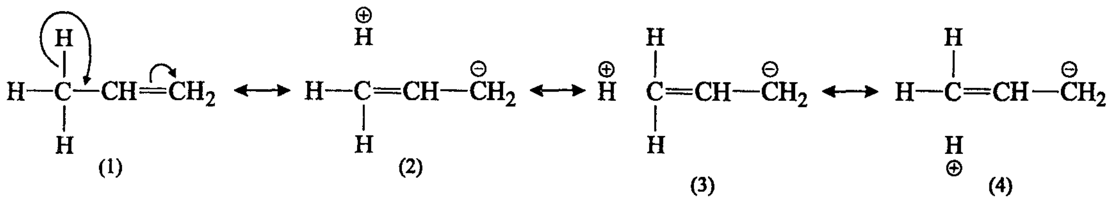
$CH_3—\overset{\oplus}{C}H_2$ $\quad$ $CH_3—\overset{\oplus}{C}(CH_3)—CH_3$

(iii) σ (C—H), odd electron (incomplete *p*-orbital) conjugation : This type of conjugation occurs in alkyl free radicals.



$CH_3—\dot{C}H_2$ $\quad$ $CH_3—\dot{C}H—CH_3$

Resonating structures due to hyperconjugation may be written involving "no-bond" between *alpha* carbon and hydrogen present on *alpha* carbon.



According to the valence bond theory there is no covalent bond between carbon and hydrogen in the resonating structures. From this point of view, hyperconjugation may be regarded as "no bond resonance". Actually the hydrogen atom does not become free to move from its original position. Above resonating structures only suggest that (i) there is some ionic character between C—H bond and (ii) carbon-carbon double bond acquires some single bond character.

From the above resonating structures one can very easily conclude that :

Number of resonating structures = Number of α-hydrogens + 1

Structure	Number of α-hydrogens	Number of resonating structures
$CH_3—CH=CH_2$	3	4
$CH_3—CH_2—CH=CH_2$	2	3
$CH_3—\overset{\oplus}{C}H_2$	3	4
$CH_3—\overset{\oplus}{C}H—CH_3$	6	7
$CH_3—\underset{\underset{CH_3}{\vert}}{\overset{\bullet}{C}}—CH_3$	9	10

According to molecular orbital theory delocalisation occurs between *pi* MO of carbon-carbon double bond and MO of C—H bond of the *alpha* carbon.

Here the extended orbital does not encompass two *pi* bonded carbon atoms or two *sigma* bonded carbon atoms or *sigma* bonded carbon and hydrogen atoms only but it holds all the four atoms together (Fig. 1.9).

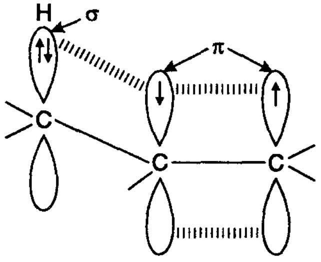
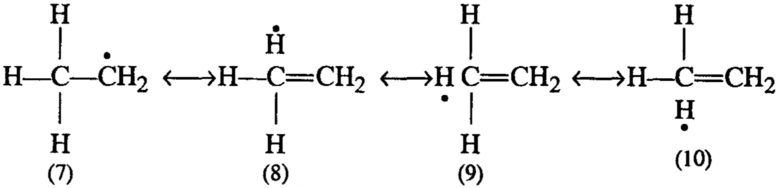


Fig. 1.9. α-π **overlap.**

In alkyl free radicals overlap takes place between molecular orbital of C—H bond and incomplete orbital of the adjacent carbon atom (Fig. 1.10). Here the extended orbital encloses the two carbons and one hydrogen.



Valence bond description

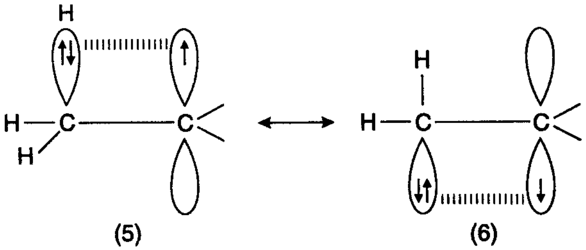


Fig. 1.10. **σ-*p* (incomlete) overlap.**

Similarly in alkylcarbocations, hyperconjugation is regarded as an overlap of the C—H, *sigma* molecular orbital and the vacant *p*-orbital of the positively charged carbon atom. Here the extended orbital formed holds the two carbon atoms and the hydrogen atom together (Fig. 1.11).

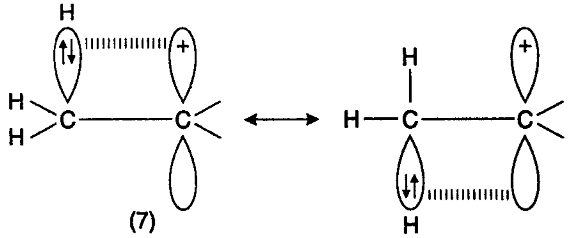
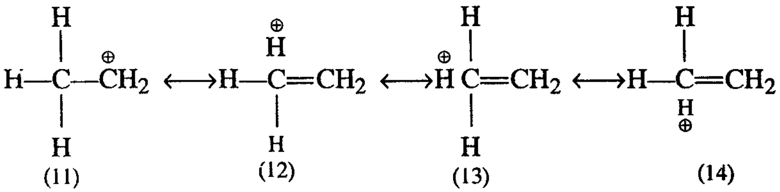


Fig. 1.11. **σ-*p* (vacant) overlap.**



Valence bond Description

Resonating structures of a given free radical possess the same number of covalent bonds. Similarly resonating structures of a given carbocation also possess the same number of covalent bonds. Hyperconjugation in which resonating structures possess the same number of covalent bonds is known as **isovalent hyperconjugation**.

Physical and chemical properties of compounds, in which hyperconjugation phenomenon can be possible, can be explained by hyperconjugative effect.

(1) Stability of Alkenes : On the basis of heat of hydrogenation stability order of the different alkenes has been found as follows :

Tetrasubstituted > Trisubstituted > Disubstituted > Monosubstituted > $CH_2{=}CH_2$

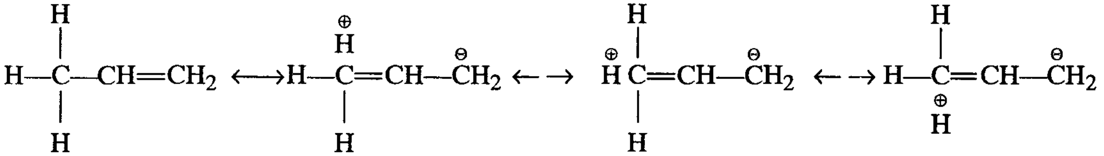
Stability in Decreasing Order

This stability order of alkenes can be explained on the basis of hyperconjugation :

Structure	$CH_3{-}\underset{CH_3}{C}{=}\underset{CH_3}{C}{-}CH_3$	$CH_3{-}\underset{CH_3}{C}{=}CH{-}CH_3$	$CH_3{-}CH{=}CH{-}CH_3$	$CH_3{-}CH{=}CH_2$
Number of *alpha* hydrogens	12	9	6	3
Number of resonating structures	13	10	7	4

We know that the greater is the number of resonating structures, the more will be stability of the system. Thus tetrasubstituted alkene is the most stable and ethylene is the least stable.

(2) Carbon-carbon double bond length in Alkenes : Due to the hyperconjugation single carbon-carbon bond of an alkane acquires some double bond character and carbon-carbon double bond acquires some single bond character. Thus due to the hyperconjugation carbon-carbon double bond length of substituted alkenes is always more than the ethylene.



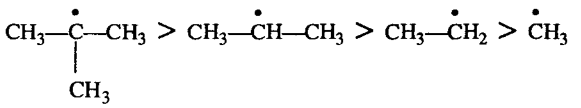
$$\mathrm{H{-}\underset{H}{\overset{H}{C}}{-}CH{=}CH_2 \longleftrightarrow H{-}\underset{H}{\overset{\overset{\oplus}{H}}{C}}{=}CH{-}\overset{\ominus}{C}H_2 \longleftrightarrow \overset{\oplus}{H}\,\underset{H}{\overset{H}{C}}{=}CH{-}\overset{\ominus}{C}H_2 \longleftrightarrow H{-}\underset{\underset{H}{\oplus}}{\overset{H}{C}}{=}CH{-}\overset{\ominus}{C}H_2}$$

$$\mathrm{CH_2\underset{\underset{1.34Å}{\uparrow}}{=}CH_2 \qquad CH_3{-}CH\underset{\underset{1.39Å}{\uparrow}}{=}CH_2}$$

Hyperconjugation also decreases C- -H bond length and C—C bond length.

$$\mathrm{CH_3\underset{\underset{1.54Å}{\uparrow}}{-}CH_3 \qquad CH_3\underset{\underset{1.50Å}{\uparrow}}{-}CH{=}CH_2}$$

(3) Stability of alkyl free radicals : Stability order of different types of alkyl free radicals is as follows :



$$\mathrm{CH_3{-}\underset{CH_3}{\overset{\bullet}{C}}{-}CH_3 > CH_3{-}\overset{\bullet}{C}H{-}CH_3 > CH_3{-}\overset{\bullet}{C}H_2 > \overset{\bullet}{C}H_3}$$

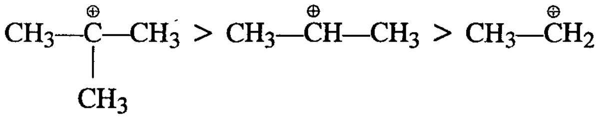
Stability in decreasing order

This order of stability can be explained by hyperconjugation as follows :

Structure	$\mathrm{CH_3{-}\underset{CH_3}{\overset{\bullet}{C}}{-}CH_3}$	$\mathrm{CH_3{-}\overset{\bullet}{C}H{-}CH_3}$	$\mathrm{CH_3{-}\overset{\bullet}{C}H_2}$
Number of resonating structures	10	7	4

Thus stability of tertiary is more than the secondary which is more than the primary free radical.

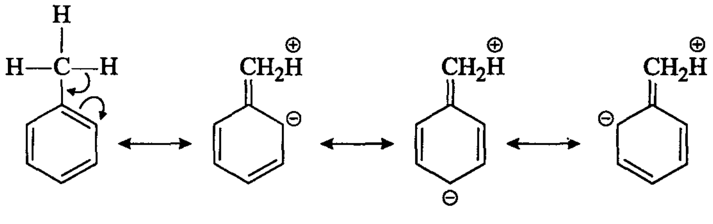
(4) Stability of alkyl carbocations : Stability order of different alkyl carbocations is as follows :



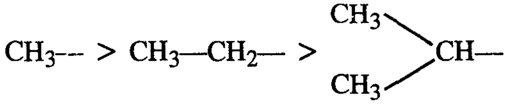
$$\mathrm{\underset{3^\circ}{CH_3{-}\underset{CH_3}{\overset{\oplus}{C}}{-}CH_3} > \underset{2^\circ}{CH_3{-}\overset{\oplus}{C}H{-}CH_3} > \underset{1^\circ}{CH_3{-}\overset{\oplus}{C}H_2}}$$

The above order can be explained by number of resonating structures of these carbocations.

(5) Electron donating power of alkyl group in alkylbenzenes : Alkyl group of alkyl benzene is *ortho-para* directing group and activating group for electrophilic aromatic substitution reactions. This property of alkyl group can be explained by hyperconjugation.



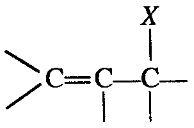
The electron-donating power of alkyl group depends on the number of *alpha* hydrogens of the alkyl group. The electron-donating power of some alkyl groups in decreasing order is as follows :



$$CH_3\text{—} > CH_3\text{—}CH_2\text{—} > (CH_3)_2CH\text{—}$$

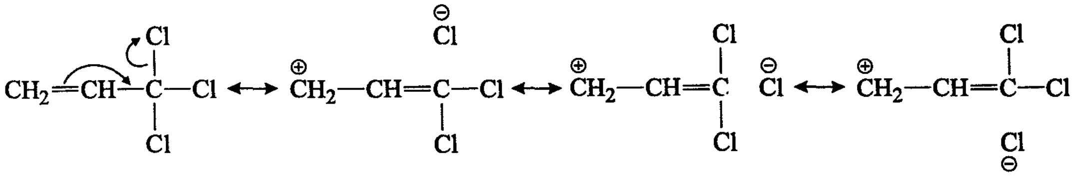
Reverse Hyperconjugation

Phenomenon of the hyperconjugation is also observed in the system given below :

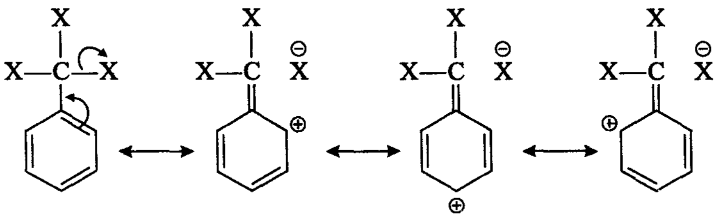


where X = halogen

In the given system, the effect operates in the reverse direction. Hence, the conjugation in such system is known as reverse hyperconjugation.



The *meta* directing influence of CX_3 group in C_6H_5—CX_3 for electrophilic aromatic substitution reaction can be explained by this effect.



1.2.8 Aromaticity. The Hückel $(4n + 2)\,\pi$ Rule

It is clear that benzene is an especially stable molecule. A number of other compounds have a similar special stability, which is called *aromaticity*. To be aromatic a compound must conform to all the following criteria :

(1) The molecule should be cyclic.

(2) There should be a p-orbital on every atom of an aromatic ring, *i.e.*, cyclic molecule is **fully conjugated**.

(3) Aromatic rings are planar. This planarity allows the p-orbitals on every atom to overlap.

(4) The cyclic arrangement of p-orbitals in an aromatic compound must contain $(4n + 2)\,\pi$-electrons, where n is an integer (0, 1, 2, 3 ...). In other words, aromatic compounds have 2, 6, 10, 14, 18, ..., π electrons.

These criteria for aromatic behaviour were first recognised in 1931 by Erich Hückel. They are often called collectively the **Hückel $4n + 2$ rule** or simply the $4n + 2$ rule. This rule is mainly used for **annulenes**. Annulene is a general name for monocyclic hydrocarbons with alternating single and double bonds. The ring size of an annulene is indicated by a number in bracket. Since the carbon atoms occur as doubly bonded pairs, an annulene must have an even number of carbons. Thus benzene is [6] annulene, cyclooctatetraene is [8] annulene. The general formula of annulenes is $(CH)_{2n}$.

Benzene conforms to the $(4n+2)$ rule because it contains a planar, continuous ring of atoms with a total of six π-electrons.

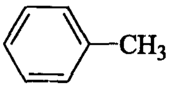
The alkene 1, 3, 5-hexatriene is not aromatic.

$$CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2$$

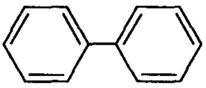
1, 3, 5-hexatriene

This compound has six π-electrons and all *p*-orbitals are parallel. However, this compound is not aromatic because the six π-electrons are not present in a *cyclic* arrangement, this compound does not meet the criteria of aromaticity.

Toluene and biphenyl are both aromatic.



Toluene

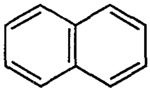
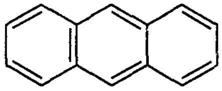
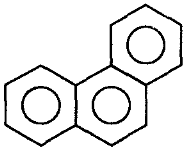


Biphenyl

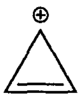
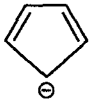
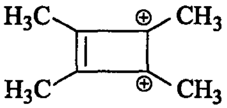
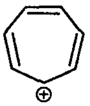
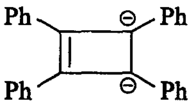
The benzene ring in toluene meets all of the criteria for aromaticity. The methyl group is a substituent group and is not part of the aromatic system of π-electrons. Each ring of biphenyl is a separate aromatic π-electron system. We do not count the number of π-electrons in both rings together because all of them are not part of one continuous cycle.

Hückel $4n+2$ rule of aromaticity can also be applied to fused polynuclear compounds. This rule can also be applicable to cyclic, planar conjugated ions (cations as well as anions). Some examples of these classes are :

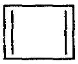
[A] Fused ring compounds :

Structure	(4n+2)π electrons
 Naphthalene	10
 Anthracene	14
 Phenanthrene	14

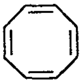
[B] Ions :

Structure	(4n + 2) π electrons	Structure	(4n + 2) π electrons
	2		6
	2		6
	6		

Neither of the following hydrocarbons are aromatic because they fail to meet the *fourth* criterion : they do not have $(4n + 2)$ π-electrons.



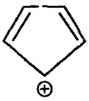
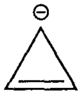
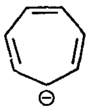
1, 3-cyclobutadiene
(not aromatic)



1, 3, 5, 7-cyclooctatetraene (COT)
(not aromatic)

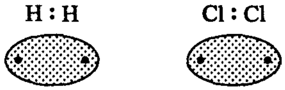
These compounds have $(4n)$ π-electrons. In fact, planar compounds containing continuous rings of $(4n)$ π-electrons are specially **unstable**, they are said to be **antiaromatic**. In other words, a molecule with $(4n)$ π-electrons is destabilised by resonance. Cyclobutadiene is, antiaromatic because it is planar and has $(4n)$ π-delocalised electrons. **On the other hand cyclooctatetraene is not an antiaromatic because it is not a planar compound. It has tube shaped geometry.**

Cyclic, planar. conjugated ions having $(4n)$ π-electrons are also antiaromatic. Some examples are given below :

Structure	**(4*n*) π-electrons**
	4
	4
	8

1.2.9 Inductive and Field Effects

If the atoms in a covalent bond have similar electronegativity (similar attractions for electrons), the bonding electrons are shared equally. Consider, for example, the hydrogen and chlorine molecule. Since two hydrogen atoms or two chlorine atoms obviously have identical electronegativities, the electron pair is shared equally and the molecular orbital (σ bond) is symetrically distributed.



There is no positive and negative end. Such a bond is said to be a **non-polar bond.**

However, in the covalent bond between hydrogen and chlorine, the electron pair is not shared equally because chlorine has a greater electronegativity than hydrogen and therefore, the electron pair shifts towards the more electronegative atom. This causes polarisation in the bond. The more electronegative atom acquires a partial negative charge (δ^-) and the counter part acquires a partial positive charge (δ^+). This type of bond, which involves the unequal sharing of electron pair between two different atoms of different electronegativities, is called polar **covalent bond**. Polar covalent bond is intermediate between an ionic and covalent bond. In that, although one atom has a greater share of the paired electrons than the other, the electrons are not actually transferred, a contrast to the ionic bond. The symbol δ (delta) is used to signify that only partial charges are formed and not full ions in contrast to ionic compounds.

A polar covalent bond can be represented as

$$\overset{\delta+}{A}—\overset{\delta-}{B}$$

If molecule has more than two atoms in a chain such as C_3—C_2—C_1—X with a more electronegative atom X at one terminal, the partial positive charge (δ^+) over C_1 does not remain localised. Since C_1 is positively charged, it will attract towards itself the electron pair forming the covalent bond between C_1 and C_2. This will cause C_2 to acquire a small positive charge, but the charge will be smaller than that on C_1, because the effect of the X atom has been transmitted through C_1 to C_2. Similarly, C_3 acquires a positive charge which will be smaller than that on C_2. ***This type of electron displacement along a chain of atoms due to the presence of a polar bond is known as Inductive Effect.*** **This effect is a permanent effect and decreases rapidly as the distance from the source (X)** increases. It is important to note that the electron pairs, although permanently displaced, remain in the same orbital. Inductive effect **operates through σ bonds.**

For the measurement of relative **Inductive effect**, H is chosen as a reference standard and (+) or (–) sign is assigned to group having relative electron attracting or repelling character, respectively.

***–I* Effect :** Any atom or group which attracts electrons more strongly than hydrogen is said to have negative inductive effect (—*I* effect). Following groups have been arranged in decreasing order of negative inductive effect :

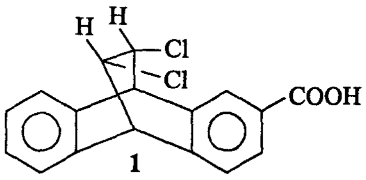
$$\overset{\oplus}{N}R_3 > NO_2 > SO_2R > CN > SO_2Ar > COOH > F > Cl > Br > I > OAr > COOR$$
$$> OR > COR > SH > SR > OH > NH_2 > Ar$$

***+I* Effect :** The atoms or groups which attract electrons less strongly than hydrogen are said to have positive inductive effect (+*I* effect). The following groups have been arranged in decreasing order of +*I* effect :

$$\overset{\ominus}{O} > C\overset{\ominus}{O}O > CR_3 > CHR_2 > CH_2R > CH_3 > D$$

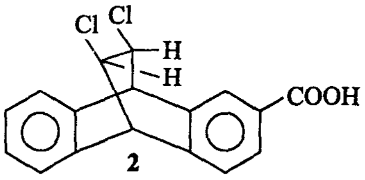
–*I* groups are electron-withdrawing groups and +*I* groups are electron-donating groups.

The field effect arises due to the presence of polar bonds in a molecule and it is transmitted not through bonds but through the environment (space or solvent molecules) around the molecules. It is often very difficult to measure the inductive and field effects separately. However, it has been done in many cases, because the field effect depends on the geometry of the molecule but the inductive effect depends only on the nature of the bonds. For example, in isomers **1** and **2** the inductive effect of the chlorine atoms on the COOH group (and hence the acidity) should be the same because the same bonds intervene; but the field effect is different because the chlorines are closer in space to COOH in **1** than they are in **2**. Thus, a comparison of the acidity of **1** and **2** clearly shows that a field effect is truly operating. The greater acidity of **2** than the **1** is due to the stabilisation of the carboxylate group by the +ve ends of the carbon-chlorine dipoles through the field effect in **2**. On the other hand, in **1** the –ve ends of the carbon-chlorine dipoles, which are closer to the carboxylate group, destabilise it due to repulsive interaction through the field effect.



1

pKa = 6.07



2

pKa = 5.67

Applications of Inductive Effect

(A) Magnitude of positive charge : The magnitude of positive charge on cations can be compared by *+I* or *–I* groups present in it. Suppose a carbocation is :

$$\overset{\oplus}{C}H_2—G$$

where, G = + *I* group or *–I* group

Case I : Suppose G is *+I* group, then

$$\overset{\oplus}{C}H_2 \leftarrow G$$

(i) Magnitude of positive charge will be decreased by *+I* group, and

(ii) More is the *+I* power of the group, less will be magnitude of positive charge.

$$\text{Hence, magnitude of positive charge} \propto \frac{1}{+I \text{ power of the group}}$$

Case II : Suppose G is *–I* group, then :

$$\overset{\oplus}{C}H_2 \rightarrow G$$

(i) Magnitude of positive charge will be increased by *–I* group, and

(ii) More is the *–I* power of the group, more will be magnitude of the positive charge.

Hence magnitude of positive charg ∝ – *I* power of the group.

(B) Magnitude of negative charge :

(i) Magnitude of negative charge $\propto \dfrac{1}{-I \text{ power of the group}}$

(ii) Magnitude of negative charge ∝ + *I* power of the group

(C) Stability of Non-conjugated Cations and Anions : Stability of non- conjugated charged species can be compared by the following rules :

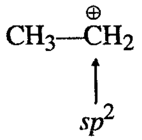
Rule 1 : Less is the magnitude of charge, more will be stability of the charged species.

Stability of similar charged species (*i.e.*, stability between cations or stability between anions) can be compared by this rule in those cases where :

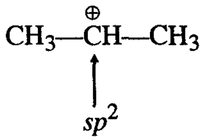
(i) Charge is present on the same atoms in all species, and

(ii) Hybridisation of atoms bearing the charge should be the same in all species.

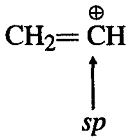
For example :


$\underset{sp^2}{CH_3—\overset{\oplus}{C}H_2}$

(I)


$\underset{sp^2}{CH_3—\overset{\oplus}{C}H—CH_3}$

(II)


$\underset{sp}{CH_2=\overset{\oplus}{C}H}$

(III)

Stability of cations I and II can be compared by rule-1 because positive charge in (I) and (II) is present on the same atom (*i.e.*, carbon) and hybridisation of $\overset{\oplus}{C}$ is the same in both the cases.

Stability of (I) and (III) cannot be compared by rule-1 because hybridisation of $\overset{\oplus}{C}$ in (I) and (III) is different.

Rule 2 : For maximum stability, positive charge should be present on electropositive atom in cation or negative charge should be present on electronegative atom in anion.

This rule can be used in those cases where hybridisation of atoms bearing charge is different. Thus stability of cations (I) and (III) or (II) and (III) can be compared by this rule.

(1) Stability of Alkyl Carbocation :

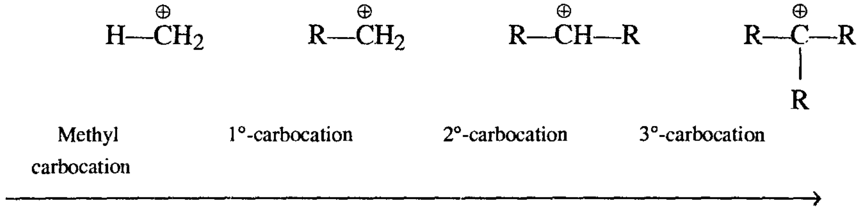
$$\text{Stability of alkyl carbocation} \propto \frac{1}{\text{magnitude of positive charge}} \qquad \text{...(i)}$$

$$\text{Magnitude of positive charge} \propto \frac{1}{+I \text{ power of the group (i.e., alkyl group)}} \qquad \text{...(ii)}$$

From (i) and (ii)

Stability of alkyl carbocation $\propto +I$ power of the group present on $\overset{\oplus}{C}$

Thus tertiary alkyl carbocation is more stable than secondary which is more stable than primary carbocations.



$$\underset{\text{Methyl carbocation}}{H{-}\overset{\oplus}{C}H_2} \qquad \underset{1^\circ\text{-carbocation}}{R{-}\overset{\oplus}{C}H_2} \qquad \underset{2^\circ\text{-carbocation}}{R{-}\overset{\oplus}{C}H{-}R} \qquad \underset{3^\circ\text{-carbocation}}{R{-}\underset{R}{\overset{\oplus}{C}}{-}R}$$

$$\xrightarrow{\hspace{12em}}$$

(i) Number of $+I$ groups on $\overset{\oplus}{C}$ is in increasing order

(ii) $+I$ power on $\overset{\oplus}{C}$ is in increasing order

(iii) Magnitude of positive charge is in decreasing order

(iv) Stability is in increasing order

(2) Stability of Alkyl Carbanion :

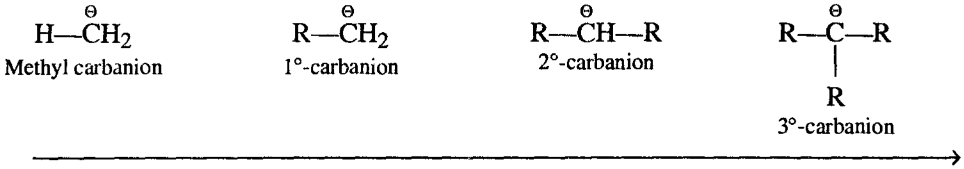
$$\text{Stability of alkyl carbanion} \propto \frac{1}{\text{magnitude of negative charge}} \qquad \text{...(i)}$$

$$\text{Magnitude of negative charge} \propto +I \text{ power of the group (i.e., alkyl group)} \qquad \text{...(ii)}$$

From (i) and (ii)

$$\text{Stability of alkyl carbanion} \propto \frac{1}{+I \text{ power of the alkyl group present on } \overset{\ominus}{C}}$$

For example :



$$\underset{\text{Methyl carbanion}}{H{-}\overset{\ominus}{C}H_2} \qquad \underset{1^\circ\text{-carbanion}}{R{-}\overset{\ominus}{C}H_2} \qquad \underset{2^\circ\text{-carbanion}}{R{-}\overset{\ominus}{C}H{-}R} \qquad \underset{3^\circ\text{-carbanion}}{R{-}\underset{R}{\overset{\ominus}{C}}{-}R}$$

$$\xrightarrow{\hspace{12em}}$$

(i) Number of alkyl groups on $\overset{\ominus}{C}$ is in increasing order

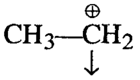
(ii) $+I$ power on $\overset{\ominus}{C}$ is in increasing order

(iii) Negative charge on $\overset{\ominus}{C}$ is in increasing order

(iv) Stability is in decreasing order

(3) Stability of Alkyl and Vinyl Carbocations :

Stability of these two types of species can be compared by rule 2.



$$CH_3{-}\overset{\oplus}{C}H_2$$

$\downarrow$

sp^2-hybrid carbon, less electronegative

Positive charge is present on less electronegative carbon.

$CH_2{=}\overset{\oplus}{C}H$

$\downarrow$

sp-hybrid carbon, more electronegative

Positive charge is present on more electronegative carbon

Hence, alkyl carbocation is always more stable than vinyl carbocation.

(4) Stability of Alkyl, Vinly and Acetylenic Carbanions : Stability of these three species can be compared by rule 2.

(I) $CH_3{-}\overset{\ominus}{C}H_2$

$\downarrow$

sp^3-hybrid carbon, less electronegative than *sp*^{2} carbon

Negative charge is present on less electronegative carbon.

(II) $CH_2{=}\overset{\ominus}{C}H$

$\downarrow$

sp^2-hybrid carbon, more electronegative than *sp*^{3} carbon

Negative charge is present on more electronegative carbon

(III) $CH{\equiv}\overset{\ominus}{C}$

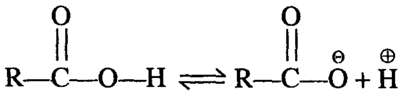
$\downarrow$

sp-hybrid carbon, more electronegative than *sp*^{2} carbon.

Negative charge is present on most electronegative carbon

Hence, acetylenic carbanion is more stable than vinylic carbanion which is more stable than alkyl carbanion.

(D) Strength of Carboxylic Acids : Acid strength is measured by the position of equilibrium of ionisation in water.



$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}H \rightleftharpoons R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\ominus}{O} + \overset{\oplus}{H}$$

The further the ionisation go to the right, the greater the acid strength. In other words.

$$Ka = \frac{\left[R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\ominus}{O}\right][\overset{\oplus}{H}]}{[RCOOH]}$$

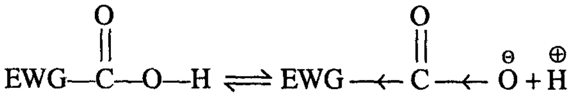
Acid strength ∝ *Ka*

or Acid strength ∝ concentration of acid anion

or Acid strength ∝ stability of acid anion

Thus strength of acid is the function of stability of acid anion.

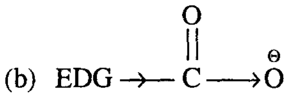
The influence of the inductive effect on acidity can be summarised as follows :

(a) 

$$EWG{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}H \rightleftharpoons EWG \leftarrow \overset{\overset{\displaystyle O}{\|}}{C} \leftarrow \overset{\ominus}{O} + \overset{\oplus}{H}$$

Electron withdrawing group (– *I* group) stabilises acid anion and strengthens the acid

or, $-I$ group increases strength of acid and thus :
Strength of acid $\propto -I$ power of the group present on —COOH

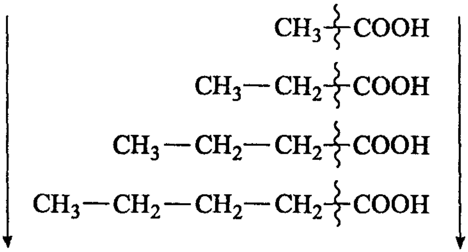

(b) $EDG \rightarrow\!- \overset{\overset{O}{\|}}{C} \longrightarrow \overset{\ominus}{O}$

Electron-donating groups (*i.e*, $+I$ group) destabilise acid anion and weaken the acid.
or, $+I$ group decreases strength of acid and thus :

$$\text{Strength of acid} \propto \frac{1}{+I \text{ power of the group present on —COOH}}$$

Consider the following homologous aliphatic acids :

Example 1.


CH_3-COOH
CH_3-CH_2-COOH
$CH_3-CH_2-CH_2-COOH$
$CH_3-CH_2-CH_2-CH_2-COOH$

+I power of alkyl groups are in increasing order

Acid strength in decreasing order

Example 2.

$Cl-CH_2-COOH \qquad Cl_2CH-COOH \qquad CCl_3-COOH$

$\longrightarrow$

$-I$ power is in increasing order,
acid strength is also in increasing order

Strength of Aliphatic Carboxylic Acids and Benzoic Acid

$\underset{\underset{+I\text{ group}}{\uparrow}}{R} \rightarrow\!-COOH \qquad \underset{\underset{-I\text{ group}}{\uparrow}}{C_6H_5} - \leftarrow\!-COOH$

Hence benzoic acid is stronger acid than aliphatic carboxylic acids but exception is formic acid. Thus

$HCOOH \qquad C_6H_5COOH \qquad RCOOH$

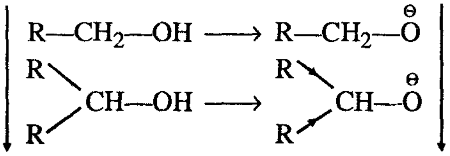
$\longrightarrow$

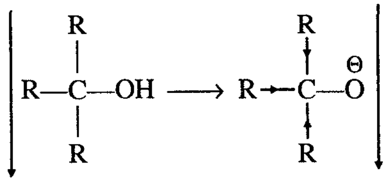
Acid strength in decreasing order

(E) Acidity of Alcohols : Acidity of alcohol depends on the stability of alkoxide ion (*i.e.*, conjugate base of alcohol) which is obtained by the dissociation of alcohols.

$$R-O-H \longrightarrow \underset{\text{Alkoxide ion}}{R-\overset{\ominus}{O}} + \overset{\oplus}{H}$$

Acid strength of alcohol $\propto$ stability of alkoxide ion





Acidity in decreasing order

Negative charge on oxygen is in increasing order; stability in decreasing order

1.2.10 Dipole Moment

As mentioned in the previous section, when two atoms of different electronegativities are joined by a covalent bond the atom which is more electronegative attracts the shared electron pair towards itself. The more electronegative atom acquires a partial negative charge and the counterpart atom acquires a partial positive charge. Development of polarisation in covalent bond constitutes a dipole. The value of dipole is called dipole moment or bond dipole moment (μ) and is expressed by the expression

$$\mu = q \times l$$

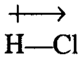
where q = charge in e.s.u.

l = bond distance in Å

The unit of dipole moment is (D) Debye unit

$$1\text{D} = 10^{-8} \text{ e.s.u.}$$

It is a vector quantity, its direction is indicated by an arrow parallel to the covalent bond and pointing towards the negative end. For example :



$$\overset{+\!\!\longrightarrow}{\mathrm{H{-}Cl}}$$

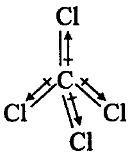
The value of dipole moment of some of the polar covalent bonds is given in Table 1.4.

Table 1.4. **Dipole moment of Some Bonds**

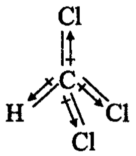
Bond	Dipole moment in D
C—H	0.4
C—F	1.41
C—Cl	1.46
C—N	0.22
C—O	0.74
C=O	2.3

The dipole moment associated with a particular bond is independent of the other bonds present in the molecule. The values in Table 1.4 may then be substituted in other real or theoretical compounds having that bonds and the dipole moment for such compounds can be calculated by vectorial addition.

The resultant of the vectorial addition of all groups yields overall dipole moment of a molecule. For example, $CHCl_3$ has a dipole moment of 1.87 D, whereas CCl_4 has no dipole moment as the resultant of four C—Cl bond moments is zero.

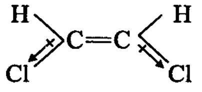


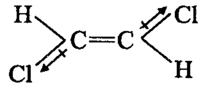
$\mu = 0$ D



$\mu = 1.87$ D

From the above examples it is clear that all molecules with polar bonds do not necessarily possess molecular dipoles, because individual bond moments are so oriented that they cancel one another. Any molecule that has a centre of symmetry will not have a dipole moment. The two geometric isomers of 1, 2-dichloroethylene illustrate this principle. Both molecules are planar, and both contain two polar carbon-chlorine bonds. The *cis* isomer has an appreciable dipole moment, since in this molecule the bond moments are so oriented as to provide overall electrical dissymmetry. The *trans* isomer has a zero dipole moment, since the two individual bond moments are aligned so as to cancel each other (as in the case of CCl_4).


cis-1,2-dichloroethene
$\mu = 1$ D

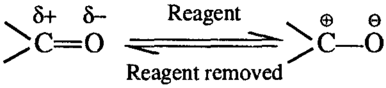

trans-1,2-dichloroethene
$\mu = 0$ D

1.2.11 Electromeric Effect (*E*)

It has been mentioned earlier that a multiple bond consists of σ and π-bonds. Due to the nature of π bonding the electrons involved in such a combination are loosely held and are easily polarisable. For example, when a multiple bond is exposed to an attacking reagent (say a nucleophile), the two electrons which form the π-bond are completely transferred to one atom or the other.

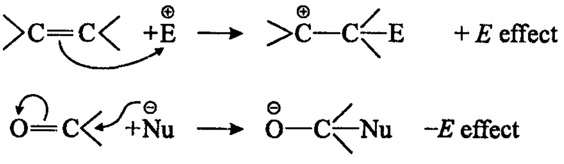
The effect, involving the complete transfer of a shared pair of electrons to one of the atoms joined by a multiple bond on the requirement of attacking reagent, is known as **electromeric effect.** This effect is a temporary effect and is brought into play on the requirement of the reagent. This effect may be illustrated with the help of the carbonyl group. The carbonyl group has a small positive charge on carbon and a small negative charge on oxygen due to the greater electronegativity of oxygen.

At the approach of a nucleophile (attacking reagent) the π-electron pair is completely transferred to oxygen atom and thus C atom acquires a positive charge and oxygen atom acquires a negative charge.



When the attacking reagent is removed, the molecule is reverted to its original electronic condition. This shows that electromeric effect is a polarisability effect and operates only in the excited sate. The electromeric effect is indicated by symbol *E* and is represented by a curved arrow (↷), the base of the arrow indicates the original position of the shared pair of electrons and the head indicates the position where the electron pair has migrated.

The electromeric effect is said to be +*E* when the electron displacement is towards the attacking reagent, and −*E* when it is away from the attacking reagent.

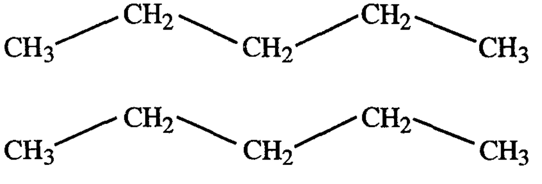


1.3 INTERMOLECULAR FORCES

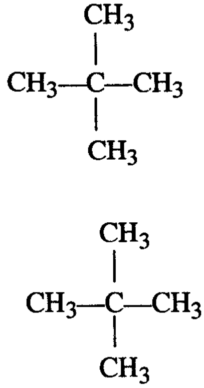
Most of the physical properties of covalent compounds depend on the nature of intermolecular interactions or intermolecular forces. There are three types of intermolecular forces which dictate the physical properties of the molecules. The three different types of forces are (i) van der Waals forces (ii) dipole association or dipole-dipole interactions (iii) hydrogen bonds.

1.3.1 van der Waals Forces

Neutral molecules have balanced number of negative electrons and positive charges on the nucleus. Yet since the electrons are in constant motion, the centre of density of negative charges does not coincide continuously with the centre of density of the positive charges. This situation produces small instantaneous local dipoles; that is, areas with a positive and negative ends which behave as small electromagnets. When molecules are close enough these dipoles attract each other. Such attraction is called van der Waals attraction or van der Waals forces. The more electrons a molecule has, the more polarisable it is, and the more important the van der Waals attraction. Thus the larger a hydrocarbon (neutral molecules) is, the more polarisable it is, the more the molecules stick together. For the van der Waals attraction to be most effective, the molecules must be able to touch large portions of their surfaces together. Two molecules of *n*-pentane can touch better than two molecules of neopentane, as shown below :



Two molecules of *n*-pentane

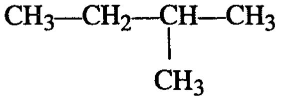


Two molecules of neopentane

Spheres have the minimum surface area for their volume of any geometrical figures. Consequently, the more spherical molecules become, the lower is their boiling points. This is a very general phenomenon. The following examples will illustrate this phenomenon :

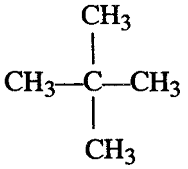
$CH_3—CH_2—CH_2—CH_2—CH_3$

n-pentane
bp 36°C



$CH_3—CH_2—CH(CH_3)—CH_3$

2-methylbutane
bp 28°C

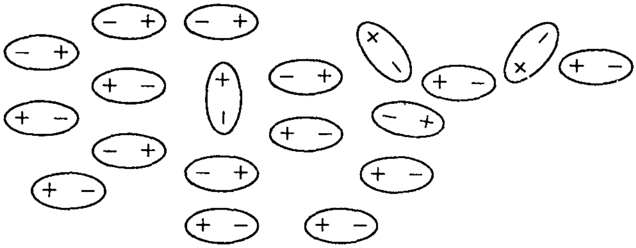


$CH_3—C(CH_3)_2—CH_3$

neopentane
bp 9.5°C

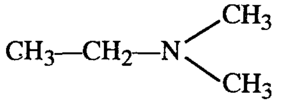
1.3.2 Dipole-Dipole Interactions

Unequal sharing of electrons in covalent bonds results in both dipoles and their magnitudes are indicated by the bond moments (μ). Strong intermolecular forces arise from interaction of the electric dipoles found in unsymmetrical molecules. In both liquids and solids, there is a strong tendency for dipoles to become aligned and to hold molecules together. As a consequence, compounds that have large dipole moments usually melt and boil at much higher temperatures than non-polar compounds of comparable molecular weight. In the liquid phase, molecules tend to orient themselves so that the positive end of the dipole of one molecule is close to the negative pole of another. Thus molecules attract one another. Thermal motions of the molecules tend to upset this order. Arrangements of molecules is shown below :

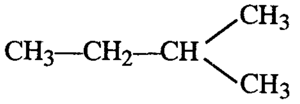


Ordered structure of liquid resulting from dipole-dipole interactions

Since this attraction (attraction due to dipole-dipole interaction) has to be overcome in order to vaporize the liquid, the polar molecules tend to have higher boiling points than do their non-polar derivatives. For example :



bp 37.5°C
MW 73

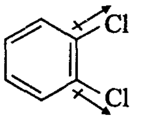


bp 30°C
MW 72

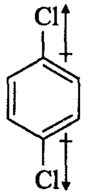
CH_3—O—CH_3
bp – 25°C
MW 46

$CH_3CH_2CH_3$
bp – 45°C
MW 44

Strong dipole-dipole interactions may arise between molecules that contain polar bonds but have no dipole moments because of their symmetry properties. The dipoles associated with bonds in two different molecules may align themselves in such a way as to provide some intermolecular compensation for charge separation. A comparison of the physical properties of *o*-chlorobenzene and *p*-chlorobenzene indicates that, although the *ortho* isomer possesses a significant dipole moment and the *para* isomer none, the two isomers have comparable boiling points and the *p*-isomer is the higher melting than the *o*-isomer.

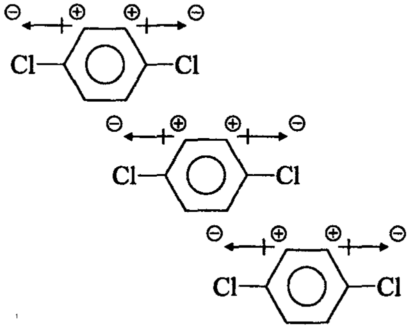


mp – 18°, bp 179°C



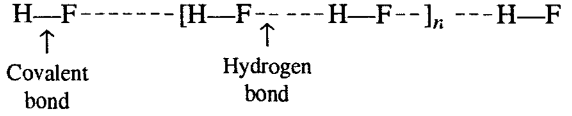
mp 53°, bp 174°C

In the liquid state, the molecules of the *para* isomer can arrange themselves in the manner formulated below :



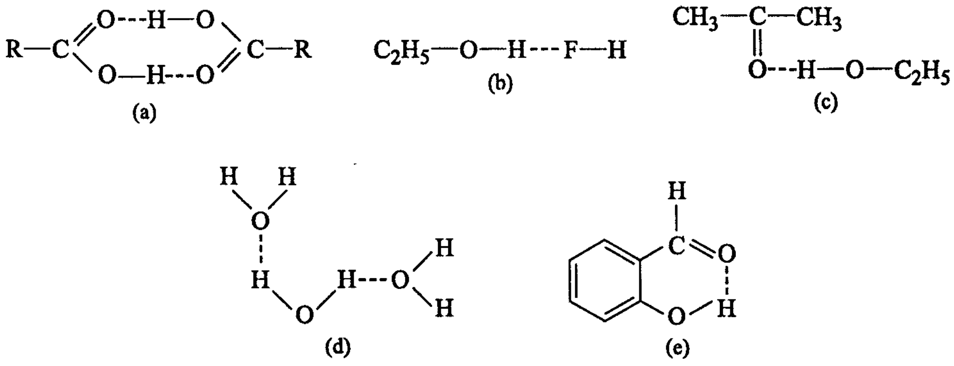
1.3.3 Hydrogen Bonding

When a hydrogen atom is bonded covalently to a highly electronegative atom having a small nucleus (like O, N, F, S, etc.), the bonding electron pair is drawn almost completely towards the electronegative atom. Such hydrogen atom acquires a special ability to attract and associate with the other electron rich atoms or group of atoms (O, N, F, etc.) towards itself. This attraction or weak link established between hydrogen and a second electronegative atom or group is known as hydrogen bond. In hydrogen bonding hydrogen atom may act as a bridge between two electronegative atoms (same or different), holding one electronegative atom by a covalent bond and the other by electrostatic force. This kind of electrostatic attraction is a special case of dipole-dipole association and is of great practical importance. Usually a hydrogen bond is represented by a dashed line rather than by the solid line used for a covalent bond.



$$\underset{\substack{\uparrow\\ \text{Covalent}\\ \text{bond}}}{H\text{—}F}\text{-------}[H\text{—}\underset{\substack{\uparrow\\ \text{Hydrogen}\\ \text{bond}}}{F\text{---}}\text{---}H\text{—}F\text{--}]_n\text{---}H\text{—}F$$

Being electrostatic in nature, it is much weaker than a normal covalent bond. The hydrogen bond energy is only 2–10 kcal/mole as compared to the covalent bond energy of 50–100 kcal/mole, but it is greater than van der Waals attraction which is < 1 kcal/mole. A hydrogen bond in H—Z will be effective only when Z is strongly electronegative and is small in size. When the electronegativity is not high or if the atom (Z) has a large atomic radius, the electrostatic forces will be weak and the hydrogen bond will not be very effective. For example, chlorine which has electronegativity comparable to that of nitrogen, still does not form effective hydrogen bond due to its relatively large size.

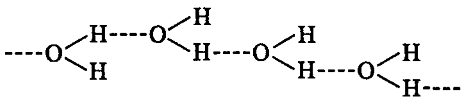


Hydrogen bonding in different molecules

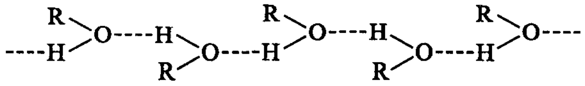
The strongest and the most important hydrogen bonds are those in which both of the electronegative atoms involved are O, N or F.

The hydrogen bonds are of two types :

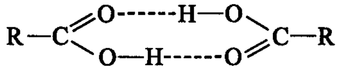
(a) Intermolecular hydrogen bond : Intermolecular hydrogen bond is formed between atoms of two or more molecules, resulting in the association of molecules. For example, water and alcohols are associated as polymeric aggregates in liquid and solid states whereas carboxylic acids and amides exist as dimer in the liquid and gaseous phase due to intermolecular hydrogen bonding.



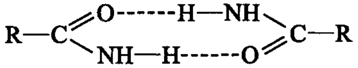
Polymeric form of water molecule (intermolecular hydrogen bond)



Polymeric form of alcohol molecule (intermolecular hydrogen bond)

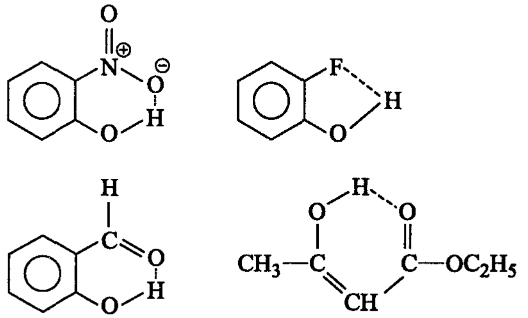


Dimeric form of carboxylic acids (intermolecular hydrogen bonding)



Dimeric form of amides (intermolecular hydrogen bonding)

(b) Intramolecular hydrogen bonding : Intramolecular hydrogen bond is formed between two atoms within the same molecule. This results in the formation of five or six membered ring (chelate ring).



Intramolecular hydrogen bonding

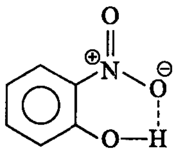
Effect of Hydrogen Bonding on Properties

Hydrogen bonding has marked effect on the properties of involved molecules, such as mp, bp, solubility, acidity, spectra, chemical properties of some functional groups and biological properties.

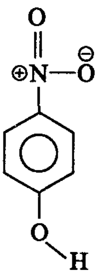
1. M.P. and B.P. : Intermolecular hydrogen bonding resulting in the association of molecules raises melting and boiling points because some extra amount of energy is required to break the hydrogen bond. For example :

$CH_3—O—CH_3$	CH_3CH_2OH	H_2S	H_2O
M. Wt. 46, b.p. – 25°C	M. Wt. 46, b.p. 78°C	M. Wt. 34, b.p. – 59.5°C	M. Wt. 18, b.p. 100°C
(Intermolecular hydrogen bonding not possible)	(Strong intermolecular hydrogen bonding)	(No intermolecular hydrogen bonding)	(Strong intermolecular hydrogen bonding)

On the other hand, the intramolecular hydrogen bonding decreases the mp and bp because it prevents association through intermolecular hydrogen bonding. For example, *o*-nitrophenol has mp 45°C (steam volatile) while *p*-nitrophenol has mp 114°C (non-volatile in steam).



Forms stable six-membered chelate ring by intramolecular hydrogen bonding which prevents association through intermolecular hydrogen bonding.

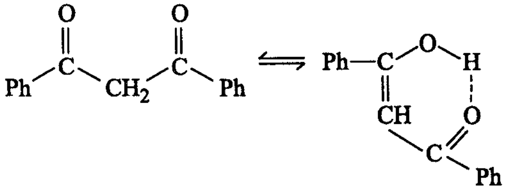


— NO_2 and — OH are too distant, hence no chelation through intramolecular hydrogen bonding is possible. Association due to intermolecular hydrogen bonding occurs which raises the mp.

2. Solubility : Solubility of a substance increases tremendously when hydrogen bonding is possible between solute and solvent. For example, solubility of alcohols and sugars in water. Where hydrogen bonding with solvent molecules is not possible the solubility is of very low order, *e.g.*, ethers, esters and hydrocarbons are very less soluble in water.

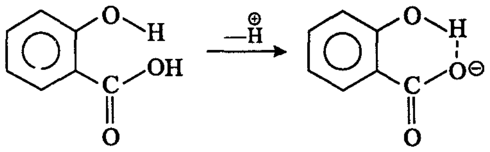
The intramolecular hydrogen bonding hinders water solubility of substances owing to their failure to form association with water molecules, *e.g.*, *o*-nitrophenol is less soluble in water than *p*-nitrophenol because the former forms intramolecular hydrogen bond while the latter does not.

3. Chemical properties : Some chemical properties are also influenced by hydrogen bonding. One of the most important is the absence of functional group properties in typical cases. Almost complete inactivity of carbonyl as well as hydroxyl function in dibenzoylmethane is largely due to very effective intramolecular hydrogen bonding. Dibenzoylmethane neither forms Schiff bases nor addition compounds with HCN (properties of C=O group). It does not undergo acetylation with acetic anhydride and does not liberates N_2 with diazomethane (properties —OH group).



4. Spectral properties : Hydrogen bonding shifts the positions of bands (peaks) in ultraviolet (UV), infrared (IR) and ^1H NMR spectra.

5. Acidity of carboxylic acids : If one or two hydroxyl groups are *ortho* to carboxylic function, the resulting intramolecular hydrogen bonding stabilises the carboxylate ion and so increases the dissociation (acidity) of the acid, *e.g.* :



pKa = 2·98, the *pKa* of the *p* isomer is 4·58 and that of benzoic acid is 4·17

For similar reasons maleic acid (*pKa* = 1.92) is more acidic than fumaric acid (*pKa* = 3.02).

1.4 INCLUSION COMPOUNDS

For decades the choleic acids, the blue colour of starch iodine mixture and the hydrate of chlorine gas were chemical oddities. Suddenly, following the accidental discovery of the crystalline urea complex of octyl alcohol by Bengen in 1940, there was a tremendous burst of activity and interest in these compounds by the oil companies. It was soon discovered that these complexes, referred to as **inclusion compounds**, have several valuable commercial and laboratory uses.

The inclusion compounds are of two general types, the **cage** or **clathrates** (*Gr* = lock) and the **channel** compounds.

Cage Compounds (Clathrates)	Channel Compounds
Quinols Gas hydrates, etc.	Urea complexes, cyclodextrins, chloleic acids, biphenyls, etc.

These compounds have one underlying principle in common : their formation depends on the spatial "fitting in" of the guest molecules into the crystal lattice cavities or the "holes" of liquid aggregates of host molecules.

There is no chemical affinity between the **host** and **guest** molecules in the usual sense, *e.g.*, inclusion compounds of even the inert gases have been formed. Inclusion compound formation depends upon the size and shape of the **guest** molecules and the reciprocal size of the cavities created by the host molecules. This brings about a very close contact of the molecules, and the short-range van der Waals forces become significant factors for compound formation.

1.4.1 Cage Compounds

(i) The first clathrate compounds, hydroquinone —H_2S was reported by Wohler in 1849.

The quinols, which are hydroquinone and phenol inclusion compounds [Fig. 1.12] have been studied in greater detail. The clathrate formation arises by three hydroquinone molecules forming a cup through hydrogen bonds and two such units forming cage for guest molecules. Compound formation dependant upon the size of the guest molecules. For example, hydroquinone will form quinols with methyl alcohol and argon but not with eltyl alcohol (too large) or helium (too small).

(ii) Hydrates : The gas and salt hydrates consist of crystalline compounds in which water molecules form cavities within which guest molecules (gases : CO_2, SO_2, Cl_2, Kr, CH_4 etc. salts : ammonium salts) are trapped. Cubic unit cell is formed by polyhedra made up of twenty or more water molecules held together by hydrogen bonds.

The first gas hydrate, chlorine hydrate ($6Cl_2 . 46\, H_2O$) was discovered by Davy (1810). Gas hydrates are now used for desalting seawater.

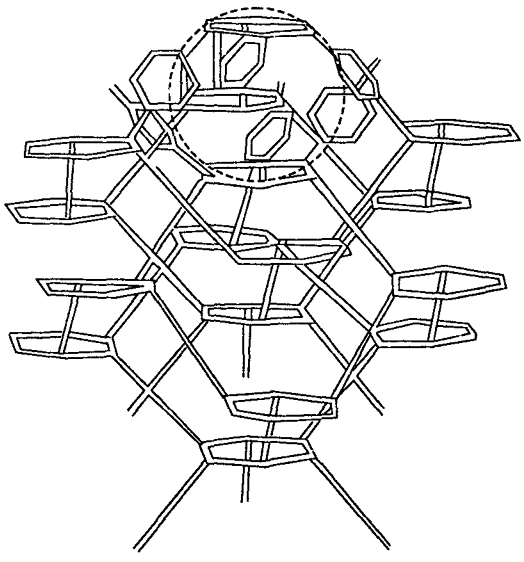


Fig. 1.12. Structure of quinol clathrates.

1.4.2 Channel Compounds

The most common example of this class is the **urea complexes**. Guests of urea complexes are *n*-alkanes and their straight chain derivatives. In the presence of straight chain hydrocarbons, urea

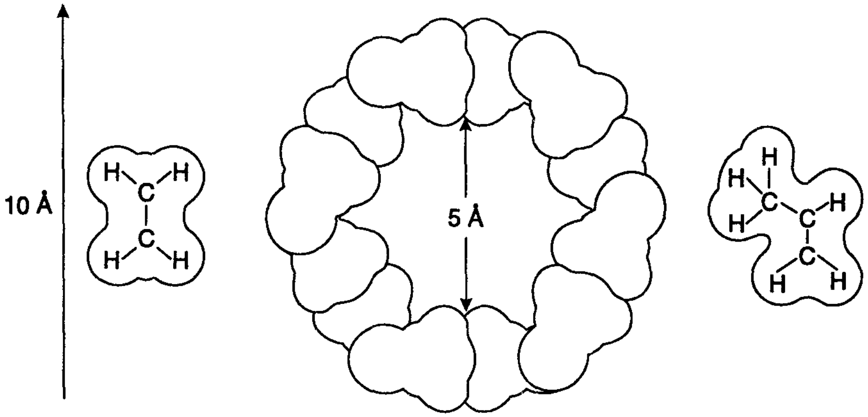


Fig. 1.13. Dimensions of the urea channel compared to the van der Waals diameters of long-chain and branched-chain hydrocation molecules.

crystalises in the form of parallel tubes or helices with the urea molecules arranged stepwise in head to tail hydrogen bonding and forming hexagonal unit cells. The diameter of the central channel is about 5Å which is just the right size to hold straight-chain hydrocarbon molecules [or their straight-chain derivatives] in a planar, zig-zag configuration (Fig. 1.13). On the other hand, branched chains are too large to fit into the channel and rarely form inclusion compounds with urea. Inclusion compound formation occurs most readily with straight chains of six carbon atoms or more. About 0.7 molecules of urea are required per —CH_2— group of the guest molecule. X-ray diffraction investigations show that urea normally crystallises in a tetragonal structure, but in a helical inclusion compound, the N—H---O bond distances are 0.05Å shorter than in tetragonal urea. Apparently in the presence of the guest molecules urea can crystallise in the helical structure and the complex owes its stability largely to the formation of strong hydrogen bonds and van der Waals forces between the closely packed molecules.

The heats of formation of the urea complexes is about 1 kcal/mole of urea or 1–2 kcal per —CH_2— unit of guest molecule.

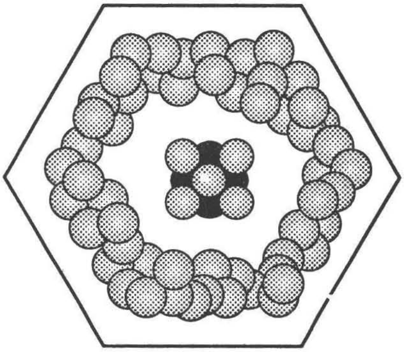


Fig. 1.14. Guest molecule in a urea lattice.

1.4.3 General Methods of Preparation of Inclusion Compounds

Inclusion compounds can be prepared by the following general methods :

(i) Crystallisation of host in the presence of guest molecules.

(ii) If host is soluble in guest component, crystallisation of host from a solution in which guest is solvent.

(iii) A common solvent (which itself is not clathrated) can be used if host is insoluble in guest component.

(iv) Urea complexes are prepared by mixing hot methanolic solution of urea and of the guest and allowing to crystallise upon cooling.

(v) The quinol-inert gas, clathrates are obtained by crystallising hydroquinone under pressure of the noble gas.

1.4.4 Important Uses of Inclusion Compounds

The most common inclusion compound used in analytical chemistry is the use of starch-iodine compound. If starch has some impurities such as fatty acids, then it will not trap iodine to give a blue colour. The general use of inclusion compounds fall into two main categories :

(1) Resolution of Mixtures :

(i) Removal of straight chain hydrocarbons present in petroleum through urea complexation from hydrocarbon mixture.

(ii) Removal of free fatty acids from oils or waxes by treatment with moist urea.

(iii) Separation of saturated and unsaturated fatty acids by urea adduct formation.

(iv) *cis-trans* isomers can be separated by urea complexation.

(v) Separation of benzene from cyclohexane (both having very close boiling points). Both can be separated by treating the mixture with wet thiourea and filtering out the cyclohexane complex. The complex when shaken with water gives pure cyclohexane as water dissolves thiourea.

(2) Storage of substances : Certain substances can be protected for long time in the form of inclusion complexes. For example, auto-oxidation of oleic acid does not occur when the acid is in the form of urea complex.

The clathrates of inert gases provide a convenient method of despersing the gases without restoring to high pressure cylinders.

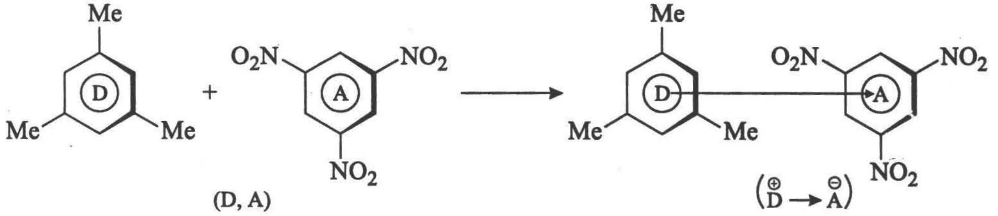
1.4.5 Charge Transfer Complexes

Molecular adducts formed by mixing an electron-rich molecule (called donor molecule, D) and an electron-defficient molecule (called acceptor molecule, A) in 1 : 1 ratio are termed as **charge transfer complexes.** A donor molecule is a molecule capable of donating either *non-bonding* or π-electrons. These complexes are considered to be hybrids of the following resonance forms :

$$D + A \rightleftharpoons \underset{(1)}{D\text{-----}A} \longleftrightarrow \underset{(2)}{\overset{\oplus}{D}\overset{\ominus}{A}}$$

Form (1), being the major contributor, does not involve formal covalent bond and the binding forces between these molecules may **be weak coulombic forces.** A bonding of such type which results from attractive forces between donor and acceptor molecule is called *charge transfer interaction.*

Formation of the so called picrate by the action of picric acid and an aromatic hydrocarbon probably represents the most common example of such addition compounds. The nitro groups rather than a hydroxyl group are essential for the success of the reaction, as not only picric acid but other aromatic compounds such as 1, 3, 5-trinitrobenzene, form similar addition compounds. In these complexes the aromatic rings are held in parallel planes.



Charge transfer complex between picric acid and 1, 3, 5-trimethyl benzene

The formation of charge-transfer complex is facilitated by the presence of electron- donating substituents in donor molecule and electron-withdrawing substituents in acceptor molecule. The distance between the donor and accepter molecules in charge transfer complexes is 3–3.5Å. The extent of charge-separation in a charge-transfer complex is often reflected in ground state properties such as dipole moment. Charge transfer complexes display significant dipole moment.

VERY SHORT ANSWER QUESTIONS

1. Which of the following compounds has a longer C=C bond and why?

$$CH_3—CH=CH_2 \text{ and } CH_2=CH_2$$

2. An aqueous solution of tropylium bromide gives light yellow precipitate of AgBr on treatment with $AgNO_2$. Explain.
3. Why is *o*-nitrophenol is steam volatile but *p*-nitrophenol is not?
4. Explain why the boiling point of ethylene glycol is much lower than that of glycerol?
5. Which of the following species are aromatic?

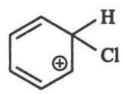

I


II


III


IV


V



VI

6. In with of the following species all the carbon atoms are in sp^2 hybrid state?

$CH_2{=}CH{-}\overset{\oplus}{C}H_2$

I

II

III

$CH_2{=}C{=}CH_2$

IV

$CH_2{=}CH{-}CH_2{-}CH{=}CH_2$

IV

VI

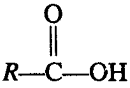
7. Which of the following are planar molecules?
   - (a) $CH_2{=}CH{-}CH{=}CH_2$
   - (b) Chlorobenzene
   - (c) Formic acid
   - (d) Acetone
   - (e) Formaldehyde
   - (f) Cyclohexene

8. Arrange the following compounds according their decreasing bond lengths :

   (a) $CH_2{=}CH_2$ (b) $HC{\equiv}CH$ (c)  (d) $CH_3{-}CH_3$

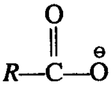
9. Which of the following compounds are polar and which are nonpolar?
   - (a) CO_2
   - (b) CCl_4
   - (c) CH_3OH
   - (d) CH_3Cl
   - (e) *p*-dichlorobenzene
   - (f) *o*-dichlorobenzene

10. Which of the following is more stabilised by resonance and why?



$R{-}\overset{\overset{O}{\|}}{C}{-}OH$

(I)



$R{-}\overset{\overset{O}{\|}}{C}{-}\overset{\ominus}{O}$

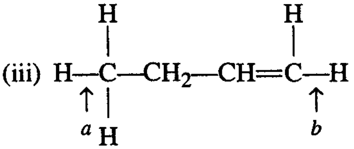
(II)

PROBLEMS WITH SOLUTIONS

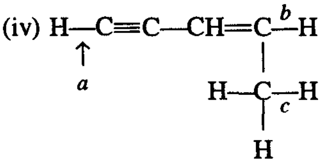
1. In which of the following compounds delocalized bonding is not possible?
   - (a) 1, 3-butadiene
   - (b) 1, 4-pentadiene
   - (c) 1, 3, 5-hexatriene
   - (d) benzene
2. In which of the following compounds C—H bond length is minimum?
   - (a) ethane
   - (b) ethene
   - (c) 1, 2-dichloroethene
   - (d) 1, 2-dichloroethane
3. Arrange the following in order of increasing bond strength :
   - (i) $N{\equiv}N$, $H_2N{-}NH_2$, $HN{=}NH$
   - (ii) Cl_2, I_2, F_2, Br_2
   - (iii) N_2, O_2, F_2
4. In the following structures some bonds are labelled *a*, *b*, *c*. List these bonds in order of decreasing bond length :

   (i) $CH_3\underset{\underset{c}{\uparrow}}{-}CH_2\underset{\underset{b}{\uparrow}}{-}CH\underset{\underset{a}{\uparrow}}{=}CH_2$

   (ii) $CH_3\underset{\underset{a}{\uparrow}}{-}CH_2{-}C\underset{\underset{c}{\uparrow}}{\equiv}C\underset{\underset{b}{\uparrow}}{-}CH_3$

   (iii) 

   $H\underset{\underset{a}{\uparrow}}{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}CH_2{-}CH{=}\overset{\overset{H}{|}}{C}\underset{\underset{b}{\uparrow}}{-}H$

   (iv) 

   $H\underset{\underset{a}{\uparrow}}{-}C{\equiv}C{-}CH{=}\underset{\underset{H-\underset{\underset{H}{|}}{C}\overset{c}{-}H}{|}}{C}\overset{b}{-}H$

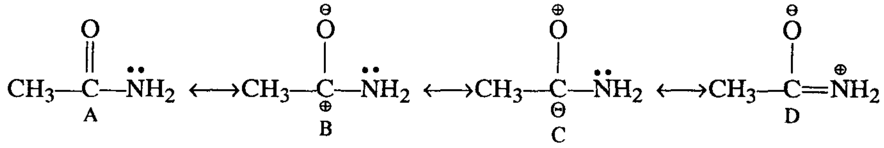
5. Which among the given compounds is most stable?
   - (a) 1-butene
   - (b) *trans*-2-butene
   - (c) *cis*-2-butene
   - (d) 2, 3-dimethyl-2-butene

6. Which of the following resonating structures is the major contributor to the resonance hybrid?

$$\underset{(I)}{CH_3-CH_2-\overset{\oplus}{C}H-\underset{\bullet\bullet}{\overset{\bullet\bullet}{O}}-CH_3} \longleftrightarrow \underset{(II)}{CH_3-CH_2-CH=\underset{\bullet\bullet}{\overset{\oplus}{O}}-CH_3}$$

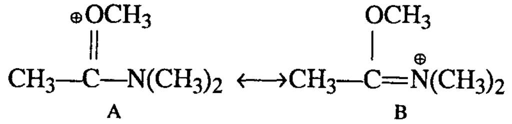
(a) I
(b) II
(c) both have equal contribution
(d) they are not resonating structures

7. In each of the following sets, which resonating structure is the major contributor to the real structure?



(i) $\underset{A}{CH_3-\overset{\overset{O}{\|}}{C}-\ddot{N}H_2} \longleftrightarrow \underset{B}{CH_3-\overset{\overset{\ominus}{O}}{\overset{|}{\underset{\oplus}{C}}}-\ddot{N}H_2} \longleftrightarrow \underset{C}{CH_3-\overset{\overset{\oplus}{O}}{\overset{|}{\underset{\ominus}{C}}}-\ddot{N}H_2} \longleftrightarrow \underset{D}{CH_3-\overset{\overset{\ominus}{O}}{\overset{|}{C}}=\overset{\oplus}{N}H_2}$

(ii) $\underset{A}{CH_2=CH-\underset{\bullet\bullet}{\overset{\bullet\bullet}{O}}-CH_3} \longleftrightarrow \underset{B}{\overset{\ominus}{C}H_2-CH=\underset{\bullet\bullet}{\overset{\oplus}{O}}-CH_3}$



(iii) $\underset{A}{CH_3-\overset{\overset{\oplus OCH_3}{\|}}{C}-N(CH_3)_2} \longleftrightarrow \underset{B}{CH_3-\overset{\overset{OCH_3}{|}}{C}=\overset{\oplus}{N}(CH_3)_2}$

(iv) $\underset{A}{\overset{\ominus}{C}H_2-CH=CH-\overset{\ominus}{O}} \longleftrightarrow \underset{B}{CH_2=CH-\overset{\oplus}{C}H-\overset{\ominus}{O}}$

(v) $\underset{A}{CH_2=CH-\overset{\ominus}{O}} \longleftrightarrow \underset{B}{\overset{\ominus}{C}H_2-CH=O}$

(vi) $\underset{A}{\overset{\ominus}{C}H_2-C\equiv N} \longleftrightarrow \underset{B}{CH_2=C=\overset{\ominus}{N}}$

8. Which of each of the following pairs of ions is more stable?

(i) $\underset{I}{CH_3CH_2\overset{\ominus}{O}}$ $\qquad \underset{II}{CH_2=CH-\overset{\ominus}{O}}$

(ii) $\underset{I}{(CH_3)_2\overset{\ominus}{C}-CH=O}$ $\qquad \underset{II}{(CH_3)_2\overset{\ominus}{C}-CH=CH_2}$

(iii) $\underset{I}{Me_2\ddot{N}-CH=CH-CH=\overset{\oplus}{N}Me_2}$ $\qquad \underset{II}{Me\underset{\bullet\bullet}{\overset{\bullet\bullet}{O}}-CH=CH-CH=\overset{\oplus}{N}Me_2}$

9. In which of the following organic species all the carbon atoms are in the same hybrid state?

(a) $CH_2=C=CH_2$
(b) $CH_3-\overset{\oplus}{C}H-CH_3$
(c) $CH_3-C\equiv CH$
(d) $CH_2=CH-\overset{\oplus}{C}H_2$

10. Consider the following compound :

$$\underset{1}{CH_2}=\underset{2}{CH}-\underset{3}{CH}=\underset{4}{CH_2}$$

Carbon-carbon bond length between C_2 and C_3 will be :

(a) 1.54 Å
(b) 1.34 Å
(c) 1.20 Å
(d) less than 1.54 Å and greater than 1.34 Å

11. Consider the following three halides :

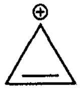
$$\underset{\text{(I)}}{CH_3CH_2{-}Cl} \quad \underset{\text{(II)}}{CH_2{=}CH{-}Cl} \quad \underset{\text{(III)}}{C_6H_5{-}Cl}$$

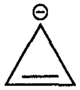
Arrange C—Cl bond length of these halides in decreasing order :

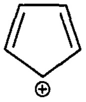
(a) I > II > III (b) I > III > II

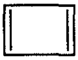
(c) III > II > I (d) II > III > I

12. Which of the following possesses aromaticity?

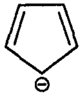
(a) 

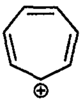
(b) 

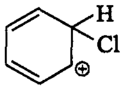
(c) 

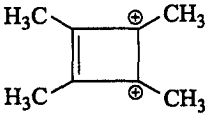
(d) 

13. Which of the following is not aromatic?

(a) 

(b) 

(c) 

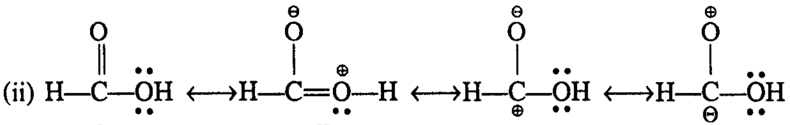
(d) 

14. Predict the most reasonable type of hybridisation and shape in species having interorbital bond angle of :

(a) 165° (b) 118° and (c) 107°.

15. Giving reason, arrange the following resonating structures in the order of decreasing stability.

(i) $\underset{\text{I}}{CH_2{=}CH{-}\ddot{\underset{..}{Cl}}\!:} \longleftrightarrow \underset{\text{II}}{\overset{\ominus}{C}H_2{-}CH{=}\overset{\oplus}{\underset{..}{Cl}}\!:} \longleftrightarrow \underset{\text{III}}{\overset{\oplus}{C}H_2{-}CH{=}\overset{\ominus}{\underset{..}{Cl}}\!:}$



$$\text{(ii)}\ \underset{\text{I}}{H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\ddot{\underset{..}{O}}H} \longleftrightarrow \underset{\text{II}}{H{-}\overset{\overset{\ominus}{\overset{\displaystyle O}{|}}}{C}{=}\overset{\oplus}{\underset{..}{O}}{-}H} \longleftrightarrow \underset{\text{III}}{H{-}\underset{\oplus}{\overset{\overset{\ominus}{\overset{\displaystyle O}{|}}}{C}}{-}\ddot{\underset{..}{O}}H} \longleftrightarrow \underset{\text{IV}}{H{-}\underset{\ominus}{\overset{\overset{\oplus}{\overset{\displaystyle O}{|}}}{C}}{-}\ddot{\underset{..}{O}}H}$$

16. Explain why 1, 3, 5-cycloheptatrienyl cation is aromatic but 1, 3, 5-cycloheptatriene is not?

17. Indicate the hybrid state of each carbon in the following chemical species :

(a) $CH_3{-}CH{=}C{=}CH{-}C{\equiv}N$ (b) $N{\equiv}C{-}C{\equiv}N$ (c) $CH_2{=}CH{-}\overset{\oplus}{C}H_2$

18. Which of the following types of compounds belong to the charge transfer complex category :

(a) Clathrates (b) Picrates

(c) Inclusion compounds (d) Channel compounds

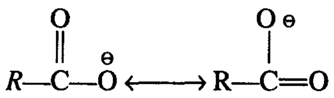
PROBLEMS FOR SELF ASSESSMENT

1. Giving examples, discuss the application of hyperconjugation in explaining the stability of olefins and carbocations.
2. Write short notes on :
   (a) Clathrates (b) Charge transfer complexes
   (c) Channel compounds
3. Discuss the following :
   (a) Inductive and field effects (b) Steric inhibition of resonance
   (c) Hückel $(4n+2)\ \pi$ rule (d) Hydrogen bonding

4. An aqueous solution of tropylium bromide on treatment with silver nitrate gives precipitate of silver bromide. How will you account for this observation?
   (**Hint.** It is largely an ionic compound because the tropylium ion is highly stabilised due to its aromaticity).
5. Define and explain the following :
   (a) Bond length (b) Bond angle (c) Bond energy
6. One mole cyclooctatetraene reacts with two moles of potassium. Comment on the stability of the compound formed.
   (**Hint.** Two moles of K remove two protons leaving behind a doubly negatively charged anion which now has 10 π electrons fitting in the Hückel rule, hence the compound is quite stable due to aromaticity).
7. Compare the following :
   (a) Resonance and hyperconjugation (b) Inductive and electromeric effects
   (c) *Sigma* (σ) and *pi* (π) bonds (d) Valence bond and molecular orbital theories
8. Giving suitable examples, discuss the following :
   (a) Delocalisation involving π, π-conjugation (b) Delocalisation involving π, *p*-conjugation
   (c) Cross-conjugation

ANSWER TO VERY SHORT ANSWER QUESTIONS

1. Because of hyperconjugation $CH_3—CH=CH_2$ has a longer C=C bond than $CH_2=CH_2$.
2. Tropylium bromide ionises to give an aromatic (stable) cycloheptatrienyl cation (tropylium ion) and bromide ion. The bromide ion reacts with $AgNO_3$ to give a light yellow precipitate of AgBr. The driving force for this ionisation is the aromatic character of the tropylium ion due to high resonance energy.
3. *o*-Nitrophenol undergoes intramolecular hydrogen bonding (chelation) whereas *p*-nitrophenol forms intermolecular hydrogen bonding (association). Therefore, vapour pressure of *o*-nitrophenol is higher than that of *p*-nitrophenol, hence the former is steam volatile.
4. Because of the presence of three —OH groups, glycerol undergoes more extensive intermolecular hydrogen bonding than ethylene glycol which has only two —OH groups.
5. II and IV are aromatic because they follow Hückel rule.
6. I, II and III.
7. (a), (b) and (e) are planar.
8. (d) > (c) > (a) > (b)
9. (a), (b) and (e) are nonpolar. (c), (d) and (f) are polar.
10. There are the following equivalent resonating structures for II, hence it is more stabilised by resonance.



$$R—\overset{\overset{\displaystyle O}{\|}}{C}—\overset{\ominus}{O} \longleftrightarrow R—\overset{\overset{\displaystyle O^{\ominus}}{|}}{C}=O$$

SOLUTIONS OF PROBLEMS

1. (b) 2. (c)
3. (i) $H_2N—NH_2, HN=NH, N\equiv N$ (ii) I—I, Br—Br, Cl—Cl, F—F
   (iii) F—F, O=O, $N\equiv N$

4. (i) $c > b > a$ (ii) $a > b > c$ (iii) $a > b$ (iv) $c > b > a$
5. (d) **6.** (b)
7. (i) A (ii) A (iii) B (iv) B (v) A (vi) B
8. (i) II (ii) I (iii) I (vi) B
9. (d) **10.** (d) **11.** (a) **12.** (a) **13.** (c)
14. (a) *sp* (linear) (b) sp^2 (trigonal planar) (c) sp^3 (tetrahedral)

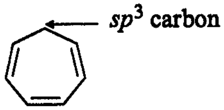
15. (i) I is more stable because it has no formal charge. III is the least stable because it has an electron deficient carbon. Thus, the order of stability is :

I > II > III

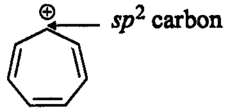
(ii) I and II have greater number of covalent bonds, hence these are more stable than either III or IV. Further, between I and II, I has no formal charge, hence is stabler than II. IV is less stable than III because in IV +ve charge is on oxygen which is more electronegative atom than the carbon on which +ve charge is present in III. Thus, the order of stability is :

I > II > III > IV

16. 1, 3, 5-Cycloheptatriene, although has 6π-electrons in three carbon-carbon double bonds, the presence of an sp^3 hybridised carbon prevents the cyclic overlap of *p*-orbitals, hence the compound is not aromatic.



Cycloheptatriene
(not aromatic)



Cycloheptatrienyl cation
(aromatic)

In 1, 3, 5-cycloheptatrienyl cation, the vacant *p*-orbital of the cationic (sp^2) carbon allows cyclic overlap of 6π-electrons, hence it is aromatic.

17. (a) $\underset{\substack{\uparrow\\ sp^3}}{CH_3}—\underset{\substack{\uparrow\\ sp^2}}{CH}=\underset{\substack{\uparrow\\ sp}}{C}=\underset{\substack{\uparrow\\ sp^2}}{CH}—\underset{\substack{\uparrow\\ sp}}{C}\equiv N$ (b) $N\equiv\underset{\substack{\uparrow\\ sp}}{C}—\underset{\substack{\uparrow\\ sp}}{C}\equiv N$ (c) $\underset{\substack{\uparrow\\ sp^2}}{CH_2}=\underset{\substack{\uparrow\\ sp^2}}{CH}—\underset{\substack{\uparrow\\ sp^2}}{\overset{\oplus}{C}H_2}$

18. (b)

Chapter 2

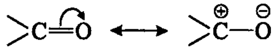
MECHANISM OF ORGANIC REACTIONS

Conversion of a chemical compound into another chemical compound is known as a **chemical reaction**. Organic reactions usually involve the fission and formation of covalent bonds. Organic reactions take place in accordance with general fundamental concepts of thermodynamics. Usually the sequence and timing of these bond breaking and bond forming processes are important in the study of these reactions. These processes may occur separately, for example, bond breaking may proceed bond formation or *vice-versa* resulting in a **step-wise reaction**. Alternatively, bond breaking and bond formation may occur simultaneously. Formation of bond and breaking of bond taking place simultaneously give rise to **synchronous** or **concerted** reactions. A reaction occurring in several steps, results in formation of reaction **intermediates** which may or may not be isolated. The concerted reactions take place via the formation of an imaginary **transition state** or **activated complex**. *A mechanism of organic reaction may be described as the detailed description of the sequence of steps in going from the reactants to the products, or the detailed path undertaken by the reactants in order to get converted into product.*

2.1 ARROW NOTATION (FORMALISM)

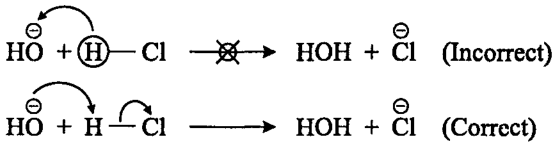
Organic reactions usually involve the fission and formation of covalent bonds. The covalent bond is often represented as a dash (–) and the movement of a pair of electrons is shown by a curved arrow (↷). In fact, arrow formalism (notation) is very important for organic reactions. Arrows in chemical drawing have specific meanings. Just as it is important to learn the structural representation and names of molecules, it is important to learn the language of **arrow formalism** in organic chemistry. The arrow formalism will help us follow the course of complex reactions only if we learn to apply it properly.

(i) *The curved arrows are used to show the movement of electrons in reactions and in resonance structures.* Therefore, curved arrows always start at the initial position of electrons and end at their final position.



$$>C{=}O \longleftrightarrow >\overset{\oplus}{C}{-}\overset{\ominus}{O}$$

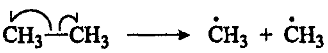
It is crucial to remember that it represents the formal flow of electrons, not the flow of atoms.



$$H\overset{\ominus}{O} + H{-}Cl \xrightarrow{\times} HOH + \overset{\ominus}{Cl} \quad \text{(Incorrect)}$$

$$H\overset{\ominus}{O} + H{-}Cl \longrightarrow HOH + \overset{\ominus}{Cl} \quad \text{(Correct)}$$

A curved arrow with a half head is called a *fish-hook*. This kind of arrow is used to indicate the movement of a single electron. In the given equation, two fish-hooks are used to show the movement of each of the two electrons in the C—C bond of ethane to a carbon atom forming two methyl radicals.



$$CH_3—CH_3 \longrightarrow \dot{C}H_3 + \dot{C}H_3$$

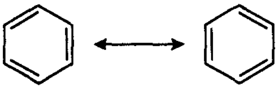
(ii) *Straight arrows point from reactants to products in chemical equations.*

$$A + B \longrightarrow C + D$$

Straight arrows with half-heads are commonly used in pairs to indicate that reaction is reversible.

$$A + B \rightleftharpoons C + D$$

A double-headed straight arrow between two structures indicates that they are resonance structures. Such an arrow does not indicate the occurrence of a chemical reaction.

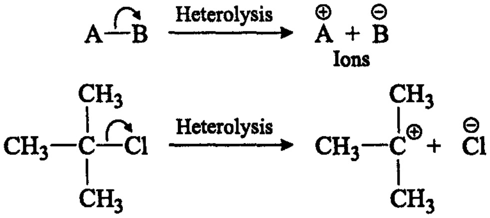


As mentioned earlier, in most reactions of organic compounds one or more covalent bonds are broken. Organic reaction mechanism thus may be divided into three basic types, depending on how the bonds are broken.

2.2 BREAKING (FISSION) OF COVALENT BONDS

There are following two types of covalent bond breaking or fission :

(i) Heterolytic bond fission or heterolysis : If a covalent bond is broken in such a way that both bonding pair of electrons are taken by only one fragment then the breaking of bond is called heterolytic bond fission or heterolysis.



$$A—B \xrightarrow{\text{Heterolysis}} \overset{\oplus}{A} + \overset{\ominus}{B}$$

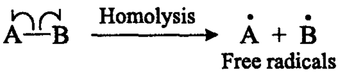
Ions

$$(CH_3)_3C—Cl \xrightarrow{\text{Heterolysis}} (CH_3)_3\overset{\oplus}{C} + \overset{\ominus}{Cl}$$

The covalent bond is represented by dash (–) and the movement of pair of electrons is shown by ↷ (curved arrow).

As a result of heterolysis ions are formed. It is the more electronegative atom which takes both the bonding pair of electrons. Heterolysis usually takes place in polar compounds and in polar solvents.

(ii) Homolytic bond fission or homolysis : If a covalent bond is broken in such a way that each fragment takes one of the bonding pair of electrons then the breaking of bond is called homolytic bond fission or homolysis.

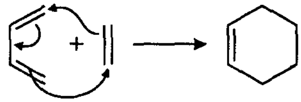


$$A—B \xrightarrow{\text{Homolysis}} \dot{A} + \dot{B}$$

Free radicals

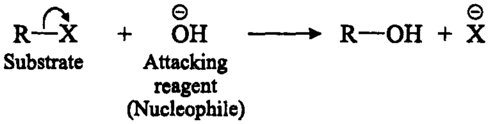
As a result of homolysis free radicals are formed which have unpaired electron(s). Homolysis is usually brought about by heat, light or organic peroxides. It is the most common mode of bond fission in the vapour phase.

It would seem that all bonds must break in one of the two ways described above to give ions or free radicals but there is a third type of mechanism in which electrons move in a close ring. There are no intermediates, ions or free radicals, and it is impossible to say whether the migrating electrons are paired or unpaired. Reactions with this type of mechanism are called **Pericyclic reactions.**



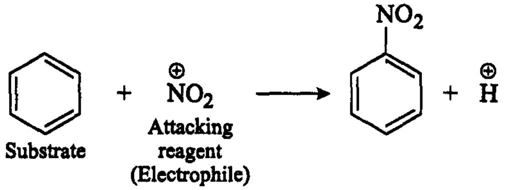
2.3 TYPES OF REAGENTS

Heterolysis of organic compounds is usually brought about by certain reagents. For a large number of reactions it is convenient to call one reactant as **substrate** (which supplies carbon to the new bond) and the other as **attacking reagent.** In heterolytic reactions the attacking reagent generally brings a pair of electrons to the substrate or takes a pair of electrons from the substrate. A reagent (reagent means attacking reagent) that brings an electron pair is called a **nucleophile** and the reaction is known is **nucleophilic reaction.** For example :

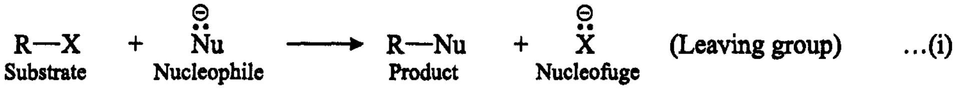


$$\underset{\text{Substrate}}{R-X} + \underset{\substack{\text{Attacking}\\ \text{reagent}\\ \text{(Nucleophile)}}}{\overset{\ominus}{O}H} \longrightarrow R-OH + \overset{\ominus}{X}$$

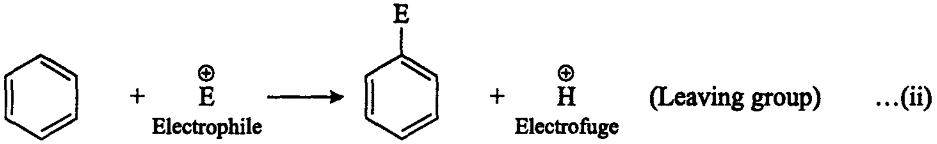
A reagent that takes an electron pair is called **electrophile** and the reaction is known as electrophilic reaction. For example :



In a reaction in which the substrate molecule becomes cleaved, the part that does not contain carbon is usually called leaving group. The leaving group that carries electron pair is called **nucleofuge.** If the leaving group comes away without the electron pair, it is called **electrofuge.** For Example :



$$\underset{\text{Substrate}}{R-X} + \underset{\text{Nucleophile}}{\overset{\ominus}{\ddot{N}u}} \longrightarrow \underset{\text{Product}}{R-Nu} + \underset{\text{Nucleofuge}}{\overset{\ominus}{\ddot{X}}} \quad \text{(Leaving group)} \quad \ldots\text{(i)}$$



2.3.1 Nucleophilic reagents or Nucleophiles

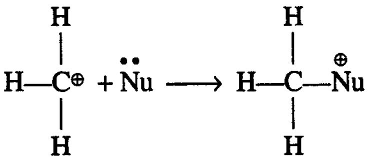
Reagents having an unshared pair of electrons are known as nucleophilic reagents or nucleophiles because they have a tendency to share this pair of electrons with electron deficient substrate. Thus nucleus loving species are known as nucleophiles. Nucleophiles can be classified into three groups :

(i) Neutral Nucleophiles : Electron rich species due to the presence of non-bonding electrons are known as neutral nucleophiles. Central atom of such species should have complete octet. They are not charged and are electrically neutral. For example :

$$R-\ddot{\underset{\cdot\cdot}{O}}-H,\ R-\ddot{N}H_2\ H-\ddot{\underset{\cdot\cdot}{O}}-H,\ R-\ddot{\underset{\cdot\cdot}{O}}-R_1$$

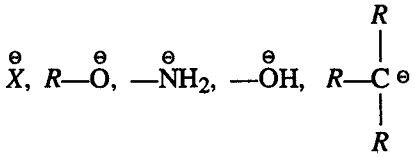
Note : Organic compounds having C—C multiple bond(s) also behave as neutral nucleophiles because such species have π electron clouds above and below the plane of the molecule.

The addition of neutral nucleophile to a positively charged substrate will give a positively charged product.



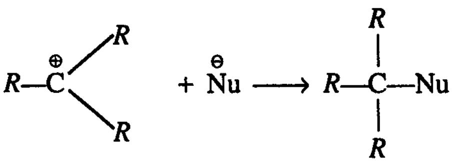
$$H_3C^{\oplus} + \ddot{Nu} \longrightarrow H_3C\text{—}\overset{\oplus}{Nu} \qquad \text{...(3)}$$

(ii) Negative Nucleophiles : Negative nucleophiles are those which carry an electron pair and are negatively charged because of one extra electron. For example :



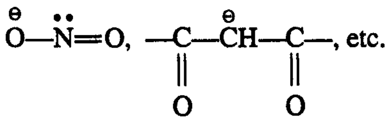
$$\overset{\ominus}{X},\ R\text{—}\overset{\ominus}{O},\ \text{—}\overset{\ominus}{N}H_2,\ \text{—}\overset{\ominus}{O}H,\ R_3C^{\ominus}$$

Addition of a negative nucleophile to a positively charged substrate results in a neutral molecule.



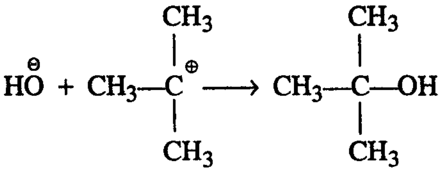
$$R_3C^{\oplus} + \overset{\ominus}{Nu} \longrightarrow R_3C\text{—}Nu$$

(iii) Ambident Nucleophiles : The nucleophiles which can attack through two or more atoms are called *ambident nucleophiles*. For example, $\overset{\ominus}{CN}$ can attack through N or C to give cyanide (*R*CN) or isocyanide (*R*NC). Other examples of ambident nucleophiles are :



$$\overset{\ominus}{O}\text{—}\ddot{N}=O,\ \text{—}\underset{O}{\underset{\|}{C}}\text{—}\overset{\ominus}{C}H\text{—}\underset{O}{\underset{\|}{C}}\text{—},\ \text{etc.}$$

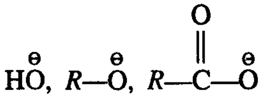
Nucleophiles can be classified according to the kind of atom that forms a new covalent bond. For example, the hydroxide ion, in the reaction given below, is an oxygen nucleophile.



$$H\overset{\ominus}{O} + (CH_3)_3C^{\oplus} \longrightarrow (CH_3)_3C\text{—}OH$$

In the product, a new carbon-oxygen bond is formed. The most common nucleophiles are oxygen, nitrogen, sulphur, halogen and carbon nucleophiles.

Oxygen Nucleophiles : $H\text{—}\ddot{\underset{\cdot\cdot}{O}}\text{—}H,\ R\text{—}\ddot{\underset{\cdot\cdot}{O}}\text{—}H,\ R\text{—}\ddot{\underset{\cdot\cdot}{O}}\text{—}R$



$$H\overset{\ominus}{O},\ R\text{—}\overset{\ominus}{O},\ R\text{—}\overset{O}{\overset{\|}{C}}\text{—}\overset{\ominus}{O}$$

Nitrogen nucleophiles : $\ddot{N}H_3,\ R\ddot{N}H_2,\ R_2\ddot{N}H,\ R_3\ddot{N},\ \ddot{N}H_2\text{—}\ddot{N}H_2,\ \overset{\ominus}{N}H_2$

Sulphur Nucleophiles : $H—\overset{\bullet\bullet}{\underset{\bullet\bullet}{S}}—H$, $R—\overset{\bullet\bullet}{\underset{\bullet\bullet}{S}}—H$, $R—\overset{\bullet\bullet}{\underset{\bullet\bullet}{S}}—R$, $R—\overset{\ominus}{S}$

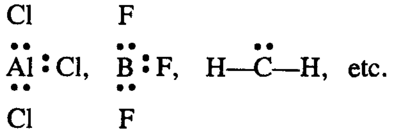
Halogen Nucleophiles : $\overset{\ominus}{Cl}$, $\overset{\ominus}{Br}$ and $\overset{\ominus}{I}$

Carbon Nucleophiles : $\overset{\ominus}{C}H_3$, $CH_3—\overset{\ominus}{C}H_2$, $\overset{\ominus}{R}$, $\overset{\ominus}{C}\equiv N$, $R—C\equiv\overset{\ominus}{C}$

2.3.2 Electrophilic Reagents or Electrophiles

An electrophile (electron loving) is a reagent that is electron deficient and the deficiency accounts for its affinity for electrons. Electrophiles can also be of two types :

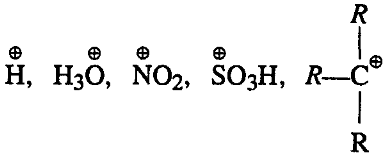
(i) Neutral Electrophiles : The neutral electrophiles, though electron deficient, do not carry positive charge. They have incomplete valence shells. The examples are $AlCl_3$, BF_3, $\ddot{C}H_2$ (carbene), etc. They are electron deficient due to incomplete outermost shell.



$$\underset{Cl}{\overset{Cl}{Al}}:Cl,\quad \underset{F}{\overset{F}{B}}:F,\quad H—\ddot{C}—H,\ \text{etc.}$$

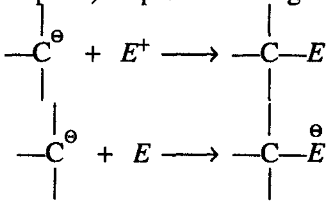
(Only six electrons instead of eight electrons in the outermost shell)

(ii) Positive Electrophiles : The positive electrophiles are those which carry a positive charge on central atom and have incomplete octet.



$$\overset{\oplus}{H},\ H_3\overset{\oplus}{O},\ \overset{\oplus}{N}O_2,\ \overset{\oplus}{S}O_3H,\ R—\underset{R}{\overset{R}{C^{\oplus}}}$$

The positive electrophile attacks the substrate (negative nucleophile) and accepts an electron pair for sharing, thus forming a neutral molecule. On the other hand, a neutral electrophile will attack an electron rich substrate (negative nucleophile) to produce a negatively charged molecule.

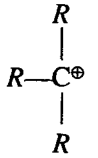


$$—C^{\ominus} + E^{+} \longrightarrow —C—E$$

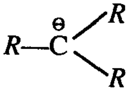
$$—C^{\ominus} + E \longrightarrow —C—\overset{\ominus}{E}$$

2.4 REACTION INTERMEDIATES

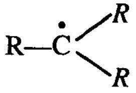
Homolytic and heterolytic bond fission results in the formation of short lived species called **reaction intermediates**. These short-lived intermediates are very reactive and are quickly converted to more stable molecules. However, under certain circumstances they are of sufficient stability to be isolated and studied. The four most common kinds of reaction intermediates with fewer than four covalent bonds at carbon are :



Carbocation



Carbanion



Free radical

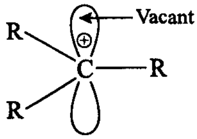
Carbene

2.4.1 Carbocations

All the cations in which the positive charge is carried by a carbon are called **carbocations** or **carbonium** ions. These are reactive intermediates in a large number of organic reactions. The reason for their reactivity is that the carbon has only six electrons in the valency shell and has a great tendency to complete its octet.

Structure of Carbocations

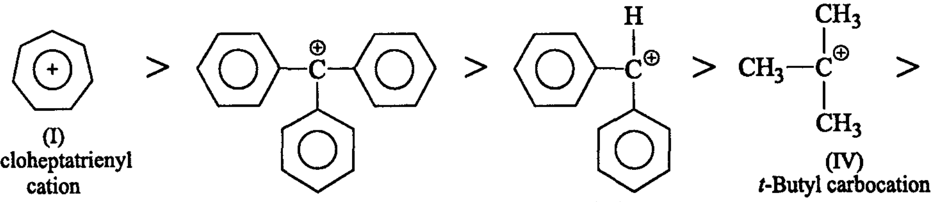
The carbon atom of carbocation is sp^2 hybridised in which the p orbital is devoid of any electron. The three bonding orbitals form three σ bonds, the remaining p orbital is vacant. This vacant p orbital makes the carbon atom electron deficient and gives it a positive charge. The carbocation thus has a planar (flat) structure having all the three σ bonds in one plane with the bond angles of 120° between them.



Stability of carbocations

The cycloheptatrienyl cation is an exceptionally stable carbocation which can be isolated and studied. At the other extreme is the methyl carbocation, which is so unstable that it has never even been detected as an intermediate in any ordinary chemical reaction. In between these two extremes there exist a whole spectrum of carbocations; some can be isolated, some are detectable but not isolable and others can be generated only under extreme conditions.

Some carbocations are listed below in order of their decreasing relative stability (in solution) :

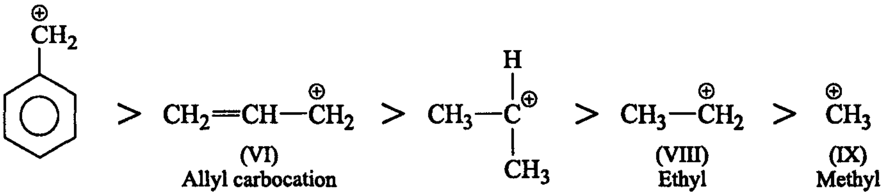


(I) Cycloheptatrienyl cation

(II) Triphenylmethyl carbocation

(III) Diphenylmethyl carbocation

(IV) *t*-Butyl carbocation



(V) Benzyl carbocation

(VI) Allyl carbocation

(VII) Isopropyl carbocation

(VIII) Ethyl carbocation

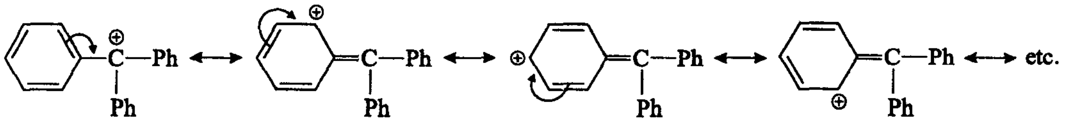
(IX) Methyl carbocation

The relative stabilities of the first five cations are easily understood on the basis of resonance. When the positively charged carbon atom is in conjugation with π-bond, the stability is greater because of increased delocalisation due to resonance and because positive charge is spread over the whole molecule instead of being concentrated on one atom.

The cycloheptatrienyl (tropylium) cation has seven equivalant resonance forms. This carbocation is aromatic in character. In aromatic carbocation there is complete delocalisation of positive charge. Due to this reason aromatic carbocations are more stable than non-aromatic carbocations. In aromatic carbocations the positively charged carbon is part of an aromatic ring.

Thus high degree of stability found experimentally is exactly what is expected for this molecule.

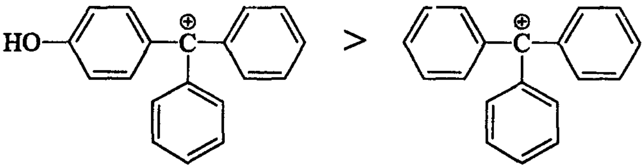
Ten resonance forms can be written for triphenyl carbocation in which positive charge is on the central carbon atom.



Thus this cation is also stabilised due to resonance.

Diphenylmethyl carbocation is less stable than the triphenylmethyl carbocation because it has fewer number of resonating forms than triphenylmethyl carbocation.

Triphenylmethyl and diphenylmethyl carbocations have been isolated as solid salts and these salts are available commercially. These carbocations are further stabilised if they have electron donating substituents (*o*, *p*-directing group, +*I* effect) in *ortho* or *p*-positions. Thus :



The next member of our series is benzyl carbocation. This has also the same type of resonance form which stabilised the triphenylmethyl carbocation. But in this case the number of resonating structures are less than triphenylmethyl and diphenymethyl carbocations. That is why it is less stable than these two.

Although triphenylmethyl, diphenylmethyl and benzyl carbocations are stabilised by resonance but they are not aromatic in character. Positive charge in these carbocations are present on alkyl carbon or on a carbon which is not part of an aromatic ring. Due to this reason they are less stable than aromatic carbocations.

The allyl carbocation has only two resonating forms, but both resonance forms are equivalent. Because of this, this ion has a stability similar to benzyl cation.

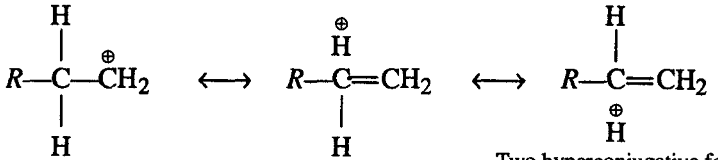
$$CH_2{=}CH{-}\overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2{-}CH{=}CH_2$$

The order of stability of alkyl carbocations is as follows :

Tertiary > Secondary > Primary

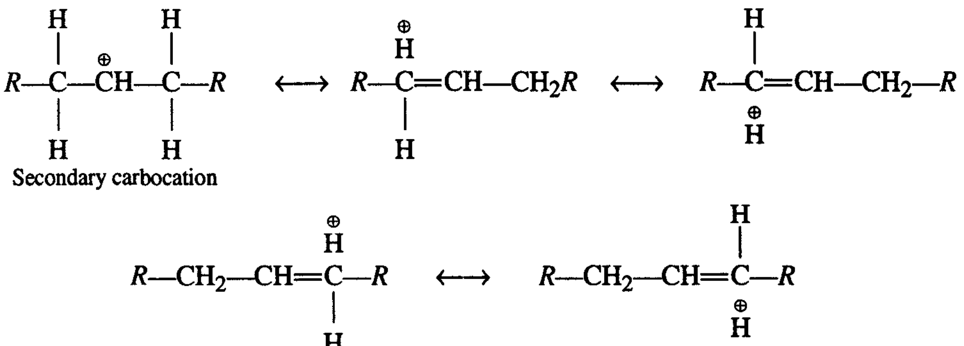
The stability order of these carbocations can be explained by hyperconjugation and by field effect (Inductive effect).

According to hyperconjugation, the σ-electrons of an α C—H bond can be delocalised into the unfilled *p*-orbital of the positive carbon atom, thus spreading the charge over all such bonds. Several hyperconjugative resonance forms can be written, each having the same number of covalent bonds as the first structure.

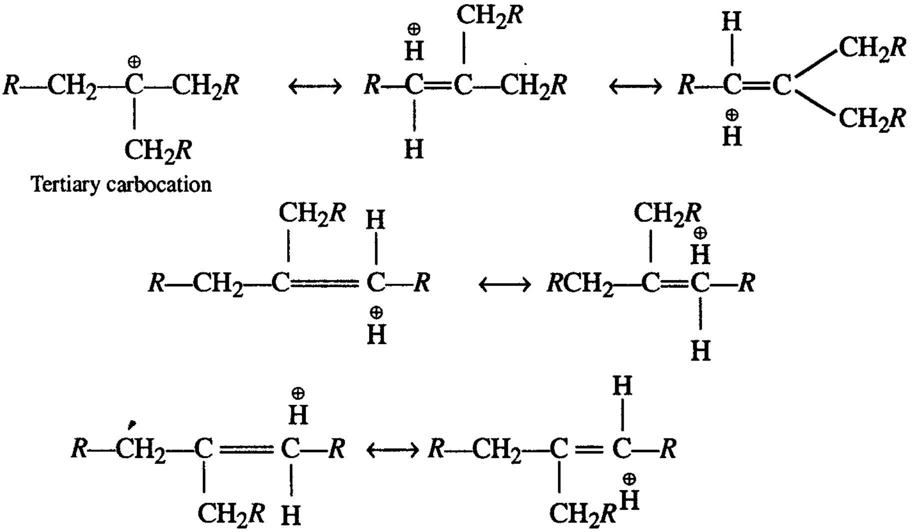


Primary carbocation

Two hyperconjugative forms



Four hyperconjugative forms



(Six hyperconjugative forms)

Since the stability of a resonating structure depends on the number of equivalent resonance structures, the tertiary is more stable than secondary and secondary is more stable than the primary carbocations. (Table 2.1).

Table 2.1 ***Stabilisation energies of carbocations***

Carbocation	Stabilisation Energy (kcal/mole)	Carbocation	Stabilisation Energy (kcal/mole)
$CH_3-\underset{CH_3}{\overset{\oplus}{C}}-CH_3$	84	$CH_2-\overset{\oplus}{C}H_2$	36
$CH_3-\underset{CH_3}{\overset{\oplus}{C}}H$	66	$\overset{\oplus}{C}H_3$	0

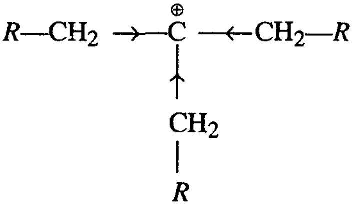
The field effect explanation is that the electron donating effect of alkyl group (+*I* effect) increases the electron density at the charge-bearing carbon, reducing the net charge on the positive carbon. Thus there is a partial neutralisation of positive charge on carbon. As a general rule greater the neutralisation of charge, greater is the stability of the charged species.

$R{-}CH_2 \rightarrow\!- \overset{\oplus}{C}H_2$

Primary carbocation

$R{-}CH_2 \rightarrow\!- \overset{\oplus}{C}H -\!\leftarrow CH_2{-}R$

Secondary carbocation



Tertiary carbocation
(maximum neutralisation of positive charge due to +*I* effect)

Formation of Carbocations

Carbocations can be generated in a variety of ways. Some of the reactions forming carbocations are given below :

(i) Direct ionisation

$$R{-}X \xrightarrow{\text{Liquid } SO_2} \overset{\oplus}{R} + \overset{\ominus}{X}$$

$$R{-}X + \overset{\oplus}{Ag} \longrightarrow \overset{\oplus}{R} + AgX\downarrow$$

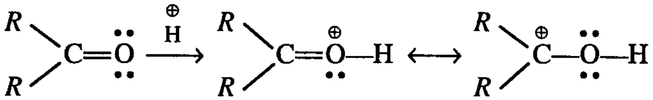
X = Cl, Br or I

($\overset{\oplus}{Ag}$ promotes the formation of carbocation by precipitation of Ag*X*)

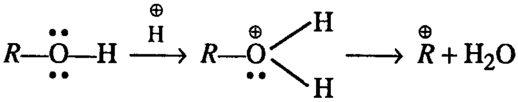
$$R{-}F + SbF_5 \longrightarrow \overset{\oplus}{R} + \overset{\ominus}{SbF_6}$$

(ii) Protonation of alkenes and carbonyl compounds

$$R{-}CH{=}CH_2 \xrightarrow{\overset{\oplus}{H}} R{-}\overset{\oplus}{C}H{-}CH_3$$



(iii) Protonation of alcohols followed by dehydration



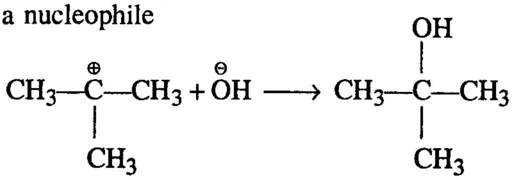
(iv) Deamination of amines with nitrous acid

$$R{-}NH_2 \xrightarrow{HNO_2} R{-}\overset{\oplus}{N}{\equiv}N \longrightarrow \overset{\oplus}{R} + N_2$$

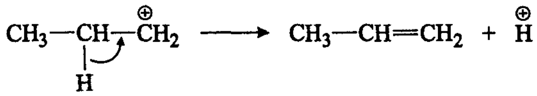
Reactions of Carbocations

Although a carbocation undergoes a variety of reactions, the common goal of all these reactions is to provide a pair of electrons to complete the octet of the positively charged carbon. A carbocation may react in any one of the following ways :

(a) Combination with a nucleophile

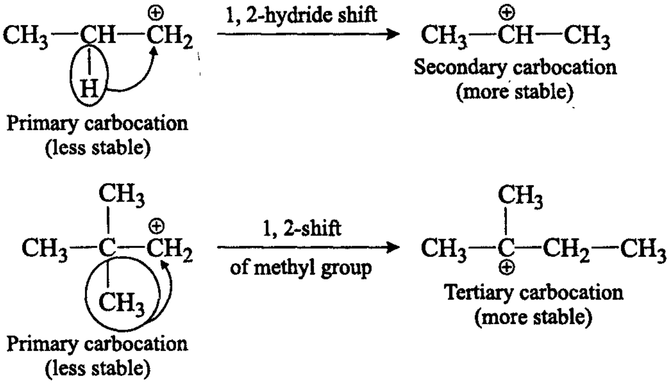


(b) Elimination of a proton



$$CH_3-\underset{\underset{H}{|}}{CH}-\overset{\oplus}{C}H_2 \longrightarrow CH_3-CH=CH_2 + \overset{\oplus}{H}$$

(c) Rearrangement to form a more stable carbocation



$$CH_3-\underset{\underset{H}{|}}{CH}-\overset{\oplus}{C}H_2 \xrightarrow{\text{1, 2-hydride shift}} CH_3-\overset{\oplus}{C}H-CH_3$$

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\oplus}{C}H_2 \xrightarrow[\text{of methyl group}]{\text{1, 2-shift}} CH_3-\underset{\oplus}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_3$$

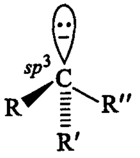
2.4.2 Carbanions

All the anions in which the negative charge is carried by a carbon are called carbanions. For example :

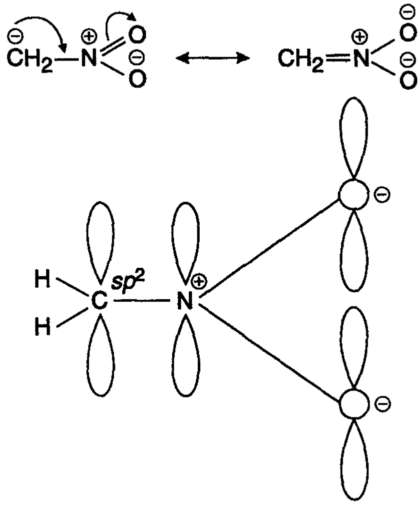
$\overset{\ominus}{C}H_3$	$CH_3-\overset{\ominus}{C}H_2$	$CH_3-\overset{\ominus}{C}H-CH_3$	$(CH_3)_3\overset{\ominus}{C}$
Methyl carbanion	Ethyl carbanion	Isopropyl carbanion	*t*-Butyl carbanion

Structure of Carbanions

A carbanion possesses an unshared pair of electrons and three pairs of bonding electrons around the central carbon atom which is sp^3 hybridised. The shape of this anion is pyramidal, similar to that of ammonia and amine molecules. Out of four sp^3 hybrid orbitals, three form σ bonds and the fourth is a nonbonding orbital containing two paired electron.



Carbanion

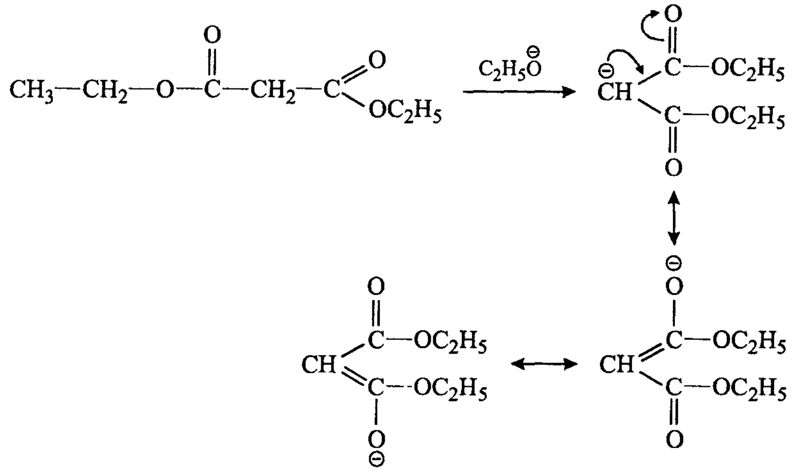


Nitromethane carbanion

Fig. 2.1. Electron delocalisation results in the formation of a double bond which requires that all the atoms involved in it should be coplanar.

The geometry of a carbanion stabilised by conjugation with substituents is, however, quite different. The carbanions which are greatly stabilised by resonance are in sp^2 hybrid state and planar in so far as the delocalised electronic system is concerned. Thus, the nitromethane anion has all of its atoms in a plane, with sp^2 hybridisation at both carbon and nitrogen (Fig. 2.1).

Similarly, malonic ester anion is planar, only the hydrogen on the ethyl group and the carbon of methyl group lie out of the molecular plane :



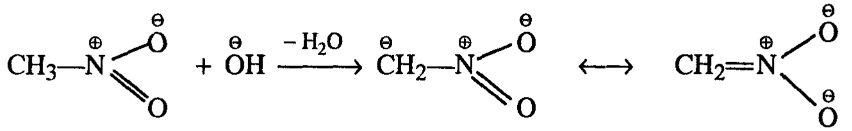
Malonic ester anion (resonance stabilised)

It is, therefore, quite reasonable to believe that the carbon atom of an unconjugated anion is sp^3 hybridised and has a pyramidal shape, whereas a carbanion conjugated with a π system is sp^2 hybridised and has a planar geometry.

Formation of Carbanions

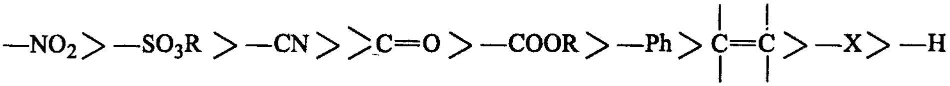
The carbanions are obtained by heterolysis of a covalent bond in which both the bonding electrons are taken by the carbon. Usually departing constituent is a proton.

The heterolytic cleavage of alkanes are very difficult process. As there is very little difference between electronegativities of carbon and hydrogen, the polarity of C—H bond is very small. In other words, hydrogen atom bonded to sp^3 carbon atom shows negligible acidity. Carbanions are formed only from those compounds which contain a functional group; capable of weakening a nearby C—H bond. Thus hydrogens on the carbon atom *alpha* to nitro, cyano, carboxylic, carbonyl and triple bond have acidic character (weak C—H bond) and can be removed as protons leaving resonance stabilised anions. For example, nitromethane is sufficiently acidic to react with aqueous alkali because the anion formed has a high degree of stability.



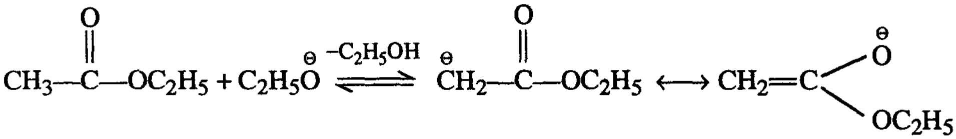
The stability of this carbanion is largely a result of the electronegativity of the oxygen atoms of the nitro group. There is stabilising —*I* inductive effect as well as a powerful resonance effect, both of which withdraw negative charge from the carbon into the nitro group.

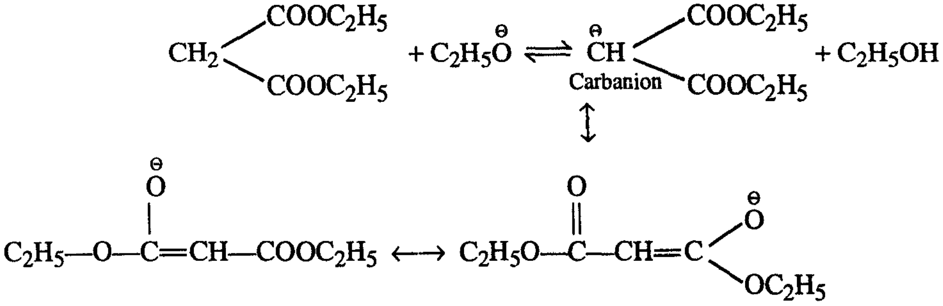
Electronegative atoms or groups, depending on their ability to withdraw electrons will lead to more or less stable carbanions. The groups are listed in order of decreasing electron withdrawing ability.



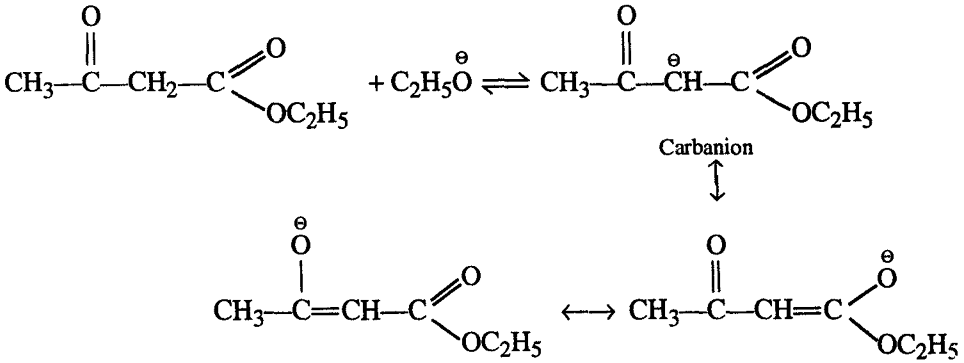
$$-NO_2 > -SO_3R > -CN > \rangle C{=}O > -COOR > -Ph > \overset{|}{\underset{|}{C}}{=}\overset{|}{\underset{|}{C}} > -X > -H$$

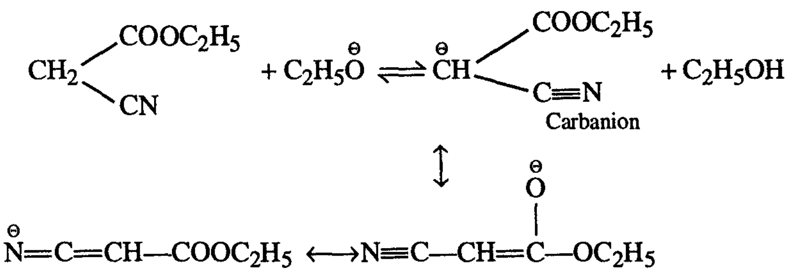
A single nitro group attached to carbon causes nitromethane to be sufficiently acidic. A group in the range from —SO$_3$*R* to —COO*R* is not electronegative enough to yield a compound with measurable acidity. But two such groups attached to the same carbon atom will remarkably enhance the acidity of a C—H bond. For example, ethyl acetate does not react with sodium ethoxide to such an extent as malonic ester and ethyl acetoacetate react.





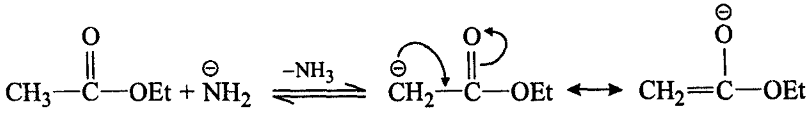
Similarly :



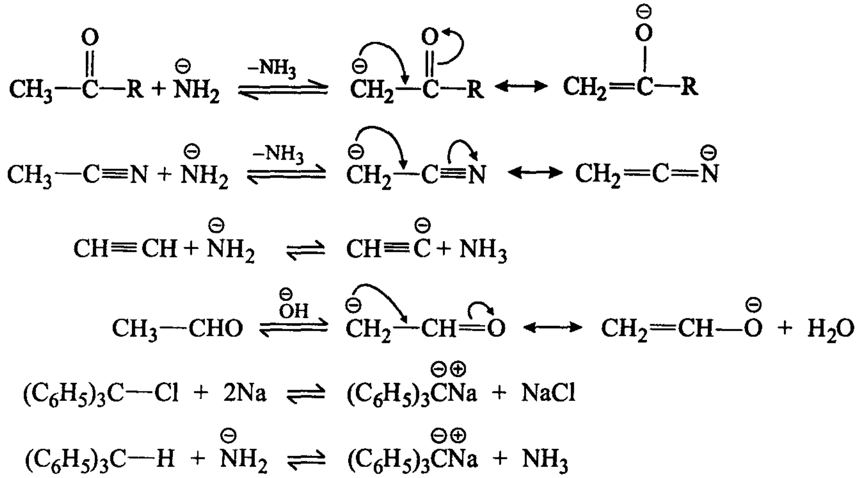


On the other hand, if strong base is used, reaction will occur with those compounds also which have only one electron withdrawing group.

For examples :



$$CH_3-\overset{O}{\overset{\|}{C}}-OEt + \overset{\ominus}{N}H_2 \xrightleftharpoons{-NH_3} \overset{\ominus}{C}H_2-\overset{O}{\overset{\|}{C}}-OEt \longleftrightarrow CH_2=\overset{\overset{\ominus}{O}}{\overset{|}{C}}-OEt$$



$$CH_3-\overset{\overset{O}{\|}}{C}-R + \overset{\ominus}{N}H_2 \xrightleftharpoons{-NH_3} \overset{\ominus}{C}H_2-\overset{\overset{O}{\|}}{C}-R \longleftrightarrow CH_2=\overset{\overset{\overset{\ominus}{O}}{|}}{C}-R$$

$$CH_3-C\equiv N + \overset{\ominus}{N}H_2 \xrightleftharpoons{-NH_3} \overset{\ominus}{C}H_2-C\equiv N \longleftrightarrow CH_2=C=\overset{\ominus}{N}$$

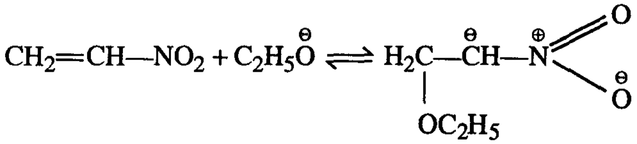
$$CH\equiv CH + \overset{\ominus}{N}H_2 \rightleftharpoons CH\equiv\overset{\ominus}{C} + NH_3$$

$$CH_3-CHO \xrightleftharpoons{\overset{\ominus}{O}H} \overset{\ominus}{C}H_2-CH=O \longleftrightarrow CH_2=CH-\overset{\ominus}{O} + H_2O$$

$$(C_6H_5)_3C-Cl + 2Na \rightleftharpoons (C_6H_5)_3\overset{\ominus\oplus}{CNa} + NaCl$$

$$(C_6H_5)_3C-H + \overset{\ominus}{N}H_2 \rightleftharpoons (C_6H_5)_3\overset{\ominus\oplus}{CNa} + NH_3$$

Carbanions are also formed when a nucleophile adds to a carbon-carbon double bond :



$$CH_2=CH-NO_2 + C_2H_5\overset{\ominus}{O} \rightleftharpoons \underset{\underset{OC_2H_5}{|}}{H_2C}-\overset{\ominus}{C}H-\overset{\oplus}{N}\begin{smallmatrix}\nearrow O \\ \searrow \overset{\ominus}{O}\end{smallmatrix}$$

Stability of Carbanions

Electron-withdrawing atoms or groups stabilise a carbanion by dispersing (delocalising) its negative charge. The following is the order of stability of simple alkyl carbanions :

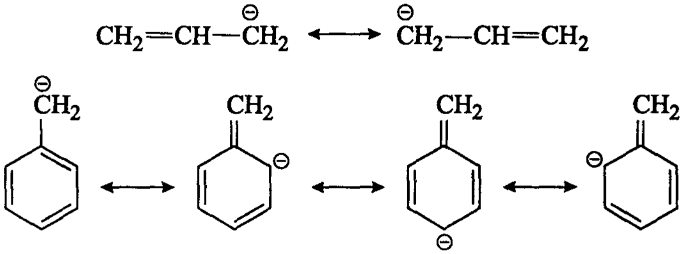
methyl > primary > secondary > tertiary

This stability order can be attributed to +*I* effect of the alkyl groups. The electron-donating alkyl groups increase the electron density on the carbanionic carbon, hence its negative charge is intensified and the carbanion is destabilised. This destabilisation increases as the number of alkyl groups attached to the carbanionic carbon increases. This explains the above order of stability of carbanions.

Many carbanions are far move stable than the simple kind of carbanions mentioned above. Their increased stability is due to certain structural features. Such types of carbanions are generally stabilised by electron-withdrawing substituents and resonance or only by resonance.

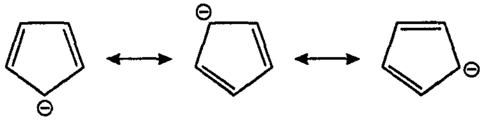
(i) Resonance : Stability of allylic, benzylic and aromatic carbanions can be explained by **resonance.**

$$CH_2=CH-\overset{\ominus}{C}H_2 \longleftrightarrow \overset{\ominus}{C}H_2-CH=CH_2$$



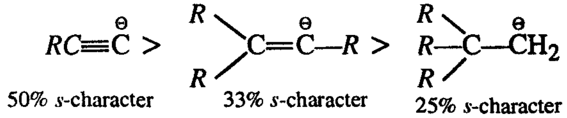
In these cases a multiple (double or triple) bond is located *alpha* to carbanionic carbon, the ion is stabilised by resonance in which the unshaired pair overlaps with the π electrons of the double bonds. This factor is responsible for the stabilisation of allylic and benzylic type of carbanions.

Aromatic carbanions are the carbanions in which the negative charge is carried by an aromatic ring carbon. These are the most stable carbanions because of their aromaticity and complete delocalisation of negative charge, for example :



(ii) Resonance and –*I* effect : When the carbanionic carbon is conjugated with a carbon-oxygen or carbon-nitrogen multiple bond (see formation of carbanions) the stability of carbanion is greater than that of benzyl and allylic type carbanions. In these cases there is a sizable inductive effect as well as a powerful resonance effect, both of which withdraw negative charge from carbon into more electronegative atoms. These electronegative atoms are better capable of bearing a negative charge than carbon.

(iii) The stability of carbanions increases with increasing *s* character of the carbanionic carbon. Thus the order of stability is :

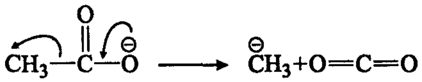


50% *s*-character 33% *s*-character 25% *s*-character

Increase *s* character means that the electrons are closer to the nucleus and hence are of lower energy.

Reactions of Carbanions

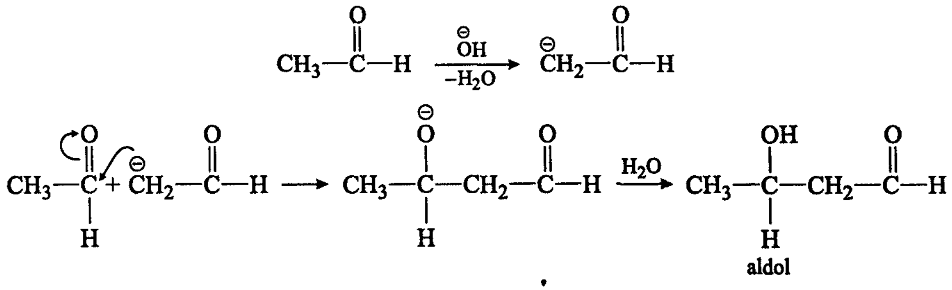
The most common reaction of carbanions is combination with a positive species (electrophile) usually a proton.



$$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{O} \longrightarrow \overset{\ominus}{C}H_3 + O=C=O$$

$$\overset{\ominus}{C}H_3 + H-X \longrightarrow CH_4 + \overset{\ominus}{X}$$

Carbanions frequently add to the carbonyl double bond (*e.g., **aldol condensation***)



$$CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow[-H_2O]{\overset{\ominus}{O}H} \overset{\ominus}{C}H_2-\overset{\overset{O}{\|}}{C}-H$$

$$CH_3-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{C}} + \overset{\ominus}{C}H_2-\overset{\overset{O}{\|}}{C}-H \longrightarrow CH_3-\underset{\underset{H}{|}}{\overset{\overset{\overset{\ominus}{O}}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-H \xrightarrow{H_2O} \underset{\text{aldol}}{CH_3-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-H}$$

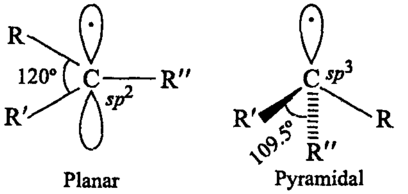
Usually, carbanions do not undergo rearrangements. However, some rearrangements involving allylic carbanions are known.

2.4.3 Free Radicals

Chemical species having one or more unpaired electrons are called free radicals. As mentioned earlier homolytic bond fission leads to the formation of free radicals. Thus free radicals are odd electron molocules, *e.g.*, $\dot{C}H_3$, $\dot{C}_2H_5$, $\dot{C}_6H_5$, $(C_6H_5)_3\dot{C}$, etc. and are highly reactive. Free radicals are paramagnetic, *i.e.*, possess a small permanent magnetic moment, due to the presence of unpaired electron. This property is used for detection of the presence of free radicals.

Structure of Free Radicals

Similar to carbanions, carbon containing an unpaired electron(s) in free radicals also may either be in *sp*^{2} hybrid state in which case the structure would be planar with odd electron in the *p* orbital or it could be *sp*^{3} hybridised which would make the structure pyramidal (non-planar) and the odd electron will be in one of the *sp*^{3} orbitals.



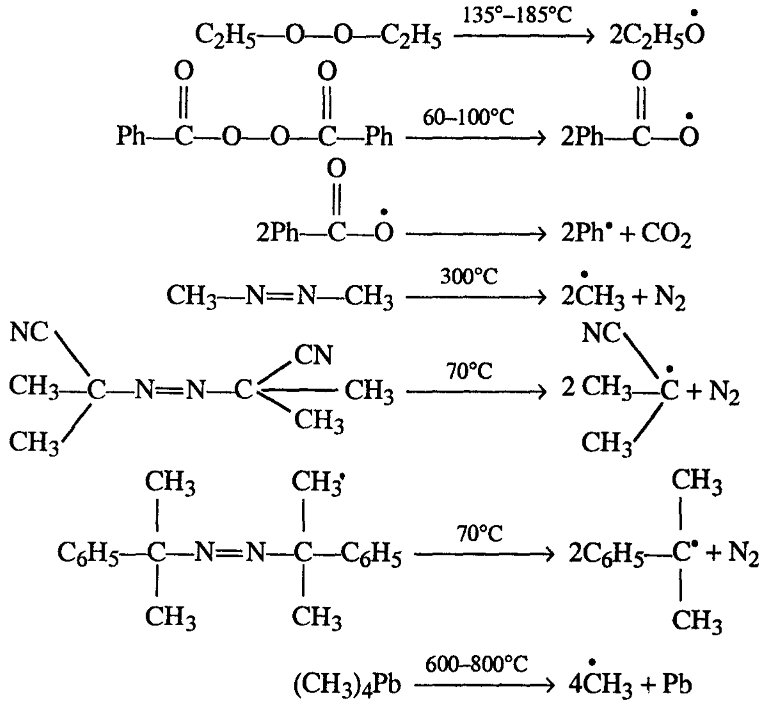
Planar Pyramidal

Physical and chemical evidences (E.S.R and stereochemistry) point to a planar configuration at the radical centre for simple alkyl radicals but not for fluorinated derivatives (*e.g.*, $\dot{C}F_3$) which prefer pyramidal shape. In resonance stabilised free radicals the radical carbon is certainly in *sp*^{2} hybrid state.

Formation of Free Radicals

Free radicals are formed by homolytic fission of a covalent bond, when a molecule is supplied with sufficient energy—thermal or photochemical.

(i) Thermal cleavage : Most of the covalent bonds are thermally stable upto a temperature of 200°C, used in solution chemistry. However, there are a few group of compunds (peroxy and azo) which undergo homolytic cleavage at temperatures below 200°C. These are designated as **initiators.** A few examples of initiators are on next page :



$$C_2H_5{-}O{-}O{-}C_2H_5 \xrightarrow{135°\text{–}185°C} 2C_2H_5\dot{O}$$

$$Ph{-}\overset{O}{\overset{\|}{C}}{-}O{-}O{-}\overset{O}{\overset{\|}{C}}{-}Ph \xrightarrow{60\text{–}100°C} 2Ph{-}\overset{O}{\overset{\|}{C}}{-}\dot{O}$$

$$2Ph{-}\overset{O}{\overset{\|}{C}}{-}\dot{O} \longrightarrow 2Ph^{\bullet} + CO_2$$

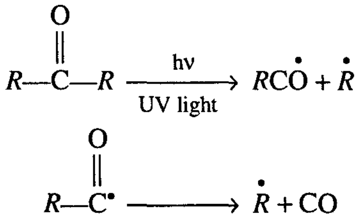
$$CH_3{-}N{=}N{-}CH_3 \xrightarrow{300°C} 2\dot{C}H_3 + N_2$$

$$(CH_3)_2C(CN){-}N{=}N{-}C(CN)(CH_3)_2 \xrightarrow{70°C} 2\,(CH_3)_2\dot{C}(CN) + N_2$$

$$C_6H_5{-}C(CH_3)_2{-}N{=}N{-}C(CH_3)_2{-}C_6H_5 \xrightarrow{70°C} 2C_6H_5{-}C^{\bullet}(CH_3)_2 + N_2$$

$$(CH_3)_4Pb \xrightarrow{600\text{–}800°C} 4\dot{C}H_3 + Pb$$

(ii) Photochemical cleavage : A second general method of obtaining radical is through irradiation with either UV or visible light. The energy transferred to the molecule by the interaction must be of the order of bond dissociation energy or greater to produce homolysis.



$$R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}R \xrightarrow[\text{UV light}]{h\nu} R\mathrm{C}\dot{\mathrm{O}} + \dot{R}$$

$$R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}^{\bullet} \longrightarrow \dot{R} + \mathrm{CO}$$

$$X_2 \xrightarrow{h\nu} \dot{X} + \dot{X}$$

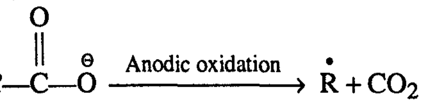
(iii) Chemical method

$$(C_6H_5)_3C\text{—}Cl \xrightarrow{Ag} (C_6H_5)_3\dot{C} + AgCl$$

(iv) Redox reactions

$$C_6H_5\text{—}\overset{\oplus}{N}\equiv N + \overset{\oplus}{Cu} \longrightarrow \dot{C}_6H_5 + N_2 + Cu^{2+}$$

$$\underbrace{H\text{—}O\text{—}O\text{—}H + Fe^{2+}}_{\text{Fenton's reagent}} \longrightarrow \dot{O}H + \overset{\ominus}{O}H + Fe^{3+}$$



$$R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}\overset{\ominus}{O} \xrightarrow{\text{Anodic oxidation}} \dot{R} + CO_2$$

Stability of Free Radicals

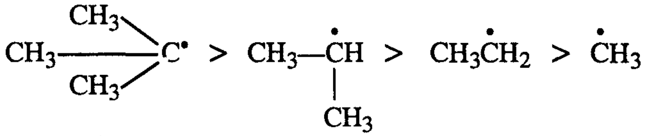
Most simple free radicals, such as methyl and *t*-butyl radicals, are highly reactive species. Even if they are kept out of contact with various other substances they cannot be obtained in any appreciable concentration because they undergo dimerization and disproportionation :

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow \underset{\text{Dimerization}}{CH_3\text{—}CH_3}$$

$$CH_3\dot{C}H_2 + CH_3\dot{C}H_2 \longrightarrow \underset{\text{Disproportionation}}{CH_3\text{—}CH_3 + CH_2{=}CH_2}$$

These two reactions are nearly instantaneous and irreversible for a free radical to have a longer lifetime, it would seem necessary that the stability of the radical be at least comparable with that of the covalent compound it would form on dimerization.

The stability of alkyl free radicals is of the following order



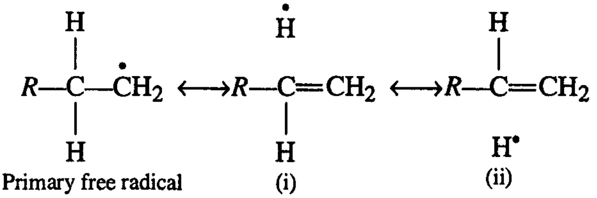
$$(CH_3)_3C^{\bullet} > CH_3\text{—}\underset{\underset{\displaystyle CH_3}{|}}{\dot{C}H} > CH_3\dot{C}H_2 > \dot{C}H_3$$

Tertiary Secondary Primary Methyl

The stability order of free radicals can be explained by hyperconjugation.

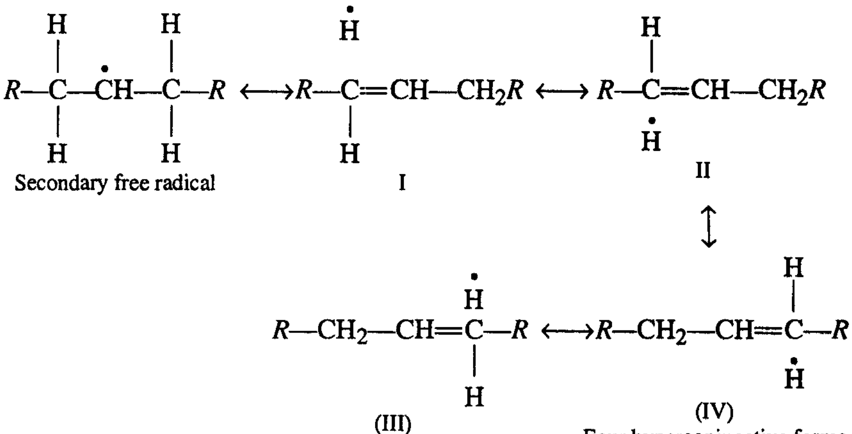
σ electrons of a *alpha* C—H bond can delocalise with the half-filled *p*-orbital of the carbon atom containing odd electron, thus spreading the odd electron over all such bonds and thereby stabilising the radical to some extent.

Several hyperconjugative resonance forms can be written each having the same number of covalent bonds as the first structure :



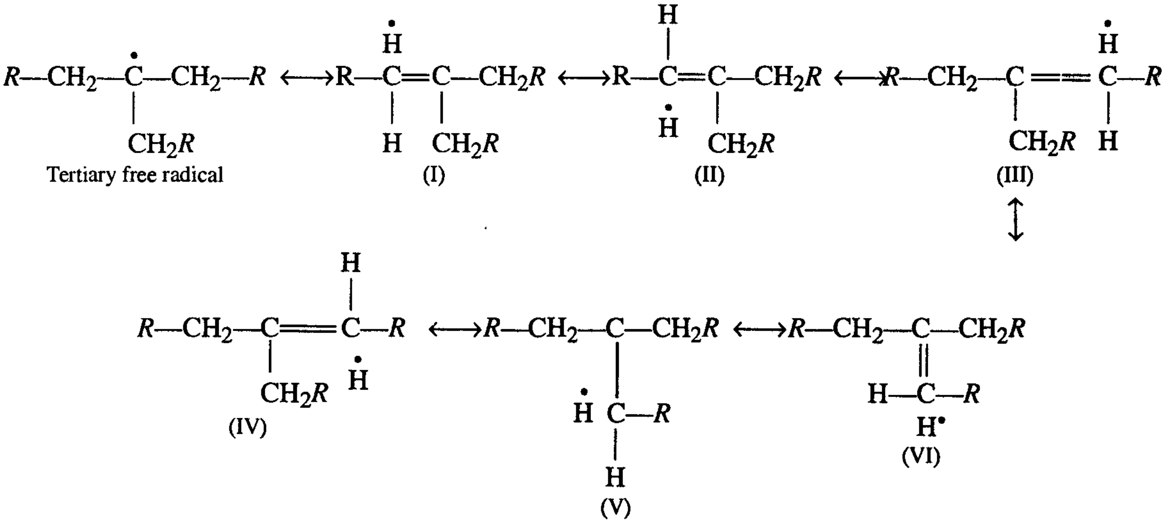
Primary free radical (i) (ii)

Two hyperconjugative forms



Secondary free radical I II (III) (IV)

Four hyperconjugative forms

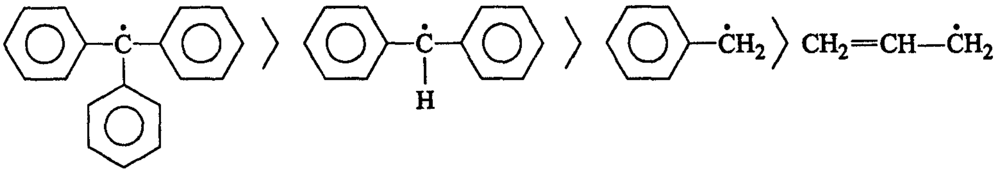


Tertiary free radical (I) (II) (III) (IV) (V) (VI)

Six hyperconjugative forms

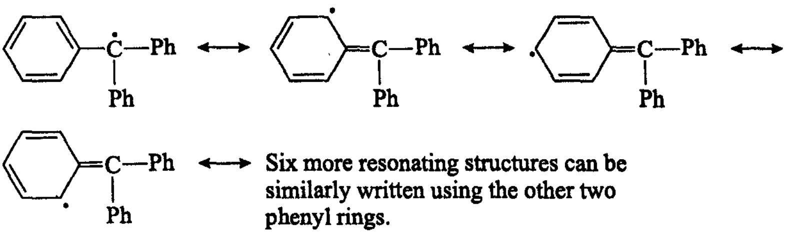
In the examples shown above, the primary free radical has only three resonating forms, the secondry radical has five and the tertiary has seven. As we know that the greater the number of equivalent resonance forms, the greater the stability of the species. Due to this, tertiary is more stable than secondary and secondary is more stable than primary free radical.

Some of the free radicals are listed below in order of their decreasing relative stability (in solution). These are more stable than the simple alkyl radicals.

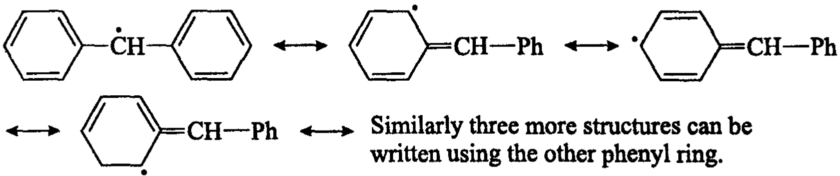

(i) (ii) (iii) (iv)

The relative stabilities of the above four radicals are easily understood on the basis of resonance. When the odd electron is in conjugation with double bond, the stability is greater because of increased delocalisation due to resonance and because odd electron is spread over whole molecule instead of being concentrated on one atom.

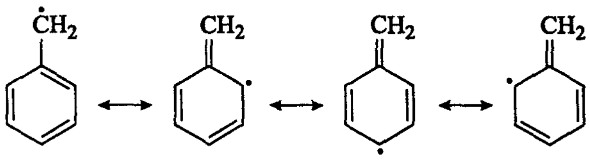
Ten resonance form can be written for triphenylmethyl free radical in which the odd electron is on the central carbon atom.


Six more resonating structures can be similarly written using the other two phenyl rings.

Similarly, diphenylmethyl free radical has seven resonance forms and benzyl free radical has four resonance forms.


Similarly three more structures can be written using the other phenyl ring.

Diphenylmethyl free radical (resonance stabilisation)


Resonance stabilisation of benzyl free radical

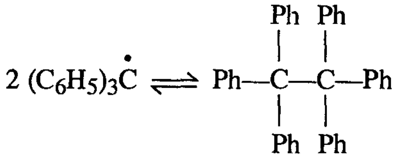
Thus triphenylmethyl free radical is more stable than the diphenylmethyl free radical because it has more number of resonating forms than the diphenylmethyl free radical. The next member is benzyl free radical. This also has the same type of resonance which stabilised the triphenylmethyl free radical. But in this case the number of resonating structures are less than triphenyl and diphenylmethyl free rdicals. Therefore, it is less stable than these two.

The allylic free radical has only two resonating forms,

$$CH_2{=}CH{-}\dot{C}H_2 \longleftrightarrow \dot{C}H_2{-}CH{=}CH_2$$

But both resonance forms are equivalent. Because of this, this free radical has a stability similar to benzyl free radical.

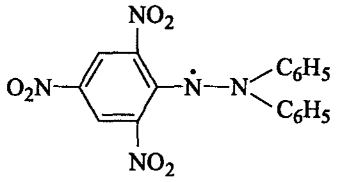
As mentioned earlier free radicals dimerise instantaneously. The triphenylmethyl radical on the other hand, is very stable and has been found to servive, if it is kept in dilute solution. At higher concentration, it is mostly dimeric, but the dimerisation is reversible.



$$2\,(C_6H_5)_3\dot{C} \rightleftharpoons Ph-\underset{Ph}{\overset{Ph}{C}}-\underset{Ph}{\overset{Ph}{C}}-Ph$$

Hexaphenylethane

Just as carbocations range from highly unstable to quite stable, so do free radicals. The most stable free radical is *N*, *N*-diphenyl picryl hydrazyl. This free radical is a commercially available soild.



Reactions of Free Radicals

The most common reactions of free radicals are the substitution and addition, for example, the halogenation of alkanes in the presence of light and the addition of HBr in the presence of a peroxide.

Halogenation of alkanes :

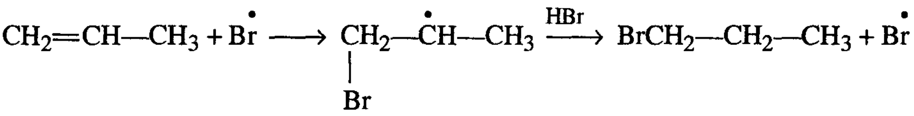
$$Cl-Cl \xrightarrow{h\nu} \dot{C}l + \dot{C}l$$

$$R-H + \dot{C}l \longrightarrow \dot{R} + H-Cl$$

$$\dot{R} + Cl-Cl \longrightarrow R-Cl + \dot{C}l$$

Free radical addition of HBr :

$$H-Br \xrightarrow{h\nu} H^{\bullet} + \dot{B}r$$



$$CH_2{=}CH-CH_3 + \dot{B}r \longrightarrow \underset{Br}{CH_2}-\dot{C}H-CH_3 \xrightarrow{HBr} BrCH_2-CH_2-CH_3 + \dot{B}r$$

Free radicals also undergo combinations of same or different radicals, or disproportionation giving a saturated and an unsaturated molecule.

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3-CH_3 \text{ combination}$$

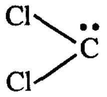
$$2CH_3\dot{C}H_2 \longrightarrow CH_2{=}CH_2 + CH_3CH_3 \text{ disproportination}$$

2.4.4 Carbenes

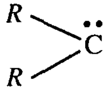
Carbenes are neutral, divalent, highly reactive carbon intermediates containing two single bonds and two non-bonding electrons around a carbon ($X-\ddot{C}-Y$).

The simplest carbene is methylene ($\ddot{C}H_2$). Other carbenes are simply named as substituted derivatives of methylene. For example :

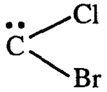
$C_6H_5-\ddot{C}H$ Phenylcarbene



Dichlorocarbene



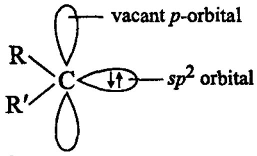
Dialkylcarbene



Bromochlorocarbene

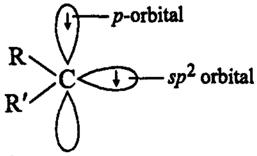
Structure of Carbenes

The carbene carbon is usually considered to be sp^2 hybridised. There are two bonding electrons (both in sp^2 orbitals) and two non-bonding electrons associated with the carbene carbon. Since the non-bonding electrons can have their spins paired or parallel, there is possibility of two electronic arrangements or spin states. Depending on this there are two kinds of carbenes : the singlet carbene and the triplet carbene. The singlet state carbene has the spins of its non-bonding electrons paired (spin multiplicity $M = 1$)*. This non-bonding electron pair is in an sp^2 orbital leaving a vacant *p*-orbital.



sp^2 singlet carbene

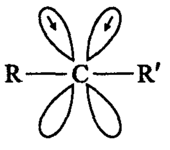
In the triplet carbene the two non-bonding electrons have parallel spins (spin multiplicity $M = 3$) and both the sp^2 and *p*-orbitals contain one electron each.



sp^2 triplet carbene

Hence triplet carbenes with their unpaired electrons exhibit properties of diradicals, and can be detected by ESR (electron spin resonance) spectroscopy.

Some carbenes have linear structure. In such cases, the carbene carbon will be in *sp* hybrid state. Two *p* orbitals remain unhybridised, and the two non-bonded electrons go into each with spin parallel according to Hund's rule because these *p* orbitals would be degenerate. This carbene will be *sp* triplet.



sp-triplet carbene

ESR spectroscopic studies have shown that triplet carbenes have bond angles of 130–150°, for example : $\ddot{C}H_2$, $Ph\ddot{C}H$, $\ddot{C}HR$, $(C_6H_5)_2\ddot{C}$, etc.

On the other hand, singlet carbenes cannot be observed by ESR spectroscopy. However, their bond angles have been found to be 100–110°. Examples are : $\ddot{C}X_2$, $\ddot{C}HX$, $\ddot{C}(OMe)_2$, etc.

---

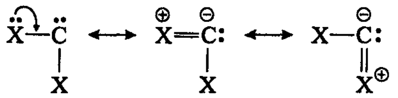
* $M = 2S + 1$, where s is the algebraic sum of the spins of the electrons in a molecule. If all the electrons have antiparallel spins, $S = 0$, hence $M = 1$ (singlet state); if there are two unpaired electrons (parallel spins) then $S = 1$, hence $M = 3$ (triplet state).

Many carbenes, like $\ddot{\mathrm{C}}\mathrm{H_2}$ exist as singlet as well as triplet. However, all carbenes have potential to exist in either the singlet or triplet state.

Some carbenes are linear but most have bent structure with bond angles between 100° and 150° suggesting an sp^2 hybridisation of the carbene carbon.

Stability of Carbenes

Generally, a triplet carbene (*e.g.*, $\ddot{\mathrm{C}}\mathrm{H_2}$) is 7.7–10 kcal/mole more stable than the singlet carbene ($\ddot{\mathrm{C}}\mathrm{H_2}$). The triplet carbene has a lower energy because with two electrons in different orbitals there is less electron-electron repulsion than that when both are in the same orbital. However, the nature of substituents has an important effect on the stability of carbenes. For example, as the substituents on the carbene carbon become better *pi* electron donors, the stability of the singlet state increases and the singlet state carbene becomes more stable than the triplet state carbene. Thus, halocarbenes are more stable in the singlet state than in the triplet state. This is because a *p*-orbital of the halogen (*X*) with a lone pair of electrons can overlap laterally with the vacant *p*-orbital of the singlet carbene, thereby stabilising the singlet state. This stabilisation is not possible in the triplet state whose *p*-orbitals are not vacant. The resonating structures are :



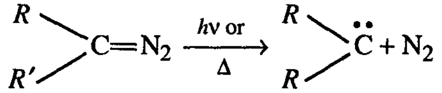
Amongst dihalocarbenes, the most stable is the singlet difluorocarbene. This can be explained as follows : Since fluorine and carbon are in the same period, their *p*-orbitals are of about the same size permitting more efficient overlapping. Furthermore, of the C—X bonds, the C—F bond length is the shortest which again provides far more extensive overlap of the respective *p*-orbitals. On this basis it can be concluded that the singlet $\ddot{\mathrm{C}}\mathrm{F_2}$ is more stable than $\ddot{\mathrm{C}}\mathrm{Cl_2}$ which is more stable than $\ddot{\mathrm{C}}\mathrm{Br_2}$.

Formation of Carbenes

Carbenes are usually generated from precursors by the loss of small, stable molecules.

(i) From diazo compounds

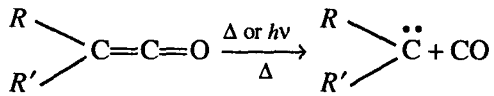
Diazo compounds easily decompose thermally and photochemically to give carbenes.



The most common diazo compound is diazomethane.

$$\mathrm{CH_2N_2} \xrightarrow[\Delta]{h\nu\text{ or}} \ddot{\mathrm{C}}\mathrm{H_2} + \mathrm{N_2}$$

(ii) From ketenes



$$\mathrm{CH_2{=}C{=}O} \xrightarrow[h\nu]{\Delta\text{ or}} \ddot{\mathrm{C}}\mathrm{H_2} + \mathrm{CO}$$

(iii) From *gem*-dihalides and trihalides

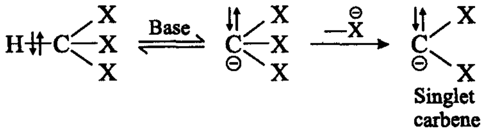
Gem-dihalides and *gem*-trihalides having at least one α hydrogen give carbene by α elimination in the presence of a strong base

$$CHCl_3 \xrightarrow[-H_2O]{\overset{\ominus}{OH}} \ddot{C}Cl_3 \longrightarrow \underset{\text{Dichlorocarbene}}{\ddot{C}Cl_2} + \overset{\ominus}{Cl}$$

The order of the ease of elimination is : *I* > Br > Cl > F. Thus CHF_2Cl gives exclusively difluorocarbene.

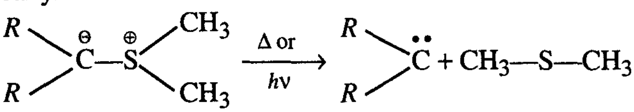
$$CHF_2Cl \xrightarrow[\overset{\ominus\oplus}{\text{e.g., }t\text{-BuOK}}]{\text{Strong base}} \overset{\oplus}{H} + \overset{\ominus}{Cl} + \ddot{C}F_2$$

α-elimination always gives singlet carbenes.

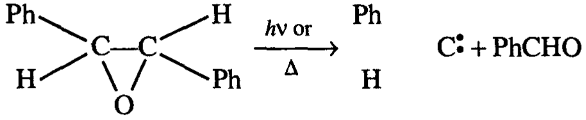


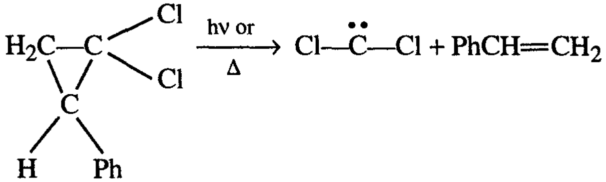
(iv) From ylides

Carbenes may be obtained from phosphorus, sulphur or nitrogen **ylide** on heating or photochemically.



(v) From small ring compounds





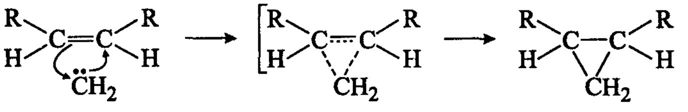
Reactions of Carbenes

Carbenes are electron deficient intermediates because the carbene carbon has only six electrons in its valency shell. Therefore, in general, carbenes are highly electrophilic in their reactions. –*I* group present on carbene carbon increases electron deficiency and hence increases the electrophilic character of the carbene.

Carbenes undergo two principal reactions, *viz.*, *cycloaddition* with alkenes, and *insertion* into a σ-bond.

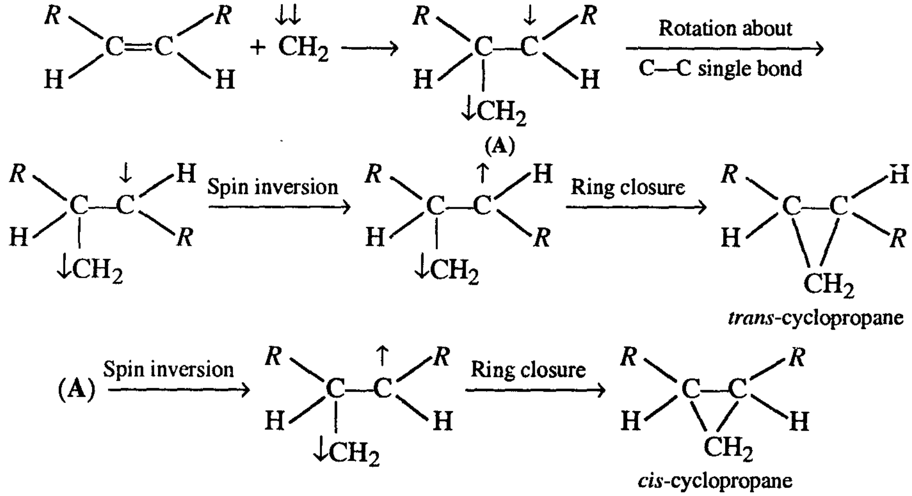
Cycloaddition to Alkenes

Addition of carbenes to alkenes gives cyclopropane derivatives. A concerted mechanism is possible for singlet carbenes, and they add stereospecifically to alkenes. As a result, the stereochemistry present in the alkene is retained in the cyclopropane.

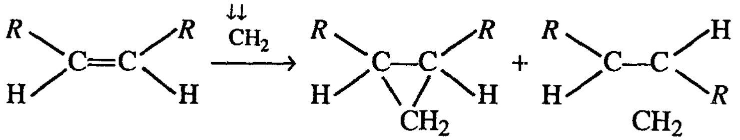


cis alkene *cis*-cyclopropane

With triplet carbenes, an intermediate diradical is involved. Ring closure to cyclopropane requires spin inversion. The rate of spin inversion is slower than the rotation about the C—C single bond. Thus, a mixture of the two possible stereoisomers is obtained from *cis* as well as *trans* alkenes, and the reaction is not stereospecific.

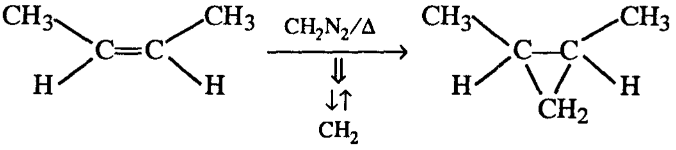


Thus,

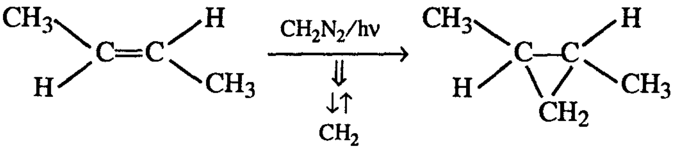


Reactions involving free carbenes are very exothermic because in these reactions there is loss of one *pi* bond and gain of two σ bonds.

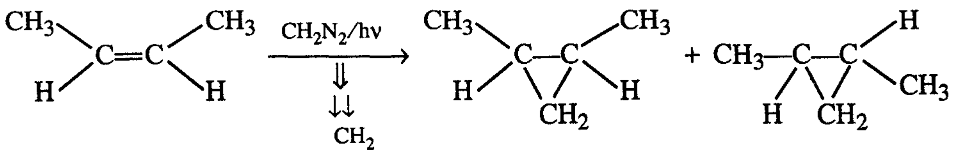
Addition of carbenes to alkenes is a very good method for the identification of singlet and triplet carbenes. For example, when *cis*-2-butene is heated with CH_2N_2, *cis*-1, 2-dimethylcyclopropane is formed. This shows that the thermal decomposition of CH_2N_2 gives singlet carbene.



Similarly it has been proved that the photolytic decomposition of CH_2N_2 in the absence of an inert gas also gives singlet carbene.

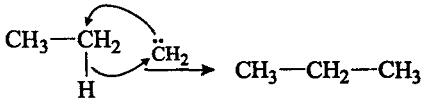


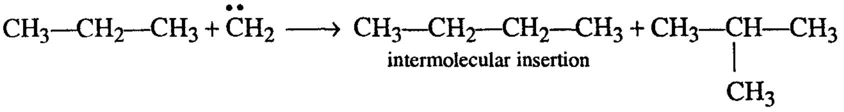
The photodecomposition of diazomethane in the presence of a large amount of an inert gas (*e.g.*, N_2) first produces singlet carbene which then collides with an N_2 molecule and loses energy to give the lower energy triplet carbene. This is proved by the formation of a mixture of the two possible stereoisomers.



Insertion into σ-bonds

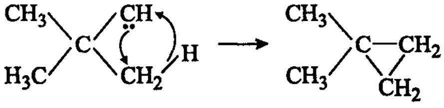
Carbenes undergo inter- and intramolecular insertion into C—H bonds, for example :





$$CH_3-CH_2-CH_3 + \ddot{C}H_2 \longrightarrow CH_3-CH_2-CH_2-CH_3 + CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_3$$

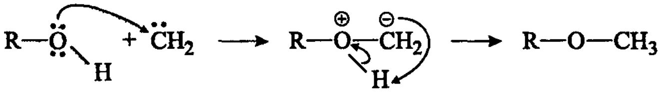
intermolecular insertion



intramolecular insertion

If there is possibility of three-, four- and five-membered rings, then the five-membered ring is preferably formed.

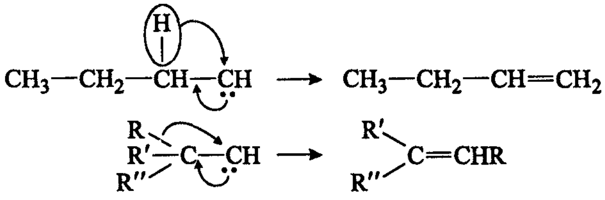
Carbenes also insert into other σ-bonds, *e.g.*, N—H, O—H, etc.



Ylide intermediate

Rearrangements of Carbenes

Alkylcarbenes can undergo rearrangements with migration of hydrogen or alkyl group. These rearrangements are so rapid that insertion reactions and addition to double bonds, which are very common to $:CH_2$, are seldom occur with alkyl or dialkylcarbenes.



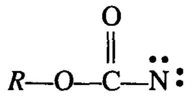
In this rearrangement migratory power of the groups in decreasing order is : H >> aryl > alkyl.

2.4.5 Nitrenes

Chemical species having a neutral, monovalent nitrogen are known as nitrenes. Nitrenes are nitrogen analogues of carbenes. Substituted nitrenes are simply named as substituted derivatives of nitrenes. For example :

$H-\ddot{N}:$	Nitrene
$C_6H_5-\ddot{N}:$	Phenylnitrene
$CH_3SO_2\ddot{N}:$	Methanesulphonylnitrene

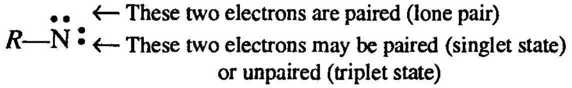
$R-\ddot{N}:$ Alkylnitrene



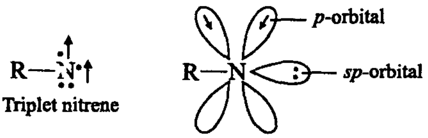
$R-O-\overset{\overset{O}{\|}}{C}-\ddot{N}:$ Carboalkoxynitrene

Structure of Nitrenes

Similar to carbenes, there are two possible spin states in which nitrenes can exist, *i.e.*, the singlet state (the two non-bonding electrons have their spins paired) and the triplet state (the two non-bonding electrons have parallel spins). In both the cases the normal lone pair remains paired.



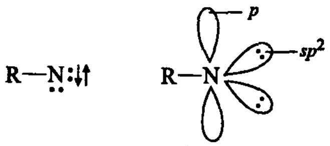
In general, nitrenes obey Hund's rule and are ground state triplets with two degenerate *p*-orbitals containing a single electron each, and the lone pair in the *sp*-orbital.



Triplet nitrene

sp-triplet nitrene

Nitrenes also exist in singlet state. Nitrogen atom in the singlet state is usually represented as sp^2 hybridised.



Singlet nitrene sp^2 Singlet nitrene

Stability of Nitrenes

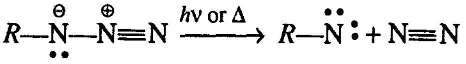
The energy difference between the singlet and triplet states is usually much larger for nitrenes than for carbenes, *i.e.*, 34.5 kcal/mole for nitrene $(:\ddot{N}H)$ and 7.7–10 kcal/mole for carbene $(\ddot{C}H_2)$. This energy difference is due to the electronegativity difference in carbon and nitrogen. Nitrogen is more electronegative than carbon, therefore holds its electrons closer to the nucleus which decreases energy and hence increases stability. Strong *pi* donor substituents such as amino groups greatly stabilise the singlet state as well as cause the nitrene to exhibit nucleophilic character. Such nitrenes are ground state singlet.

Nitrenes are characterized by spectroscopy mainly UV and IR. Nitrene $(:\ddot{N}H)$ is very transient species and it is extensively characterized by UV spectroscopy. It shows absorption maximum at 336 nm.

Formation of Nitrenes

(i) From azides

The most common method for generating nitrene intermediates is the photolysis or thermolysis of azides.



$$R-\underset{\bullet\bullet}{\overset{\ominus}{N}}-\overset{\oplus}{N}\equiv N \xrightarrow{h\nu \text{ or } \Delta} R-\ddot{N}: + N\equiv N$$

In this reaction azides may be alkyl, aryl, acyl, or sulphonyl.

$$R\text{—}SO_2\text{—}N_3 \xrightarrow{h\nu \text{ or } \Delta} R\text{—}SO_2\text{—}\ddot{N}: + N_2$$

(ii) From sulphinylamines

Sulphinylamines on thermolysis give nitrenes.

$$Ph\text{—}N{=}S{=}O \xrightarrow{\Delta} Ph\text{—}\ddot{N}: + SO$$

Sulphinylamines are readily prepared from aniline and thionyl chloride.

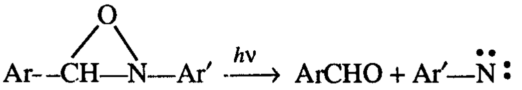
$$Ar\text{—}NH_2 + SOCl_2 \longrightarrow Ar\text{—}N{=}S{=}O + 2HCl$$

(iii) From nitro and nitroso compounds

$$ArNO_2 \xrightarrow[\Delta]{(C_2H_5O)_3P} Ar\text{—}\ddot{N}:$$

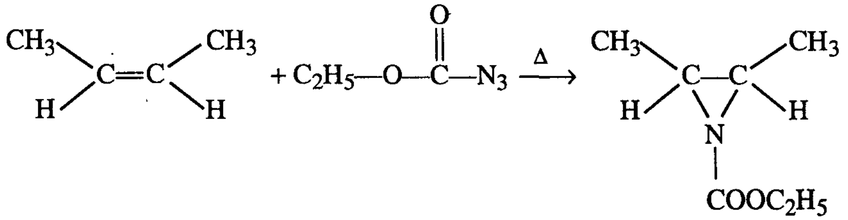
$$ArNO \xrightarrow[\Delta]{(C_2H_5O)_3P} Ar\text{—}\ddot{N}:$$

(iv) From small ring compounds

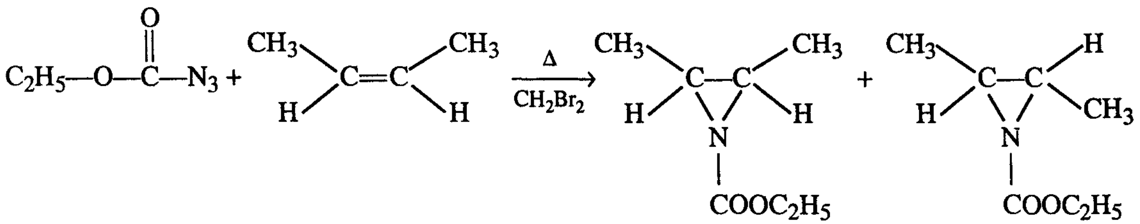


Reactions of Nitrenes

Cycloaddition to alkenes : Alkenes are nucleophiles and nitrenes, being electron deficient, are electrophiles, therefore addition reaction takes place between an alkene and a nitrene. The stereochemistry of the product depends on the spin state of the nitrene. Ethyl azidoformate on thermolysis gives singlet nitrene which adds stereospecifically to the alkene.

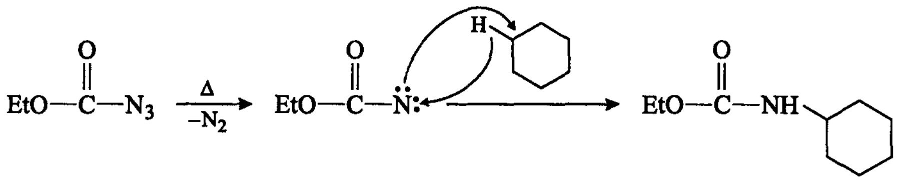


However, as the reaction mixture is diluted with an inert solvent (*e.g.*, CH_2Br_2) the singlet nitrene converts into triplet due to collisional decay and the reaction becomes non-stereospecific leading to a mixture of stereoisomers.



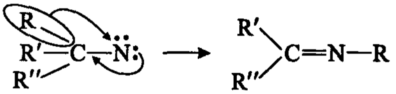
Insertion Reactions

Nitrenes undergo insertion reactions with saturated hydrocarbons.



Rearrangements of Nitrenes

Like other electron deficient intermediates with a vacant *p*-orbital such as carbocations and carbenes, nitrenes also undergo facile rearrangement in which an atom or group on the adjacent carbon migrates to electron deficient nitrogen with simultaneous formation of carbon-nitrogen double bond. Such rearrangements are called 1, 2-shifts.

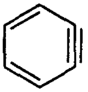


When the migrating group is hydrogen, the rearrangement is facile, hence other intermolecular reactions such as cycloaddition and insertion involving nitrenes are rarely seen. In this rearrangement migratory power of the groups in decreasing order is : H > > aryl > alkyl.

2.4.6 Benzynes (Arynes)

1, 2-Didehydrobenzene (C_6H_4) and its derivatives are called benzynes or arynes, and the simplest member is benzyne. Benzynes are neutral reaction intermediates derived from benzene ring by removing two *ortho* substituents, one in the form of electrophile and other in the form of nucleophile leaving behind two electrons to be distributed between two orbitals.

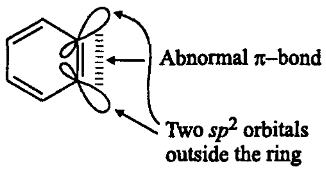
The nomenclature is derived from the fact that the C_6H_4 can be represented as an alkyne, although systematically the species should be named as 1, 2-didehydro aromatic compound, *e.g.*, 1, 2-didehydrobenzene is the systematic name for benzyne.



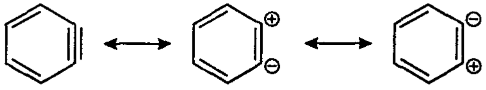
1, 2-didehydrobenzene (benzyne)

Structure and Stability of Benzynes

Benzynes can be represented by singlet molecules with a carbon-carbon triple bond. Although it has a triple bond, it is not a normal alkyne. In benzyne out of two π-bonds of the triple bond, one π-bond is normal and the other (the new one) is abnormal and is formed by lateral overlapping of two sp^2 orbitals outside the ring. This is called external π-bond. This external π-bond is very weak becuase of less efficient overlap, hence benzyne is very unstable and extremely reactive chemical species.



The structure of benzyne may also be considered as a resonance hybrid of the following resonating structures :

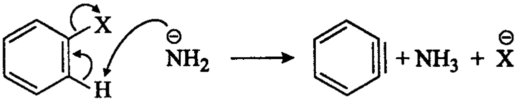


Dipolar structures explain the electrophilic character of benzynes. The resonating structures tell us that two additional electrons do not interact with the π-electron cloud involving Hückel number of π-electrons and hence they do not affect the aromaticity of the benzyne molecule.

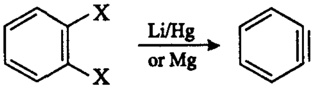
Formation of Benzynes

(i) From halobenzenes

When halobenzenes are treated with a strong base, *e.g.*, sodamide in liquid ammonia, or phenyllithium or alkyllithium, formation of benzyne takes place.

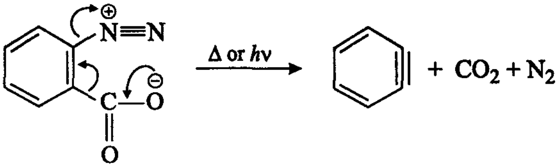


(ii) From *o*-dihalobenzenes



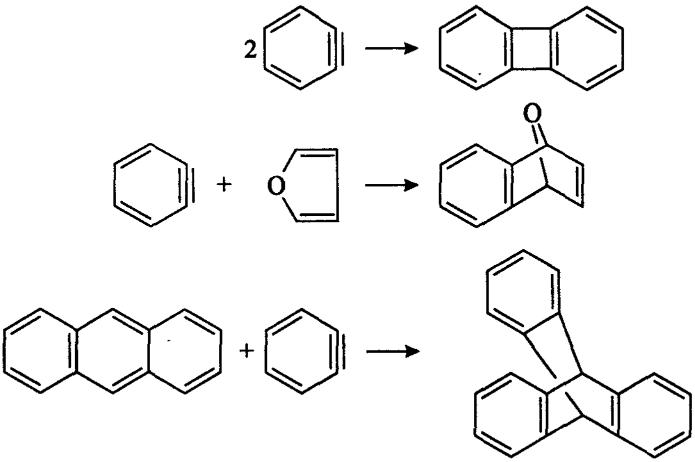
(iii) From benzenediazonium-2-carboxylic acid

This is a very convenient method for generating benzyne.



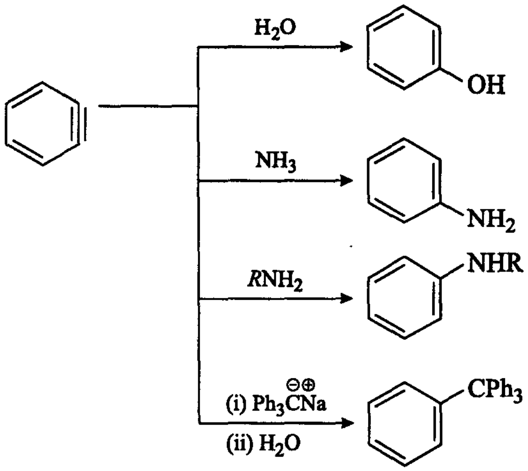
Detection of Benzynes

The transient existence of benzynes as reaction intermediates is detected by spectroscopy or by their dimerisation and trapping through cycloaddition reaction.

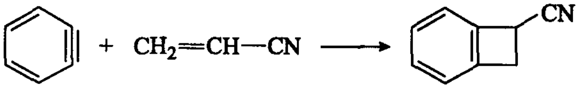


Reactions of Benzynes

Besides the above dimerisation and cycloaddition reactions, benzynes undergo nucleophilic addition with a variety of nucleophiles.



Benzynes react with olefins to form four-membered rings, for example :



2.5 FORMAL CHARGES

Formal charges may be described as the excess or lack of electrons on an atom in the molecule as compared to the free atoms. Because such charges usually affect the chemical reactions of such species, it is important to know how to tell where the charge is located.

To calculate formal charges, we simply count how many electrons contribute to the charge of each atom and compare that number with the number of valence electrons in the *free neutral atom* (given by the group number in the periodic table). The electrons that contribute to an atom's charge are :

(1) All its unshared (non-bonding) electrons; plus.

(2) Half the (bonding) electrons it shares with other atoms, or one electron of each bonding pair.

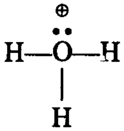
The formal charge can be summarised in the formula :

$$\begin{aligned}\text{Fromal charge} &= (\text{Number of valence electrons in a neutral atom}) \\ &\quad -\frac{1}{2}\,(\text{number of shared electrons}) \\ &\quad - \text{number of unshared electrons}\end{aligned}$$

or in a simplified form,

Formal charge = (group number) − (number of bonds on that atom + number of non-bonding electrons)

Let us apply this definition to the hydronium ion.



$$H{-}\overset{\oplus}{\ddot{O}}{-}H \quad (\text{with } {-}H \text{ below } O)$$

For each hydrogen atom

Number of valence electron in the hydrogen atom = group number = 1

Number of non-bonding electrons = 0

Half the number of shared electrons (or number of bonds present on a hydrogen atom) = 1
Therefore, the formal charge = 1 – (1 + 0) = 0

For the oxygen atom

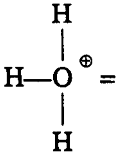
Number of valence electrons in oxygen atom (or group number of oxygen) = 6

Number of non-bonding electrons = 2

Number of bonds present on oxygen = 3

Therefore, the formal charge = 6 – (2 + 3)
= + 1

Thus it is the oxygen atom that carries positive charge in the hydronium ion. It should be noted that the net (overall) charge on the ion is the sum of the formal charges of all the atoms in the structure :

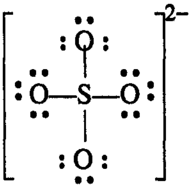


$$\text{Net charge of } \mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{O}}{}^{\oplus}} = \text{formal charge of H} + \text{formal charge of O}$$

$$= 3\,(0) + 1 = +1$$

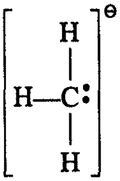
The following are some other examples of calculation of formal charges of each atom and the net charge of the structure :

(i)



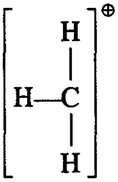
Formal charge of S = 6 – (4 + 0) = +2
Formal charge of each O = 6 – (1 + 6) = – 1
Net charge = 1 (+ 2) + 4 (– 1) = – 2

(ii)



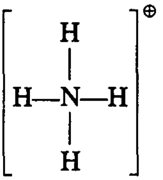
Formal charge of each hydrogen = 1 – (1 + 0) = 0
Formal charge of carbon = 4 – (3 + 2) = – 1
Net charge = (3 (0) + 1 (–1) = – 1

(iii)



Formal charge of each hydrogen = 1 – (1 + 0) = 0
Formal charge of carbon = 4 – (3 + 0)= + 1
Net charge = 3 (0) + 1 (1) = + 1

(iv)



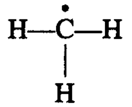
$$\left[\begin{array}{c}H\\ |\\ H-N-H\\ |\\ H\end{array}\right]^{\oplus}$$

Formal charge of H = 1 − (1 + 0) = 0

Formal charge of N = 5 − (4 + 0) = + 1

Net charge = 4 (0) + 1 (+ 1) = + 1

(v)



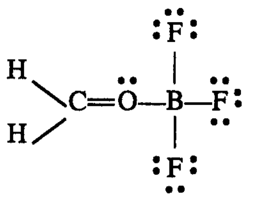
$$\begin{array}{c}\bullet\\ H-C-H\\ |\\ H\end{array}$$

Formal charge of H = 1 − (1 + 0) = 0

Formal charge of C = 4 − (3 + 1) = 0

Net charge = 3 (0) + 1 (0) = 0

There may be many neutral molecules (*i.e.*, with a net charge of zero) in which two or more of the atoms possess nonzero formal charges which cancel each other, for example :



Formal charge :

H = 1 − (1 + 0) = 0

C = 4 − (4 + 0) = 0

O = 6 − (3 + 2) = + 1

B = 3 − (4 + 0) = − 1

F = 7 − (1 + 6) = 0

Net charge = 2 (0) + 1 (0) + 1 (+ 1) + 1 (−1) + 3 (0) = 0

In this molecule oxygen has + 1 and boran −1 charge but the net charge on the molecule is zero, *i.e.*, it is a neutral molecule.

2.6 TYPES OF ORGANIC REACTIONS

Any classification of organic reactions must emphasize the changes that occur in the carbon bondings of the substrate at the site of the reaction. Thus a large variety of organic reactions may be placed in the following major categories :

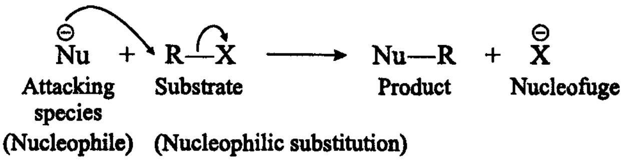
(1) Substitution reactions (2) Addition reactions (3) Elimination reactions

(4) Molecular rearrangements (5) Molecular reactions

(1) Substitution Reactions

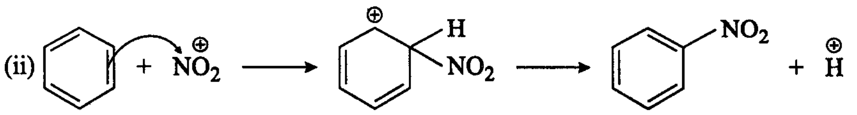
The replacement of an atom or group by any other atom or group is known as **substitution or replacement reaction.** In such reactions an attacking species of one type (nucleophile, electrophile or free radical) replaces another group of the same type.

(i)



$$\overset{\ominus}{Nu} + R-X \longrightarrow Nu-R + \overset{\ominus}{X}$$

(ii)



(Electrophilic substitution) Product Electrofuge

(iii)

$$CH_4 + \overset{\bullet}{Cl} \longrightarrow \overset{\bullet}{C}H_3 + HCl$$

Methyl free radical

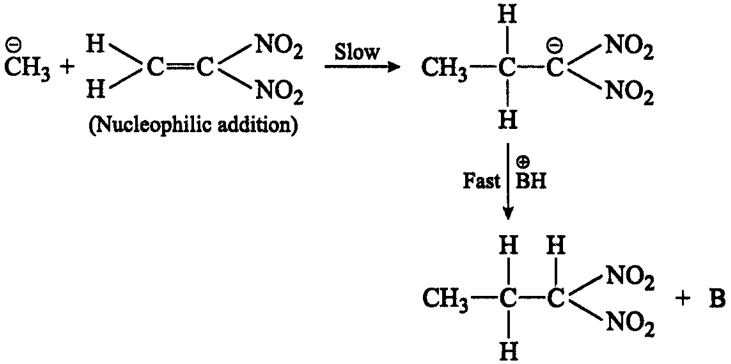
$$\overset{\bullet}{C}H_3 + Cl_2 \longrightarrow CH_3\text{—}Cl + \overset{\bullet}{Cl}$$

Methyl free radical

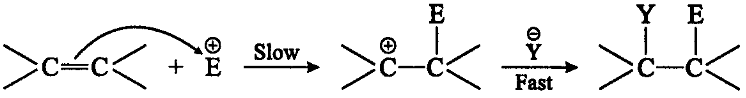
(Free radical substitution)

(2) Addition Reactions

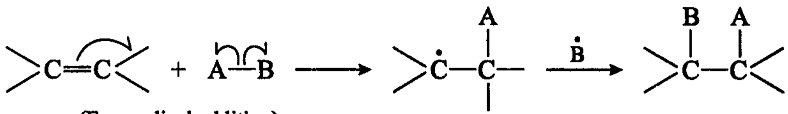
A reaction in which two molecules combine to give a single molecule of product is known as **addition reaction.** Addition reactions involve an increase in the number of groups attached to the substrate, and therefore a decrease in the degree of unsaturation of the substrate is an addition reaction. Most commonly, an addition involves the gain of two atoms or groups (one electrophile and one nucleophile, or both free radicals) at each end of the bond or ends of a system. As with substitution reaction, here also the attacking species may be a nucleophile, electrophile or free radical.



(Nucleophilic addition)



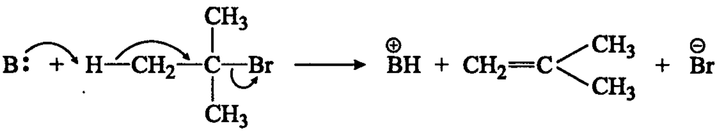
(Electrophilic addition)



(Free radical addition)

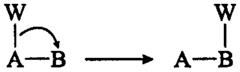
(3) Elimination Reactions

The reactions involving removal of atoms or goups from a molecule without their replacement by other atoms or groups are known as **elimination reactions.**



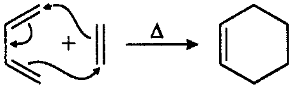
(4) Molecular Rearrangements

Reactions involving migration of an atom or group from one atom to another (*i.e.*, change in the bonding sequence within a molecule) are known as **molecular rearrangements or rearrangement reactions.**



(5) Molecular Reactions (Pericyclic Reactions)

Intra- or intermolecular processes involving concerted reorganisation of electrons within a closed loop of interacting orbitals are called molecular or pericyclic reactions. The most important example of such type of reactions is the well known *Diels-Alder* reaction.



2.7 ENERGY CONSIDERATIONS—THERMODYNAMICS OF REACTIONS

Thermodynamics is the study of energy changes and equilibrium positions involved in chemical and physical transformations. Chemical thermodynamics deals only with the relative stabilities of reactants and products in terms of energy.

If thermodynamics predicts that a reaction will not occur under certain conditions then it is no use trying it because it would not occur. However, even if a reaction is thermodynamically possible, it will be of little use unless its reaction rate is fast enough.

The study of thermodynamics involves the use of various functions, *e.g.*, *P, V, T, U, H, G, S*. These are variables whose values depend only on the state of the system and are independent of the path by which this is reached.

Let us now consider some thermodynamic applications. If *U* is the internal energy of a system at pressure *P* (atmospheres) and volume *V* (litres), then *H*, the enthalpy (heat content) of the system, is defined by the equation :

$$H = U + PV \qquad \text{...(i)}$$

Thus, when the reaction is carried out, the change in enthalpy of the reaction is given by the equation :

$$\Delta H = \Delta U + \Delta(PV) \qquad \text{...(ii)}$$

where *U* is the internal energy, *P* is pressure and *V* is volume.

For a reaction occurring at a constant pressure (most solution reactions) the change in enthalpy is the heat of reaction *qp* :

$$\Delta H = qp = \Delta U + P\,\Delta V \qquad \text{...(iii)}$$

If heat is absorbed by the reaction, *qp* has a positive value, and if heat is given off by the system *qp* is negative.

For reactions performed at a constant pressure, the heat of reaction *qp* is identical with the enthalpy of reaction Δ*H*. For reactions in which the volume remains constant (reactions run in a closed container such as a bomb calorimeter), the heat of reaction is :

$$qv = \Delta H - V\,\Delta P = \Delta U \qquad \text{...(iv)}$$

when the reaction is carried out at constant temperature, the enthalpy change, Δ*H*, is difference between the enthalpy of the product and reactant. If heat is evolved, Δ*H* is negative. In this case the product has a smaller enthalpy than the reactant and such a reaction is said to be exothermic. If, however, heat is absorbed, ΔH is positive and the reaction is said to be endothermic, and the product has a larger enthalpy than the reactant.

All chemical reactions are reversible, and reactants and products interconvert to different degree. When the concentration of reactants and products do not change, the reaction is said to be in a state of equilibrium. In several cases equilibrium lies extensively (say more than 99%) on the side of the products. When this occurs, the reaction is said to have gone to completion. In such cases the arrow indicating the reverse reaction is usually omitted. A chemical reaction proceeds when it has a favourable equilibrium, or, in other words, when the products are more stable than the reactants. The equilibrium constant of a reaction depends on the enthalpy change (ΔH) which is the quantity of heat released or absorbed and on the entropy change (ΔS) which is a measure of the energy consumed (or released) in the reaction to create more disorder (or order) in products relative to reactants. When entropy change is taken with the absolute temperature (T) it gives the free energy change (ΔG) according to the relationship :

$$\Delta G = \Delta H - T\,\Delta S$$

it should be noted that a reaction proceeds in the forward direction only when ΔG of the relation is negative. A positive ΔG, on the other hand, indicates that the reaction has a tendency to go backward. For an equilibrium reaction :

$$A + B \rightleftharpoons C + D$$

ΔG is always zero.

The relationship between the equilibrium constant (K) and ΔG is given by the equation :

$$\Delta G = -2.303\,RT \log K \qquad \text{...(v)}$$

where K = equilibrium constant
R = gas constant
T = absolute temperature

For many reactions entropy effects are small and it is the enthalpy that mainly determines whether the reaction can take place spontaneously. However, in certain type of reactions entropy is important and can dominate enthalpy.

2.8 KINETICS OF REACTIONS

Kinetic studies deal with the rates of reactions and their dependence on the concentration of the various reacting species. In contrast to the thermodynamics, time is the most important variable in kinetics. The rate of reaction is defined as the amount of reactant that is consumed in unit time or the amount of product formed in unit time. The equation relating reaction rate and molar concentration is called **rate law**. The constant K is the rate constant or specific rate, the exponent of the concentration factor is the reaction order for that substrate and the sum of the exponents of the concentrations is the order of reaction.

Consider the following reaction :

$$\mathrm{A + B \longrightarrow products} \qquad \text{...(vi)}$$

If it were found experimentally that the rate was proportional to the concentration of A and to the square of the concentration of B, the rate law would be written as :

$$\text{rate} = K\,[\mathrm{A}]\,[\mathrm{B}]^2 \qquad \text{...(vii)}$$

The above reaction is first order with respect to A and second order with respect to B, the reaction itself being therefore a third order (2 + 1 = 3) reaction.

For the reaction of the type :

$$\mathrm{A \longrightarrow C + D} \qquad \text{...(viii)}$$

the rate = K [A]

i.e., the reaction rate is dependant on concentration of A only and is a first order reaction.

For the type of reaction :

$$A + B \longrightarrow C + D \qquad \text{...(ix)}$$

$$\text{rate} = K\,[A]\,[B]$$

In this case rate is dependant on the concentration of A and B and is a second order (1 + 1 = 2) reaction.

The above two reactions may also proceed as :

$$A + B \xrightarrow{\text{Slow}} \underset{\text{Intermediate}}{[A - B]^{\neq}} \xrightarrow{\text{Fast}} C + D \qquad \text{...(x)}$$

$$\text{rate} = K\,[A]\,[B]$$

$$A \xrightarrow{\text{Slow}} \underset{\text{Intermediate}}{[A]^{\neq}} \xrightarrow{\text{Fast}} C + D \qquad \text{...(xi)}$$

$$\text{rate} = K\,[A]$$

Both these reactions (x) and (xi) are two-step reactions involving the formation of intermediate. When more than one step is involved in a reaction, it is known as multistep reaction. The rate of such a reaction is equal to the rate of the slowest step, known as the **rate-determining step** and kinetics of the reaction is kinetics of the slowest step.

In other words, the kinetics of the overall reaction is identical with the kinetics of the rate-determining step because the overall rate of the reaction is equal to the rate of the slowest step.

The **molecularity** of reaction on the other hand may be defined as the number of species that are undergoing covalency change in the rate-determining step. The order of reaction is determined experimentally, whereas molecularity is a theoretical concept. Further, the order of reaction can be a fraction, whereas molecularity shall always be a whole number. The kinetic order of any single step of a reaction is the same as the molecularity of that step.

2.9 REACTIVITY AND RATES OF REACTIONS

Up to this point, we have written rate expressions for various reactions in terms of a rate constant *K*. Every reaction has a characteristic rate constant, and if the reaction has several steps, each step is associated with a rate constant. Obviously, one important feature that causes a reaction to occur in preference to another or that causes one step in a multistep sequence to be slower than the others is the magnitude of the individual rate constants. Two important theories which explain the difference in rate constants are :

(i) Collision theory (ii) Transition State theory

Before discussing these theories, we shall first discuss the following :

Energy Profiles or Reaction Coordinate Diagrams : The energy changes that take place during the course of a reaction, as reactants are converted into products, can be visualised using a reaction profile (reaction coordinate diagram). In a reaction coordinate diagram, the energy of the species involving in the reaction is plotted against the progress of the reaction. A reaction progresses from left to right. Starting with the reactants and ending with the products. The energy of reactant is plotted on the left hand side on the *x*-axis, and the energy of the products is plotted on the right hand side of the *y*-axis. The more stable the species, the lower is energy. A typical reaction coordinate diagram of the following reaction is shown in Fig. 2.2.

$$CH_3I + \overset{\ominus}{Cl} \longrightarrow CH_3Cl + \overset{\ominus}{I}$$

(i) Collision Theory : collision theory is based on the kinetic theory of gases. *According to the collision theory, chemical reactions occur due to collisions of the molecules.* The rate at which a

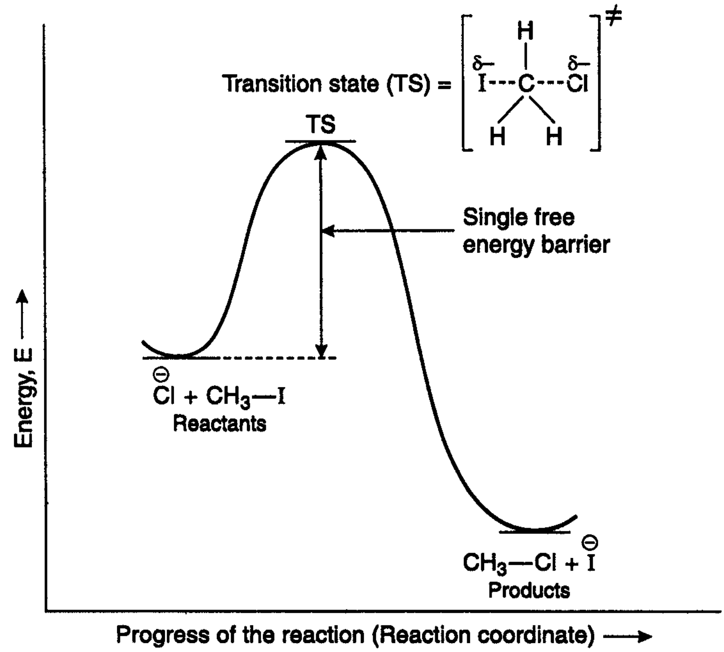


Fig. 2.2. Reaction coordinate diagram for the reaction between CH_3—I and $\overset{\ominus}{Cl}$

chemical reactions between two molecules (say A and B) occurs cannot be faster than the rate at which they collide. Thus, a knowledge of the number of collisions taking place per unit time should give us information about the rate of a reaction. Certainly increasing the concentrations of A and B will increase the frequency of collisions, because there are more molecules to collide (doubling the concentration of A or B should double the frequency of collisions, etc.). An increase in temperature should also increase the rate of collisions, because the molecules will move faster and collide more often. The rate of reaction, however, does not depend only on the frequency of the collisions as it has been found that only one in every 10^{15} collisions lead to products. To account for this, it is suggested that reaction will occur only when the molecules collide with energy greater than a certain minimum amount. This minimum amount of energy that must be provided by a collision for reaction to take place is called the **activation evergy**, *Ea*. When collisions occur with less than this amount of energy, they are elastic, the atoms bounce apart and no reaction takes place. Activation energy is required even for a thermodynamically favoured reaction, as energy is needed for breaking the bonds in the reactants before new bonds are formed in the products. The reason is that, although the bonds in the products are more stable than those in the reactants, bonds must be broken (requiring energy) before new bonds are completely formed as the reaction proceeds. Thus, there is a certain geometrical arrangement of atoms which is of higher energy than that of either the reactants or the products. This region of highest energy on the reaction pathway is called an **activated complex**. Reactants have to pass through this highest energy state before their conversion to products. The situation can be pictured in terms of an energy profile for a typical reaction (Fig. 2.3).

The difference between the average energy of the starting materials and energy of the activated complex is *Ea* (the activation energy) and only those molecules of starting material which have this amount of energy will be able to react on collision. However, there is further limitation, that is the colliding activated molecules must be effectively oriented with respect to each other for successful combination. In other words, the activated molecules must be suitably oriented to react when they

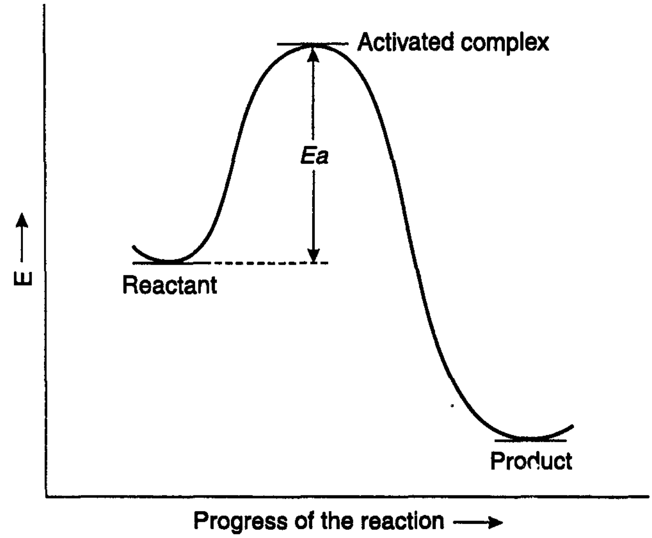


Fig. 2.3. Free energy profile for a one step reaction.

collide. This limitation is referred to as probability factor P, with this the rate of reaction can be expressed as follows :

$$\text{Rate} = P\, Ze^{-Ea/RT} \qquad \ldots\text{(xii)}$$

where Z = number of collision per unit time

P = Probability factor

Ea = Activation energy

(ii) Transition State Theory : A more modern approach to reaction rates and one which is also applicable to reactions in solution, is the transition state theory (sometimes called the absolute rate theory). The objective of this theory is to bring to bear on the problem of reaction mechanisms the very powerful principles of thermodynamics. This is the theory that is most generally applied in organic chemistry today.

According to the transition state theory, when two molecules come together in a collision that leads to products, they pass through a configuration of maximum potential energy called the transition state (TS). Transition state is often abbreviated as ≠ (double dagger) as a superscript. It does not deal with collisions and their probabilities, but relates the rate of reaction to the rate at which the system passes through a transition state.

In the transition state theory, the reactants and transition state or activated complex are taken to be in equilibrium, the equilibrium constant being designated $K^{\neq}$. According to this theory all activated complexes go on to the product at the same rate so that the rate constant of the reaction depends only on the position of equilibrium between the reactants and the activated complex. Hence, the rate constant of the reaction is dependant on the equilibrium constant which can be related to free energy change by :

$$\Delta G^{\neq} = -2.303\, RT \log K^{\neq} \qquad \ldots\text{(xiii)}$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} = -2.303\, RT \log K^{\neq} \qquad \ldots\text{(xiv)}$$

$\Delta G^{\neq}$ = free energy of activation

The equilibrium constant $K^{\neq}$ is defined like other equilibrium constants as :

$$K^{\neq} = \frac{[\text{Transition state}]}{[\text{Starting materials}]} \qquad \ldots\text{(xv)}$$

Statistical mechanics has been used to show that all transition states go on to their respective products at the same rate. This universal rate constant is K_BT/h. At 25°C $K_BT/h = 6 \times 10^{12}\ \text{sec}^{-1}$. Thus the rate of all chemical reactions can be expressed as :

$$\text{rate} = \frac{K_BT}{h}\,[\text{Transition state}] \qquad \text{...(xvi)}$$

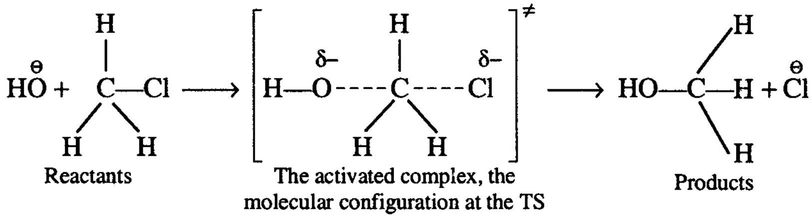
and from the equation (xvi) we can write

$$\text{Rate} = \frac{K_BT}{h}\,K^{\neq}\,[\text{Starting materials}] \qquad \text{...(xvii)}$$

and from the equation (xv) we can write

$$K = \frac{K_BT}{h}\exp\frac{-\Delta G^{\neq}}{RT} \qquad \text{...(xviii)}$$

Thus, higher the value of $\Delta G^{\neq}$, smaller will be the rate constant. Fig. 2.4 represents a free energy diagram according to the transition state theory of the reaction :



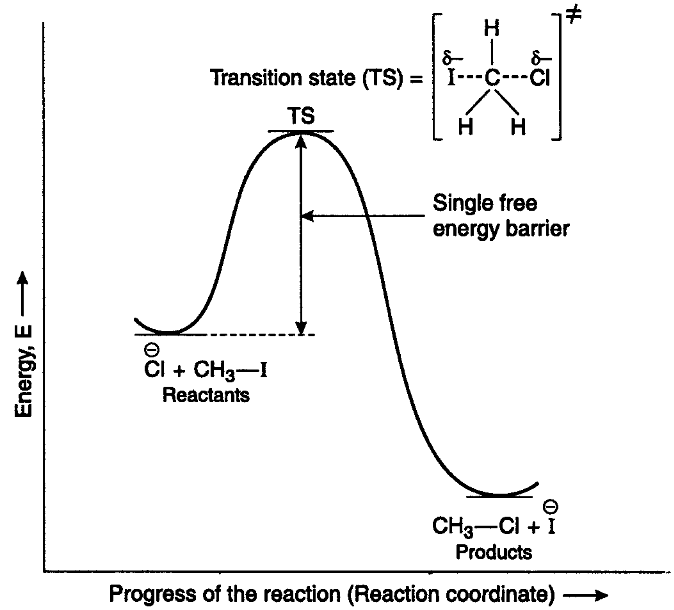


Fig. 2.4. Free energy profile for a one step reaction.

The transition state is the state of the highest potential energy acquired by the reactant during the transformation. The molecular complex which exists at the TS in equilibrium with the reactants and products is called the *activated complex*. It possesses a definite geometry and charge distribution. Due to high energy, it is highly unstable and cannot be isolated or detected. Since $\Delta G^{\neq}$ is the energy barrier, the greater the height, slower will be the reaction.

Multistep reactions may also be represented by such free energy diagrams. These reactions usually involve the formation of one or more intermediates and there are two or more transition states each with higher energy than that of the reactants, intermediates and products. Fig. 2.5 shows a free energy diagram for a simple reaction.

$$\underset{\text{Reactants}}{A+B} \xrightarrow{\text{Slow}} \underset{\text{Intermediate}}{I} \xrightarrow{\text{Fast}} \underset{\text{Product}}{C+D} \qquad \text{...(xix)}$$

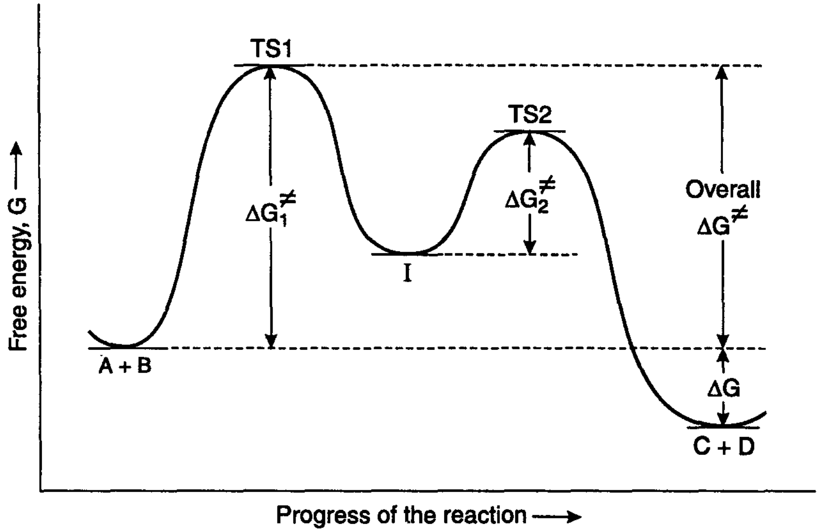


Fig. 2.5. Energy profile for a two step reaction with a less stable intermediate.

The energy well or minimum in the curve represents an intermediate in the reaction. There are two transition states, each with an energy higher than the intermediate. The deeper the well, the more stable the intermediate. Minima in free energy profile diagram correspond to real species which have a finite though very short existence. These intermediates may be carbocations, carbanions, carbenes, free radicals, nitrenes, benzynes. These intermediates do not live long (because $\Delta G_2^{\neq}$ is small) but rapidly go on to products. Maxima in these curves do not correspond to actual species but only to transition states in which bond breaking and/or bond making have partially taken place.

The rate of reaction is dependant on the slowest step, *i.e.*, the first step (equation xix) and the free energy of activation for the first step is highest. Thus the overall rate of reaction is dependant only on the difference of free energy of reactants and the highest point (corresponding to a transition state T_1) on the free energy curve. In a two step reaction, therefore, there are two transition states and one intermediate. The conversion of intermediate to products in the above reaction will not effect the rate as it will convert to products more rapidly than the reactants are converted to intermediate.

Now consider the following reaction (xx)

$$\mathrm{A+B} \xrightarrow{\text{Fast}} \mathrm{I} \xrightarrow{\text{Slow}} \mathrm{C+D} \qquad \text{...(xx)}$$

Fig. 2.6. represents the reverse situation in two step reaction. In this case the intermediate is very stable and the second step is thus rate determining.

It is also noted that the number of transition states in a multistep reaction is always equal to the number of steps and number of intermediate is always **one less** than the number of steps.

Intermediates are real chemical species (normal covalent molecules or ions) having a definite geometry and finite lifetimes. These can be isolated in many cases. If they are too unstable to be

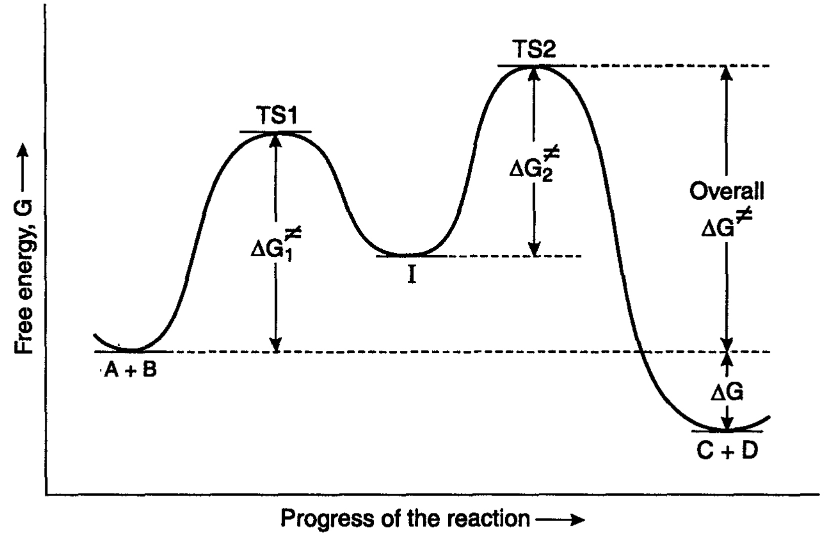


Fig. 2.6. Energy profile for a two step reaction with a stable intermediate.

isolated, their properties can be studied directly by methods such as spectroscopy, or alternatively they can be trapped by suitable reagents with which they are known to react.

On the other hand, *the transition state is not a normal covalent molecule (or ion) as some bonds are partially broken, while others are partially formed. The TS is the state of the highest potential energy in a reaction pathway. These cannot be isolated or directly detected.*

2.10 HAMMOND POSTULATE

As mentioned above, transition state is not a normal covalent molecule as some bonds are partially broken whereas others are only partially formed. According to Hammond postulate, in any individual step in a reaction, the geometry and structure of the transition state resemble either the

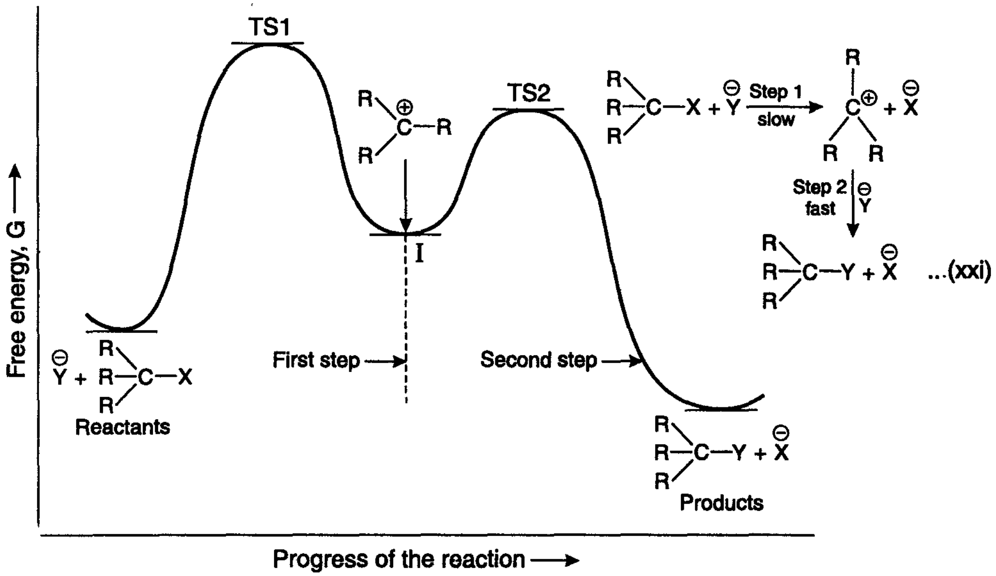
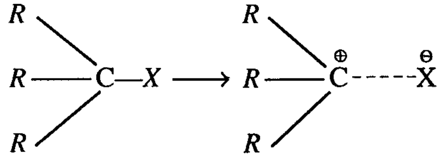


Fig. 2.7. Energy profile of the two step reaction described by equation (xxi).

reactants or the products or the intermediate depending on which of these is closer in free energy to the transition state. This implies that in an endothermic step the TS resembles the products and that in exothermic step the transition state resembles the reactants.

For example, in the reaction shown in Fig. 2.7 the first step is endothermic and therefore the TS resembles the intermediate state I to a greater extent than the starting reactants. The second step is exothermic and the TS for this step resembles the intermediate state more than the final products.

Thus, the TS may be described as *reactant-like*, *product-like* or *intermediate-like* depending upon the proximity of the former with any one of the latter. Hammond postulate is often useful to explain the observed rate and course of reactions, *e.g.*, it is well known that branching at the α carbon enhances the rate of SN1 reactions. Generally, it is related to the stability of carbocations, but the rate enhancement does not depend upon the stability of carbocations. Rather it depends upon the ease with which the TS leading to carbocation is reached, *i.e.*, upon $\Delta G^{\neq}$. As the TS is not **amneable** we use Hammond postulate assuming that in this reaction, the TS is carbocation-like and any factor that lowers the energy of the carbocation will lower the energy of the TS. Hence, such a TS is reached more readily lowering the value of $\Delta G^{\neq}$.



Carbocation-like
TS

2.11 CATALYSIS

A catalyst is a substance which increases the rate of a chemical reaction without itself being consumed in the process. Because the rate of reaction is determined by the activation energy, the catalyst functions by providing a new reaction pathway which has a lower activation energy. The common example used to illustrate the action of a catalyst is the reaction between an alkene and hydrogen. Hydrogenation of alkene is an exothermic reaction. However, despite the favourable thermodynamics,

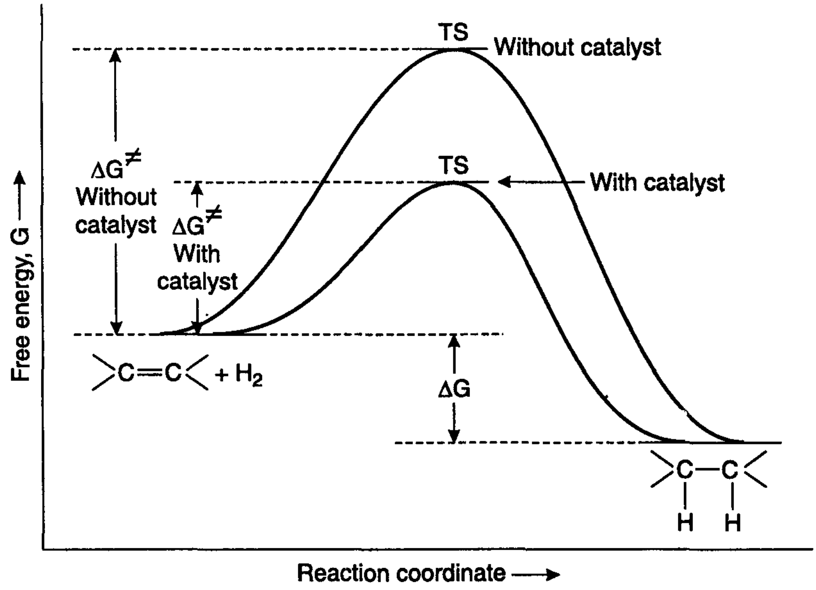


Fig. 2.8. Energy profile for the uncatalysed and catalysed reaction.

no reaction occurs when the alkene and hydrogen are simply mixed together. This is because the activation energy for this reaction is too high. When a dispersed metal such as palladium is added, the uptake of hydrogen is smooth and quantitative. The metal catalyst serves to lower the activation energy for the overall reaction. This effect is shown in Fig. 2.8 with the aid of an energy diagram.

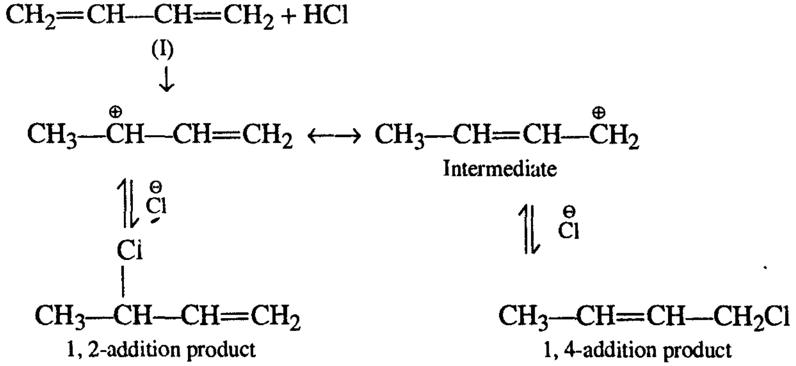
Note that ΔG of reaction is not altered by addition of the catalyst, the rate is merely increased because $\Delta G^{\neq}$ is decreased. The catalyst is not consumed in the overall reaction. If combines with the reactants in the initial step and is regenerated at a later stage of the reaction.

2.12 KINETIC AND THERMODYNAMIC CONTROL OF REACTIONS

When a reaction produces more than one product, *the product which is formed the most rapidly is called the kinetically controlled product* (or kinetic product). *The most stable product is called the thermodynamically controlled product* (or thermodynamic product). Reactions that produce the kinetic product as the major product are called kinetically controlled reactions (with lower $\Delta G^{\neq}$). Reactions that produce thermodynamic product as the major product are called thermodynamically controlled reactions (with lower ΔG). When a reaction is *under kinetic control, the relative amounts of the products depend on the rate at which they are formed* ($\Delta G^{\neq}$). When a reaction is *under thermodynamic control, the relative amounts of the products depend on their stabilities* (ΔG).

If a reaction producing more than one product is reversible and is stopped well before the equilibrium has been established, then the reaction will be kinetically controlled because more of the faster formed product will be present. However, if the reaction is allowed to attain equilibrium, then the thermodynamic (most stable) product will be predominant (or exclusive) product and the reaction will be thermodynamically controlled.

For example, addition of HCl to 1, 3-butadiene (I) clearly demonstrates the importance of kinetic and thermodynamic control in product composition.



$$\underset{\text{(I)}}{CH_2{=}CH{-}CH{=}CH_2} + HCl$$

$$\downarrow$$

$$CH_3{-}\overset{\oplus}{C}H{-}CH{=}CH_2 \longleftrightarrow \underset{\text{Intermediate}}{CH_3{-}CH{=}CH{-}\overset{\oplus}{C}H_2}$$

$$\Big\downarrow\!\!\uparrow \overset{\ominus}{Cl} \qquad\qquad \Big\downarrow\!\!\uparrow \overset{\ominus}{Cl}$$

$$\underset{\text{1, 2-addition product}}{CH_3{-}\underset{}{\overset{Cl}{\overset{|}{C}}}H{-}CH{=}CH_2} \qquad \underset{\text{1, 4-addition product}}{CH_3{-}CH{=}CH{-}CH_2Cl}$$

The 1, 2- and 1, 4-addition of HCl to 1, 3-butadiene

The addition of HCl to 1, 3-butadiene can lead to two products, both derived from a common intermediate as shown above. Fig. 2.9 shows the potential energy profile for the second step in the addition.

The more stable 1, 4-addition product predominates at higher temperature, when equilibrium is more rapidly attained, even though it is formed more slowly than 1, 2-addition product ($\Delta G^{\neq}_{1,4}= > \Delta G^{\neq}_{1,2}$). At lower temperature, where the equilibrium is not attained very rapidly, the 1, 2-addition product predominates. Thus, at lower temperature the reaction is kinetically controlled, whereas it becomes thermodynamically controlled at elevated temperature.

On the basis of the above discussion, we can conclude that the product which predominates depends on the conditions under which such reactions are carried out. If the reaction is carried out

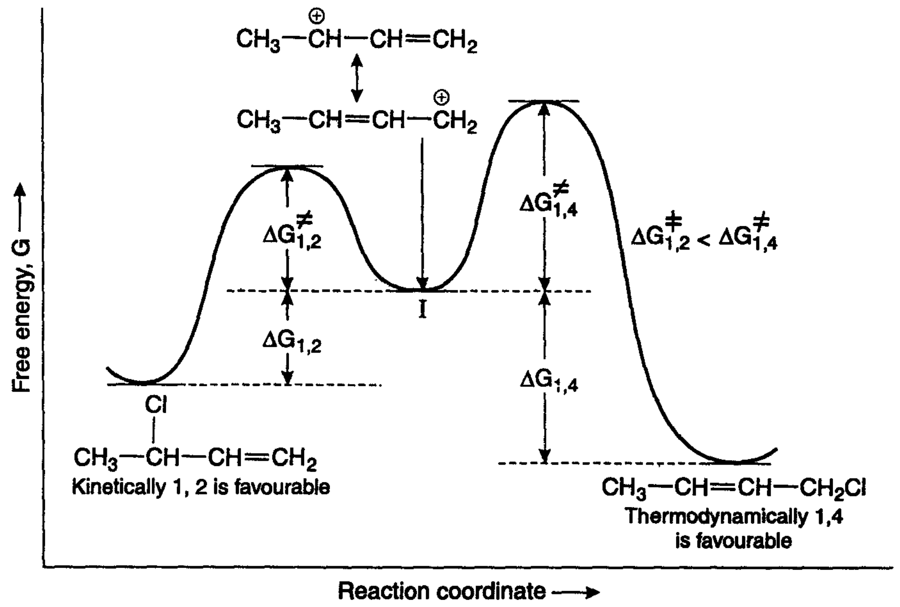


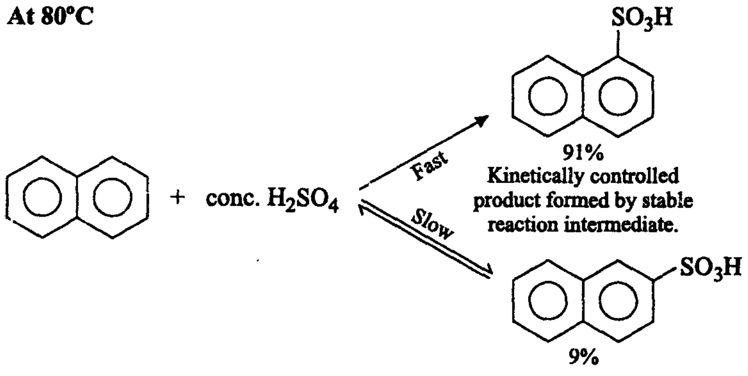
Fig. 2.9. Energy profile for the second step in the addition of HCl to 1,3 butadine.

under mild (low temperature) conditions, the major product will be the kinetic product. If the reaction is carried out under more vigorous (high temperature) conditions, the major product will be the thermodynamic product.

$$\text{Reactants} \xrightarrow[\text{(low temperature)}]{\text{mild conditions}} \text{kinetic product}$$

$$\text{Reactants} \xrightarrow[\text{(high temperature)}]{\text{vigorous conditions}} \text{thermodynamic product}$$

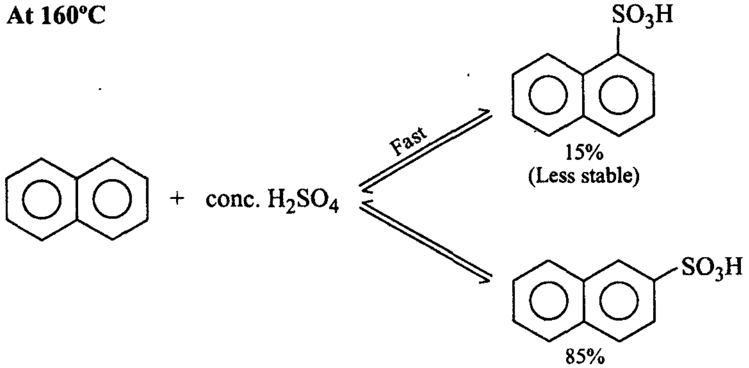
This conclusion may also be illustrated by sulphonation of naphthalene as another example of thermodynamically and kinetically controlled reactions.



91%
Kinetically controlled product formed by stable reaction intermediate.

9%

At 160°C



15%
(Less stable)

85%
Thermodynamically
more stable

2.13 METHODS OF DETERMINATION OF REACTION MECHANISMS

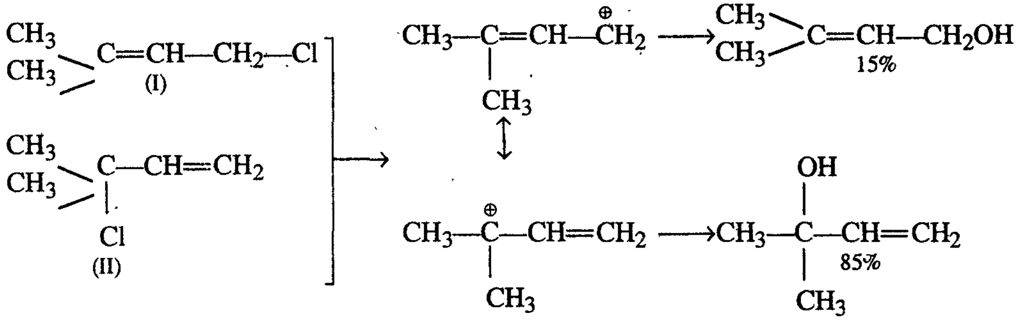
A reaction mechanism must explain all observations regarding a given chemical transformation. It should show which bonds are broken, which are formed, and the order in which this is accomplished. It should explain any change in stereochemistry, geometry and hybridisation. After characterizing the product(s), the mechanism of a reaction is determined by considering all the possibilities compatible with the experimental observations.

There are a number of commonly used methods for determining the mechanism of a reaction. These include product analysis, determination of the presence of intermediates, isotopic labelling and isotope effects, crossover experiments, stereochemical evidence, kinetic evidence and study of catalysis. It should be noted that the above order is not necessarily the order of experimentation. Furthermore, it may not be necessary to apply all the methods to determine the mechanism of a particular reaction.

2.13.1. Product Analysis

The most fundamental basis for mechanistic speculation is the identification of the reaction products and by-products (if any). The approximate yield must also be known before one starts speculating about its mechanism. Even a minor product may indicate that a competing reaction is going on, or a proposed mechanism is inadequate or incorrect. Some typical examples are :

(i) Hydrolysis of isomeric allyl chlorides (I) and (II) yields a mixture of 85% of tertiary alcohol and 15% of primary alcohol. Since product composition remains the same in either case, a common intermediate is suggested.



(ii) A little ethane invariably acompanies methyl chloride when methane is chlorinated in the presence of light. Hexafluoroethane is similarly a by product when fluorine reacts with methane. Free radical mechanism accounts for these facts readily but an ionic mechanism cannot.

$$Cl_2 \xrightarrow{h\nu} Cl^\bullet + Cl^\bullet$$

$$CH_3{-}H + Cl^\bullet \longrightarrow \overset{\bullet}{C}H_3 + HCl$$

$$\overset{\bullet}{C}H_3 + Cl_2 \longrightarrow CH_3{-}Cl + Cl^\bullet$$

$$\overset{\bullet}{C}H_3 + \overset{\bullet}{C}H_3 \longrightarrow CH_3{-}CH_3$$

$$F_2 \xrightarrow{h\nu} F^\bullet + F^\bullet$$

$$CH_4 + F^\bullet \longrightarrow \overset{\bullet}{C}H_3 + HF$$

$$\overset{\bullet}{C}H_3 + F_2 \longrightarrow CH_3{-}F + F^\bullet$$

$$CH_3{-}F + F^\bullet \longrightarrow \overset{\bullet}{C}H_2F + HF$$

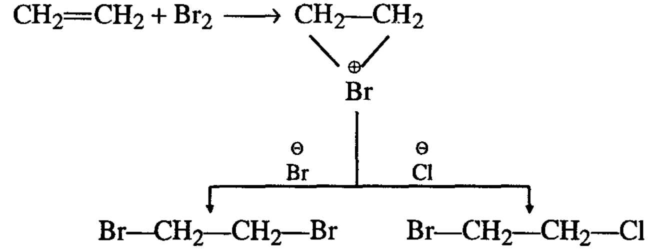
$$\overset{\bullet}{C}H_2F + F{-}F \longrightarrow CH_2F_2 + F^\bullet \longrightarrow \overset{\bullet}{C}HF_2 + HF$$

$$\overset{\bullet}{C}HF_2 + F{-}F \longrightarrow CHF_3 + HF$$

$$CHF_3 + F^\bullet \longrightarrow \overset{\bullet}{C}F_3 + HF$$

$$\overset{\bullet}{C}F_3 + \overset{\bullet}{C}F_3 \longrightarrow \underset{\text{Hexafluoroethane}}{CF_3{-}CF_3}$$

(iii) A coproduct of the reaction may throw light on the path of the reaction and suggest a mechanism in some cases. For example, 1-bromo-2-chloroethane is formed together with 1, 2-dibromoethane when bromine gives addition reaction with ethene in the presence of aqueous sodium chloride. It shows that addition of bromine does not take place in a single step and thus mechanism is as follows :



$$CH_2{=}CH_2 + Br_2 \longrightarrow CH_2{-}CH_2 \text{ (bridged by } Br^{\oplus})$$

$$\xrightarrow{Br^{\ominus}} Br{-}CH_2{-}CH_2{-}Br \qquad \xrightarrow{Cl^{\ominus}} Br{-}CH_2{-}CH_2{-}Cl$$

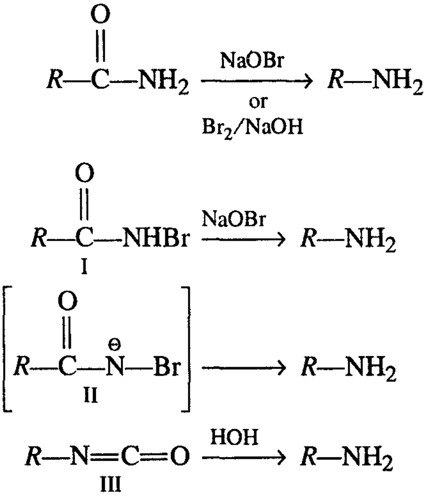
(iv) Toluene and chlorine produce benzyl chloride in the presence of light, but *o*- and *p*-chlorotoluene in the presence of iron or iodine at boiling temperature. The different products from the same reactants under different conditions indicate different mechanisms. In fact, the former follows free radical pathway, and the latter, an ionic mechanism.

2.13.2. Determination of the Presence of Intermediates

One or more intermediates may be formed in complex reactions; they may often be detected by physical methods if transient, and isolated if reasonably stable. Sometimes intermediates may be trapped by a chemical reaction with an added compound and the compound is known as trapping agent. Indirect methods may also suggest an intermediate, *e.g.*, converting a suspected intermediate into normal product under conditions of the reaction. Kinetic studies in some cases indicate the formation of an intermediate.

(i) Isolation : Occasionally, it is possible to isolate intermediates by stoping the reaction before it is completed, or by using mild conditions.

(a) Isolation of three intermediates, *N*-bromamide (I) its anion (II) and isocyanate (III) during the formation of a primary amine from an amide by the well known Hofmann rearrangement, is one of few such cases. These can be readily converted into a primary amine.



$$R\text{—}\overset{\overset{O}{\|}}{C}\text{—}NH_2 \xrightarrow[\text{or } Br_2/NaOH]{NaOBr} R\text{—}NH_2$$

$$\underset{\text{I}}{R\text{—}\overset{\overset{O}{\|}}{C}\text{—}NHBr} \xrightarrow{NaOBr} R\text{—}NH_2$$

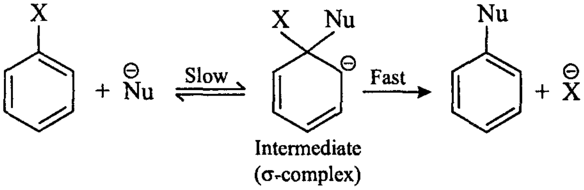
$$\underset{\text{II}}{\left[R\text{—}\overset{\overset{O}{\|}}{C}\text{—}\overset{\ominus}{N}\text{—}Br\right]} \longrightarrow R\text{—}NH_2$$

$$\underset{\text{III}}{R\text{—}N{=}C{=}O} \xrightarrow{HOH} R\text{—}NH_2$$

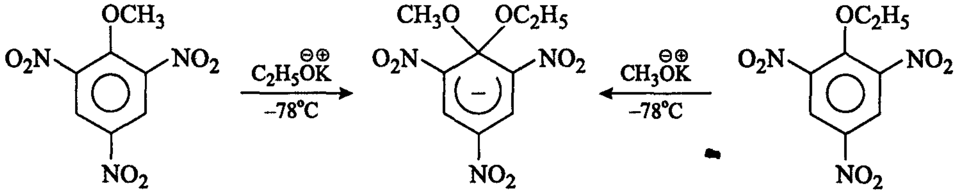
Thus any proposed mechanism for this rearrangement must account for the formation of all these intermediates.

(b) Bimolecular aromatic nucleophilic substitution reaction takes place by the formation of cyclohexadienylide anion (also known as Meisenheimer complex or σ complex).

In many cases salts of the postulated intermediates have been isolated form the reaction. A typical example is the salt (I) which is formed either by the action of potassium ethoxide on 2, 4, 6-trinitroanisole or of potassium methoxide on trinitro-pheneol.

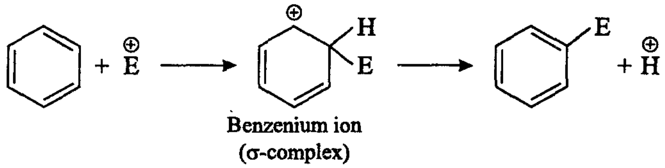


(c) Bimolecular aromatic electrophilic substitution reactions take place *via* the formation of benzenium ion (σ-complex).

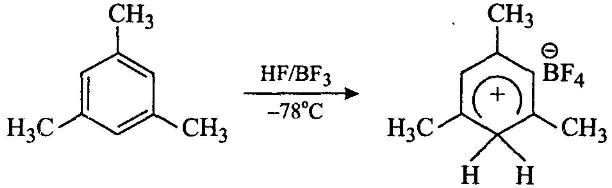


(I)

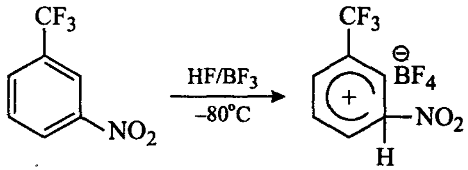
A few stable σ complexes such as (II) and (III) have been isolated from the reaction mixture and also prepared in the form of salts.



(ii) Detection of Intermediates : Unstable reaction intermediates cannot be isolated but are often detected by spectroscopic methods. For example, carbocations and carbanions are detected by



(II)
(σ-complex)



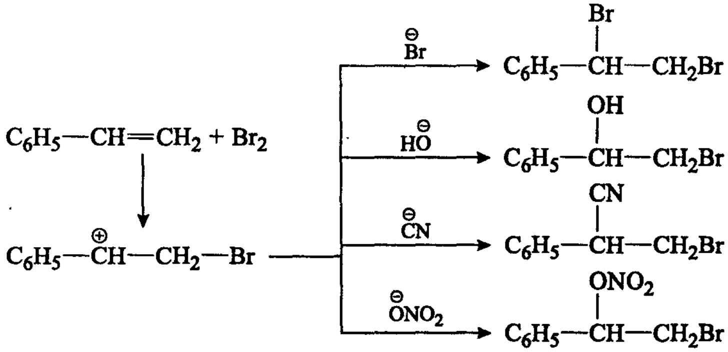
(III)
(σ-complex)

NMR; $\overset{\oplus}{NO_2}$ is detected by Raman spectroscopy, whereas free radicals and carbenes are detected by CIDNP (chemically induced dynamic polarisation which is an NMR technique) and by ESR (electron spin resonance) spectroscopy, which is also called as EPR (electron paramagnetic resonance spectroscopy.)

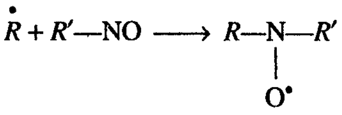
(iii) Trapping of Reaction Intermediates : Sometimes an intermediate may be detected, although it cannot be isolated, by adding a "trapping" reagent to the reaction mixture. The trapping reagent is added so that it will combine, with the intermediate to form easily identifiable product that cannot be accounted for otherwise. For example :

(a) Trapping of carbocation : Nucleophiles are commonly employed to trap carbocations. Direct evidence for the intermediacy of carbocation in the addition of a halogen to alkenes is provided by the observation that when the reaction is carried out in the presence of other nucleophiles, a mixture of products is obtained.

(b) Trapping of free radicals : Transient alkyl free radicals are trapped by nitroso compounds.

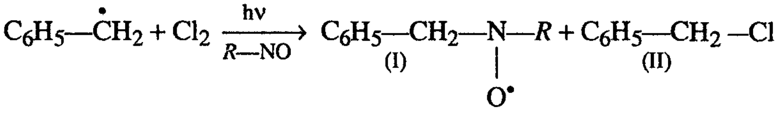


Nitroso compounds react with alkyl free radicals to form long-lived nitroxides. These nitroxides are stable.



$$\dot{R} + R'\text{—NO} \longrightarrow R\text{—}\underset{\substack{|\\ O^{\bullet}}}{N}\text{—}R'$$

Thus isolation and identification of nitroxides confirm the formation of $R^{\bullet}$ free radical in the reaction mixture. For example :

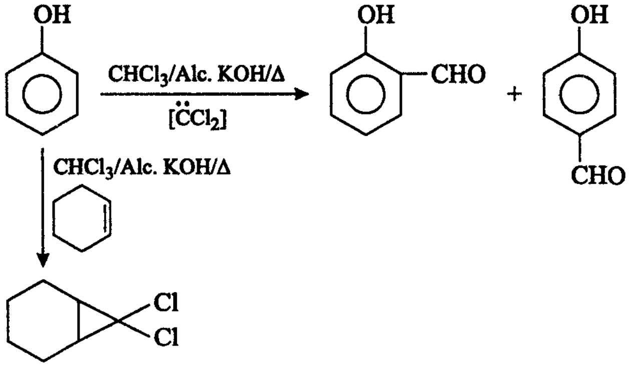


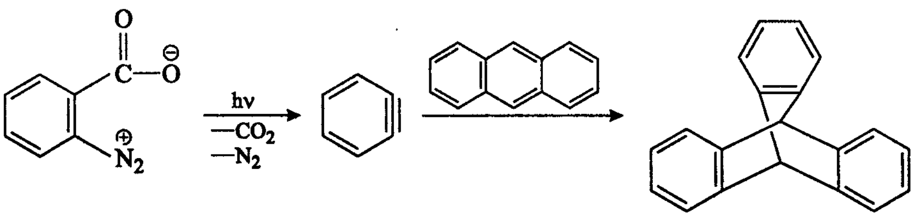
$$C_6H_5\text{—}\dot{C}H_2 + Cl_2 \xrightarrow[R\text{—NO}]{h\nu} \underset{(I)}{C_6H_5\text{—}CH_2}\text{—}\underset{\substack{|\\ O^{\bullet}}}{N}\text{—}R + \underset{(II)}{C_6H_5\text{—}CH_2}\text{—}Cl$$

Formation of product (I) in the above reaction confirms that the reaction intermediate of the reaction is $C_6H_5\text{—}\dot{C}H_2$.

(c) Trapping of carbenes and benzynes : The trapping reagent for carbenes are alkenes. The formation of cyclopropanes by the 1, 2-addition of carbenes to alkanes is probably the most characteristic reaction of carbene intermediate. This reaction is used for trapping of carbene. Thus the formation of cyclopropane derivative with alkene in the reaction confirms that intermediate of the reaction is carbene. One of the most common examples in which product formation takes place by formation of carbene as reaction intermediate is the Reimer-Tiemann reaction :

A benzyne intermediate is trapped as anthracene adduct, triptycene :



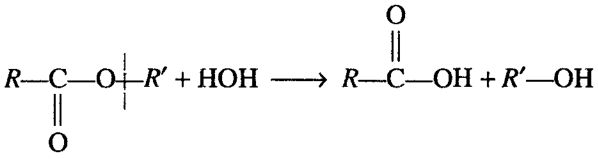


Triptycene

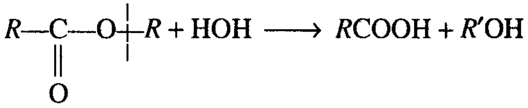
2.13.3. Isotopic Labelling and Isotope Effects

Isotopic Labelling : In non-kinetic studies, stable isotopes of carbon (^{13}C) hydrogen (D), nitrogen (^{15}N), oxygen (^{18}O), and radioactive isotopes of carbon (^{14}C), hydrogen (^{3}H), sulphur

(^{35}S), iodine (^{128}I and ^{131}I) and bromine (^{82}Br), have been introduced in strategical positions of reacting molecules to have an insight into reaction mechanisms by noting which parts of reactants form which parts of products. For example, base- catalysed hydrolysis of an ester may involve either (i) an acyl-oxygen bond fission or (ii) an alkyl-oxygen bond fission :

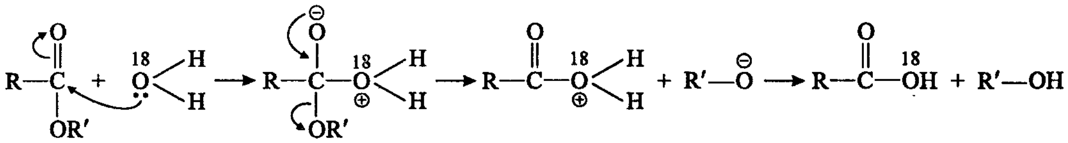
(i) 

$$R\!-\!\underset{\underset{O}{\|}}{C}\!-\!O\,|\,R' + HOH \longrightarrow R\!-\!\overset{\overset{O}{\|}}{C}\!-\!OH + R'\!-\!OH$$

(ii) 

$$R\!-\!\underset{\underset{O}{\|}}{C}\!-\!O\,|\,R + HOH \longrightarrow RCOOH + R'OH$$

What actually happens has been confirmed by hydrolysing the ester in H_2O^{18}. If the acyl-oxygen bond breaks, the labelled oxygen will appear in the acid; otherwise it will be in the alcohol.



The hydrolysis of ester yields an unlabelled alcohol and a labelled acid. This confirmed that during the course of hydrolysis acyl-oxygen bond fission occurs as follows :

Isotope Effects : In spite of their chemical similarily, the isotopes are not exactly identical and often the rate at which chemical reactions occur may vary with isotope. A difference in the rate of a reaction due to a difference in the isotope present in the reaction system is called the **isotope effect.** The ground-state vibrational energy (called the zero-point vibrational energy) of a bond depends on the mass of the bonded atoms and is lower when the reduced mass ($m_1 \times m_2/m_1 + m_2$, where m_1 and m_2 are masses of the bonded atoms) is higher. Thus, C—D, O—D, D—N bonds, etc., have lower energies in the ground state than the corresponding C—H, O—H, N—H bonds, etc. Consequently, a C—H bond is broken more readily than a C—D (or C—T) bond. Therefore, whenever a hydrogen is lost in the rate-determining step of a reaction, it will show an isotope effect on replacing the hydrogen by deuterium or tritium. Since the C—D (or C—T) bond has lower energy in the ground state than the C—H bond, if such a isotopically substituted bond is broken in the rate-determining step, then the rate will be lowered by the substitution and the isotope effect is called *primary isotope effect* because it is of relatively larger magnitude. Most of isotope effect studies have been carried out by using the more easily available deuterium.

The primary isotope effect has been used for the elucidation of mechanisms of many reactions. For example, the substitution of deuterium in the methyl groups of isopropyl bromide considerably slows down the rate of its elimination reaction with the ethoxide ion.

Reaction	*Relative rate*
$(CH_3)_2CHBr + Et\overset{\ominus}{O} \longrightarrow CH_3CH{=}CH_2 + EtOH + \overset{\ominus}{Br}$	1.0
$(CD_3)_2CHBr + Et\overset{\ominus}{O} \longrightarrow CD_3CH{=}CD_2 + EtOD + \overset{\ominus}{Br}$	0.15

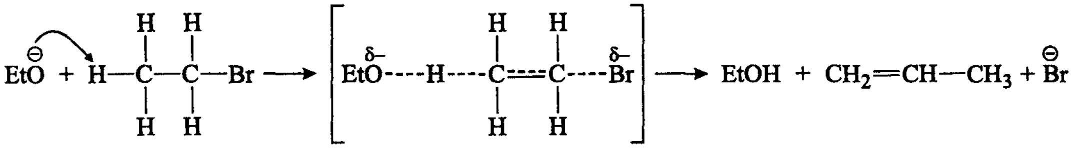
The primary isotope effect is expressed in terms of the rate ratio k_H/k_D, thus, for the above reaction it is

$$k_H/k_D = \frac{1.0}{0.15} = 6.66$$

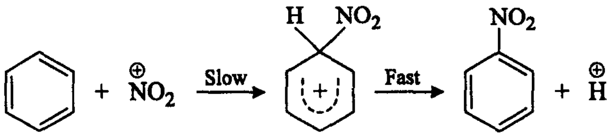
The large isotope effect clearly indicates that the rate determining step of the reaction involves C—H bond fission and rules out the mechanisms such as one given below :

$$(CH_3)_2CHBr \xrightarrow[-\overset{\ominus}{Br}]{\text{Slow}} (CH_3)_2\overset{\oplus}{C}H \xrightarrow[\text{fast}]{\overset{\ominus}{EtO}} CH_3CH{=}CH_2 + EtOH$$

The correct mechanism for the above reaction has been formulated as follows :



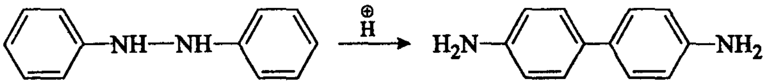
In the arenium ion mechanism, the C—H bond is not broken in the rate-determining step so no isotope effect should be found. Isotope effect has not actually been observed in most of the aromatic electrophilic substitutions. For example, the rate of nitration of C_6D_6, deuterio benzene (or C_6T_6, tritiobenzene) is the same as the rate for benzene (C_6H_6). This clearly shows that the loss of proton is not the rate-determining step. This provides a strong evidence for the following arenium ion mechanism :



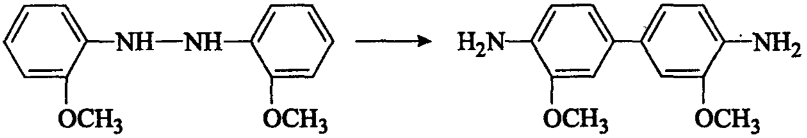
2.13.4. Crossover Experiments

Whether a rearrangement is a one-step (intramolecular) or a two-step (inter- molecular) process can be decided by carrying out the reaction with a mixture of two similarly constituted but nonidentical reactants and then analysing the products. Since the migrating group must become free in an intermolecular process, we should get a product containing fragments of both the reactants in such a process.

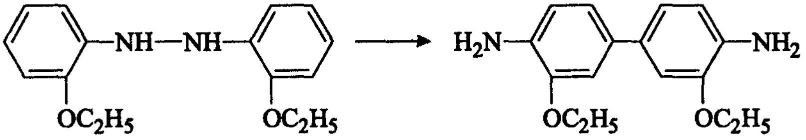
One of the most familiar examples of the use of this mode of investigation is connected with the benzidine rearrangement, a reaction in which hydrazobenzenes are converted by acid to benzidines.



If the reaction is carried out on a mixture of 2, 2′-dimethoxyhydrazobenzene and its diethoxy analogue only two benzidines can be isolated, both of them symmetrically substituted. There is no formation of unsymmetrical benzidine (III), which would result if fragments from two different hydrazobenzenes were to combine to give crossover product, is strong evidence that the rearrangement is intramolecular.



(I) (Ia)

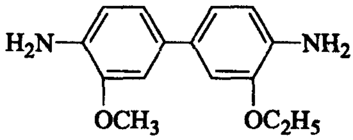


(II) (IIa)

I + II ⟶ OnlyIa + IIa

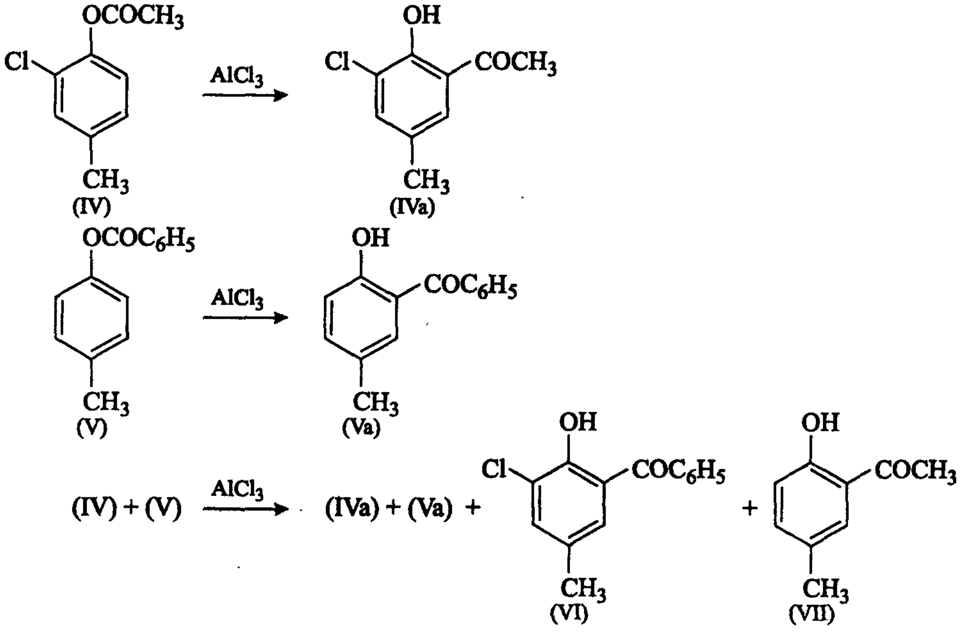
No crossover product (III) is formed :

Fries rearrangement, which involves migration of an acyl group of a phenyl ester to the benzene ring is the example of intermolecular rearrangement and this can be confirmed by crossover experiment.



(III)

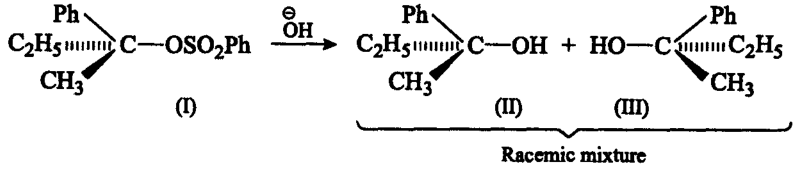
The two esters (IV) and (V), rearrange under identical conditions and at approximately the same rate to give the products (IVa) and (Va), respectively. Rearrangement of a mixture of (IV) and (V), however not only gives (IVa) and (Va) but also the cross products (VI) and (VII). Isolation of cross products unequivocally confirms that the Fries rearrangement is an intermolecular rearrangement (a two-step process). However, in certain cases crossover products have not been found; in such cases this rearrangement is intramolecular.



2.13.5. Stereochemical Evidence

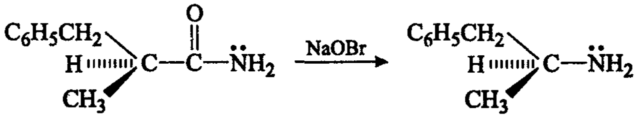
If the products of a reaction are capable of existing in more than one stereoisomeric form, the form that is obtained may give information about the mechanism.

For example, mechanism of nucleophilic substitution reactions have been investigated with optically active compounds.



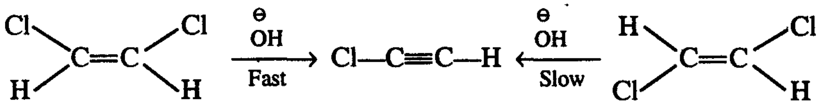
In the above case an optically active reactant yielded a product which has no optical activity (racemic mixture). Racemisation of the product indicates that the reaction passed through an intermediate that has a planar configuration, such as a carbocation, which is equally likely to be attacked by the $\overset{\ominus}{\text{OH}}$ on either side producing a mixture of equal number of molecules with inversion and retention configuration.

In the Hofmann rearrangement, if the amide used is optically active, the resulting product (amine) is also optically active. This shows that the migrating group does not become free from the remainder of the molecule for sufficient time to allow it to racemise. The configuration of the resulting amine is same as that of amide, *i.e.*, reaction occurs with retention of configuration indicating that breaking of bond and formation of bond take place simultaneously on the same side of the migrating group.



Retention of configuration

cis-1, 2-Dichloroethene undergoes elimination to give chloroacetylene 20 time faster than the corresponding *trans* isomer. This observation confirms the conclusion that the E_2 reaction proceeds with greater facility when the departing groups are *trans* than when they are *cis*.



cis
(Eliminating groups
H and Cl are *trans*)

trans
(Eliminating groups
H and Cl are *cis*)

2.13.6. Kinetic Evidence

Although a reaction mechanism cannot be deduced unequivocally from kinetic studies, knowledge of the reaction order constitutes the most important step of the investigation.

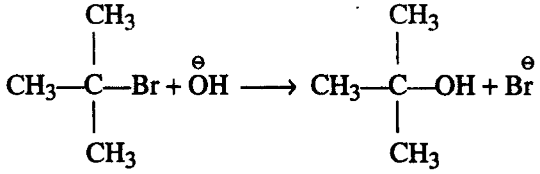
When the kinetics of the reaction between methyl bromide and sodium hydroxide are measured, the rate expression derived from the experimental data is :

$$CH_3\text{—}Br + \overset{\ominus}{OH} \longrightarrow CH_3OH + \overset{\ominus}{Br}$$

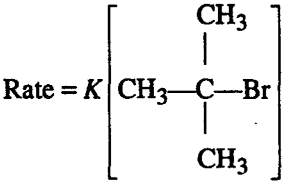
$$\text{Rate} = K\,[CH_3Br]\,[\overset{\ominus}{OH}]$$

The rate of reaction depends on the concentration of both reactants, *i.e.*, both are involved in the rate-determining step, which supports SN2 mechanism suggested for this reaction.

Similarly, when the kinetics of the reaction between *t*-butyl bromide and sodium hydroxide are measured, the rate expression derived from the experimental data is :



$$CH_3\text{—}\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{C}}\text{—}Br + \overset{\ominus}{OH} \longrightarrow CH_3\text{—}\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{C}}\text{—}OH + \overset{\ominus}{Br}$$



$$\text{Rate} = K\left[CH_3\text{—}\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{C}}\text{—}Br\right]$$

The rate of the reaction depends on the concentration of *t*-butyl bromide only, *i.e.*, only *t*-butyl bromide is involved in the rate-determining step, which supports SN1 mechanism suggested for this reaction.

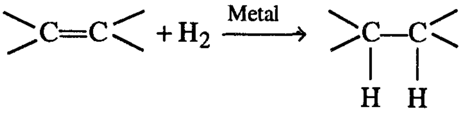
Thus, it is often possible to rule out several mechanisms merely by an inspection of the rate law.

2.13.7. Study of Catalysis

A very important question regarding any mechanism is whether or not it is catalysed or inhibited in any way. What is the effect of, for example, heat, light, acid strength or solvent? For example, does the reaction require the presence of acids, metal or peroxides? The answers to these questions provide valuable information about the mechanism of a reaction.

Examples of reactions that do require catalysts include free-radical substitution and hydrogenation of alkenes. In the former, heat or light is necessary, and a metal is necessary in the latter :

$$R\text{—H} + X_2 \xrightarrow[\text{light}]{\Delta \text{ or}} R\text{—}X + \text{H}X$$



A catalyst speeds-up a reaction by providing an alternate reaction pathway that involves but does not consume the catalyst. This alternate route has a lower $\Delta G^{\neq}$ and is therefore a more rapid reaction. Of course, just as a mechanism must be compatible with the products, so must it be compatible with its catalysts.

VERY SHORT ANSWER QUESTIONS

1. Which of the following species are paramagnetic?

(a) $C_6H_5\overset{\oplus}{C}H_2$ (b) $CH_3CO\overset{\ominus}{O}$ (c) $\dot{C}H_3$ (d) singlet carbene

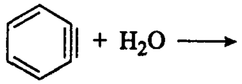
(e) $C_6H_5\overset{\ominus}{C}H_2$ (f) triplet carbene

2. Give an example of trapping of benzyne intermediate.
3. Name two reactions which occur through a carbene intermediate.
4. Give one example of a pericyclic reaction.
5. Give one example of a nucleophilic and an electrophilic substrate.
6. Pick up electrophiles and nucleophiles from the following :

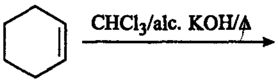
(a) $\overset{\ominus}{C}Cl_3$ (b) $CH_3\overset{\oplus}{C}H_2$ (c) BF_3 (d) $LiAlH_4$

(e) SO_3 (f) $CH_3\text{—}O\text{—}CH_3$

7. Name one reaction which is believed to occur through a nitrene intermediate.
8. Give one method each for the generation of a carbene, a nitrene and benzyne intermediate.
9. Complete the following reaction :



10. Indicate the kinetic product and the thermodynamic product formed by addition of equimolar HCl to 1,3-butadiene.
11. Give the main product of the following reaction :



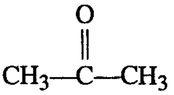
PROBLEMS WITH SOLUTIONS

1. Which among the following is an electrophile?

(a) CO_2 (b) SO_3 (c) $\overset{\oplus}{N}O_2$ (d) all of these

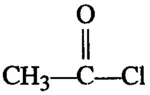
2. Which among the following compounds behave both as an electrophile as well as a nucleophile?

(1) $CH_2{=}CH_2$ (2) $CH_2{=}CH{-}\overset{\oplus}{C}H_2$ (3)



$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$

(4)



$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Cl$

Answer using the following codes :

(a) only 1 (b) 1 and 2 (c) 3 and 4 (d) 2, 3 and 4

3. Which of the following species is an ambident nucleophile?

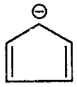
(a) $CH_3{-}\overset{\ominus}{C}H_2$ (b) $CH_2{=}CH_2$ (c) $\overset{\ominus}{N}O_2$ (d) $\overset{\ominus}{N}H_2$

4. In each of the following pairs of ions which ion is more stable?

(a) $\underset{\text{I}}{CH_2{=}\overset{\ominus}{C}H}$ and $\underset{\text{II}}{CH{\equiv}\overset{\ominus}{C}}$ (b) $\underset{\text{I}}{C_6H_5{-}\overset{\ominus}{C}H_2}$ and $\underset{\text{II}}{CH_2{=}CH{-}\overset{\ominus}{C}H_2}$

(c) $\underset{\text{I}}{CH_3{-}\overset{\ominus}{C}H{-}CH{=}CH_2}$ and $\underset{\text{II}}{\overset{\ominus}{C}H_2{-}CH{=}CH_2}$

(d)



I

and $CH_2{=}CH{-}CH{=}CH{-}\overset{\ominus}{C}H_2$

5. Arrange the following carbocations in order of increasing stability :

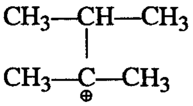
$$C_6H_5\overset{\oplus}{C}H_2,\ (C_6H_5)_2\overset{\oplus}{C}H,\ (CH_3)_3\overset{\oplus}{C},\ (CH_3)_2\overset{\oplus}{C}H,\ CH_3\overset{\oplus}{C}H_2,\ \overset{\oplus}{C}H_3$$

6. In each of the following pairs of ions which ion is more stable?

(a) $\underset{\text{I}}{CH_3CH_2\overset{\oplus}{C}H_2}$ and $\underset{\text{II}}{CH_3{-}O{-}\overset{\oplus}{C}H_2}$ (b) $\underset{\text{I}}{C_6H_5\overset{\oplus}{C}H_2}$ and $\underset{\text{II}}{CH_2{=}CH{-}\overset{\oplus}{C}H_2}$

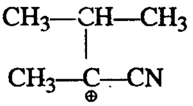
(c) $\underset{\text{I}}{CH_3{-}\overset{\oplus}{C}H_2}$ and $\underset{\text{II}}{CH_2{=}\overset{\oplus}{C}H}$

(d)



$CH_3{-}\underset{\underset{\displaystyle CH_3{-}\underset{\oplus}{C}{-}CH_3}{|}}{C}H{-}CH_3$

and

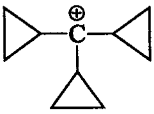


$CH_3{-}\underset{\underset{\displaystyle CH_3{-}\underset{\oplus}{C}{-}CN}{|}}{C}H{-}CH_3$

I II

7. Which of the following carbocations is most stable?

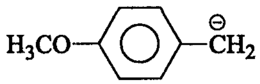
(a) $(C_6H_5)_3\overset{\oplus}{C}$ (b) $(CH_3)_3\overset{\oplus}{C}$ (c)



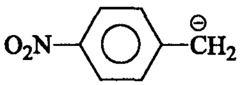
(d) $CH_2{=}CH{-}\overset{\oplus}{C}H_2$

8. Consider the following carbanions :

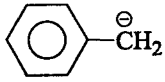
(I)



(II)



(III)



(IV)

Correct decreasing order of stability is :

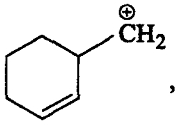
(a) II > III > I > IV (b) III > IV > I > II

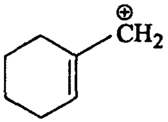
(c) IV > I > II > III (d) I > II > III > IV

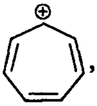
9. Arrange the carbocations in each of the following sets in increasing order of stability :

(a) $(CH_3)_2CHCH_2\overset{\oplus}{C}H_2$, $(CH_3)_2CH\overset{\oplus}{C}HCH_3$, $(CH_3)_2\overset{\oplus}{C}CH_2CH_3$
A B C

(b) $(C_6H_5)_2\overset{\oplus}{C}H$,
A


B


C

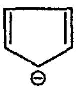
(c)

A

$(C_6H_5)_3\overset{\oplus}{C}$, $(CH_3)_3\overset{\oplus}{C}$
B C

10. Pick up the most stable and the least stable radicals from the following :

$$\dot{C}H_3,\ (CH_3)_3\dot{C},\ C_6H_5\dot{C}H_2,\ CH_3\dot{C}H_2,\ (C_6H_5)_3\dot{C}$$

11. Arrange the following carbanions in decreasing order of stability :


A

$(C_6H_5)_3\overset{\ominus}{C}$, $(CH_3)_3\overset{\ominus}{C}$, $(CH_3)_2\overset{\ominus}{C}H$, $\overset{\ominus}{C}H_3$, $CH_3\overset{\ominus}{C}H_2$
B C D E F

12. Which among the following statements is correct? Answer using the given codes.

(1) $\ddot{C}F_2$ is more stable than $\ddot{C}Cl_2$ (2) $\ddot{C}Cl_2$ is more stable than $\ddot{C}Br_2$

(3) Singlet $\ddot{C}H_2$ is more stable than triplet $\ddot{C}H_2$ (4) Singlet carbene has planar geometry

Codes :

(a) 1, 2 and 4 (b) 2 and 4

(c) 1, 2 and 3 (d) 2, 3 and 4

13. Which of the following reaction intermediates has not a planar structure?

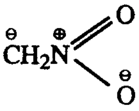
(a) Alkyl carbocation (b) Alkyl carbanion (c) Alkyl free radical (d) Singlet carbene

14. Classify the following as electrophiles and nucleophiles :

(a) $\overset{\ominus}{C}N$ (b) H_2O (c) $\overset{\oplus}{Br}$ (d) $N\overset{\ominus}{O}_2$

(e) $\overset{\oplus}{N}O_2$ (f) CH_3OH (g) $CH_2{=}CH_2$

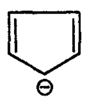
15. Indicate the geometry (planar or pyramidal) of the following :

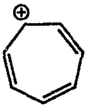
(a) $\overset{\ominus}{C}H_3$ (b) $\overset{\oplus}{C}H_3$ (c)

$\overset{\ominus}{C}H_2\overset{\oplus}{N}(=O)\overset{\ominus}{O}$ (d) $C_6H_5\dot{C}H_2$

(e) $\dot{C}F_3$ (f) singlet $\ddot{C}H_2$ (g) $\dot{C}H_3$

PROBLEMS FOR SELF ASSESSMENT

1. Discuss the following with examples :
   (a) Electrophiles
   (b) nucleophiles
   (c) Reaction Intermediates
   (d) Transition state and Activated complex
2. What is Hammond postulate. Explain with suitable example the application of Hammond postulate in determining the shape and geometry of transition state.
3. Differentiate between transition state and intermediate with the help of energy profile of a suitable reaction.
4. Draw energy profiles for the following :
   (a) A one-step reaction
   (b) A two-step reaction in which the first step is rate-determining
   (c) A catalysed and uncatalysed reaction
5. Discuss the structure of a carbocation, carbanion and free radical.
6. What are singlet and triplet carbenes? Discuss their stability and geometry.
7. With suitable examples, discuss the kinetic and thermodynamic control of reactions.
8. Illustrate use of the following techniques for determination of the mechanism of reactions :
   (a) Stereochemical studies
   (b) Crossover experiments
   (c) Product analysis
9. Define and illustrate the term isotope effect. How is it useful in ascertaining the mechanism of a reaction?
10. Discuss the structure of carbenes, nitrenes and arynes. Illustrate the technique of trapping for the detection of these intermediates.
11. Write short notes on the following :
    (a) Isotopic labelling (b) Ambident nucleophiles
    (c) Transition state theory (d) Collision theory
12. Which in each of the following pairs is more stable and why?

(a)  and $CH_2{=}CH{-}CH{=}CH{-}\overset{\ominus}{C}H_2$

(b)  and $Ph\overset{\oplus}{C}H_2$

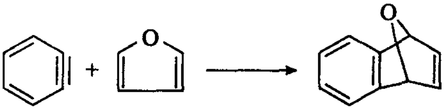
(c) $\overset{\ominus}{C}H_3$ and $\overset{\ominus}{C}Cl_3$

(d) $CH_3CH_2\overset{\oplus}{C}H_2$ and $CH_3O\overset{\oplus}{C}H_2$

13. Give two methods each for the generation of the following :
    (a) Carbocation (b) Carbanion
    (c) Free radical (d) Carbene

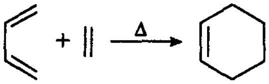
ANSWER TO VERY SHORT ANSWER QUESTIONS

1. (c) and (f) are paramagnetic.

2. 

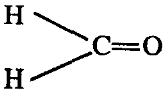
3. Reimer-Tiemann reaction and carbylamine reaction.

4. Diels-Alder reaction :



5. Alkenes and arenes are nucleophilic substrates whereas aldehydes and ketones are electrophilic substrates, for example

$CH_3—CH=CH_2$
Nucleophilic substrate



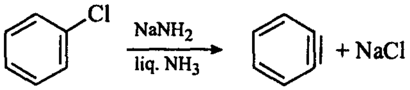
Electrophilic substrate

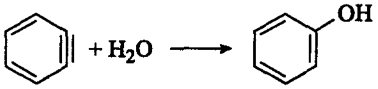
6. Electrophiles : (b), (c) and (e); nucleophiles : (a), (d) and (f).

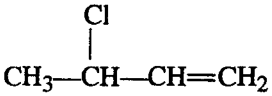
7. Hofmann bromamide reaction.

8. Carbenene : $\underset{\text{diazomethane}}{CH_2N_2} \xrightarrow{h\nu \text{ or } \Delta} \ddot{C}H_2 + N_2$

Nitrene : $\underset{\text{azide}}{R—\overset{\ominus}{\underset{\bullet\bullet}{N}}—\overset{\ominus}{N}\equiv N} \xrightarrow{h\nu \text{ or } \Delta} R—\ddot{N}\!: + N_2$

Benzyne : 

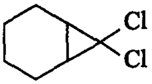
9. 

10. 

$CH_3—\overset{\displaystyle Cl}{\overset{|}{C}H}—CH=CH_2$
Kinetic product

$CH_3—CH=CH—CH_2Cl$
Thermodynamic product

(For details refer to the text)

11. 

SOLUTIONS OF PROBLEMS

1. (d) 2. (c) 3. (c)

4. (a) II (b) I (c) II (d) I

5. $\overset{\oplus}{C}H_3 < CH_3\overset{\oplus}{C}H_2 < (CH_3)_2\overset{\oplus}{C}H < C_6H_5\overset{\oplus}{C}H_2 < (CH_3)_3\overset{\oplus}{C} < (C_6H_5)_2\overset{\oplus}{C}H$

6. (a) II (b) I (c) I (d) I

7. (c)

8. (a)

9. (a) A < B < C (b) B < C < A (c) C < B < A

10. $(C_6H_5)_3\dot{C}$, most stable; $\dot{C}H_3$, least stable

11. A > B > E > F > D > C

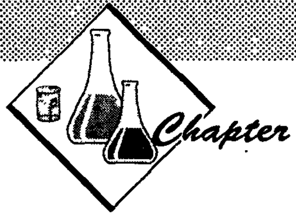
12. (a)

13. (b)

14. (c) and (e) are electrophiles; (a), (d), (f) and (g) are nucleophiles

15. (a) and (e) pyramidal; (b), (c), (d), f and (g) planar.

❑❑❑



Chapter 3

STEREOCHEMISTRY OF ORGANIC COMPOUNDS

3.0 INTRODUCTION

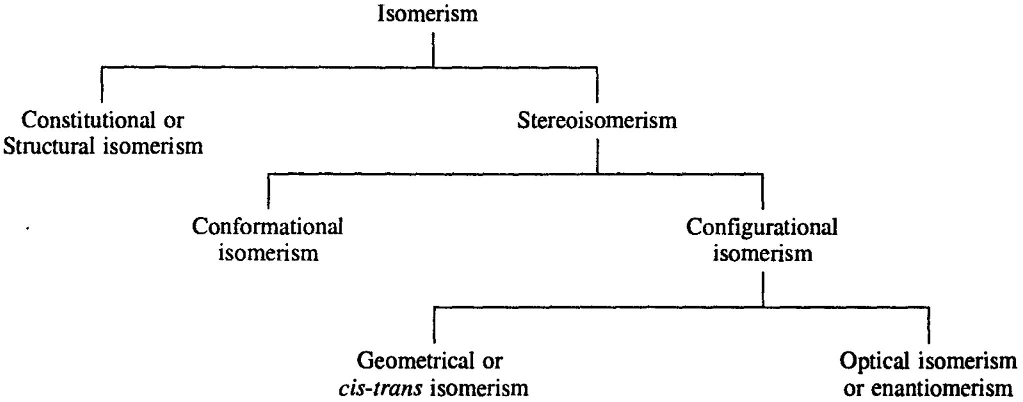
The branch of chemistry which deals with three-dimensional structures of molecules and their effect on physical and chemical properties is known as **stereochemistry** (Greek : *stereos* = solid).

3.1 ISOMERISM

Different compounds having the same molecular formula are called **isomers** (Greek : *isos* = equal; *meros* = part) and this phenomenon is known as **isomerism**.

3.2 TYPES OF ISOMERISM

There are following types of isomerism :



As shown above, isomers can be divided into two main classes : constitutional (structural) isomers and stereoisomers; the isomerisms exhibited by them are known as **constitutional (structural)** isomerism and **stereoisomerism**.

3.2.1 Constitutional Isomerism

The term constitution refers to the number, kind and connectivity of the atoms in a molecule. The connectivity describes which atom is bonded to which atom in a molecule.

The isomers which differ in the way their atoms are connected are called **constitutional isomers** and the isomerism exhibited by them is called constitutional isomerism. For examples, ethanol and dimethyl ether are isomers because they have the same molecular formula, C_2H_6O. More specifically, they are constitutional isomers because the atoms in each compound are connected differently. The oxygen in ethanol is bonded to a carbon and to a hydrogen, while the oxygen in dimethyl ether is bonded to two carbon.

CH_3CH_2OH Ethanol $CH_3—O—CH_3$ Dimethyl ether

There are various types of constitutional isomerism, *viz.*, chain isomerism, position isomerism, functional isomerism, and metamerism. Tautomerism is a special type of functional isomerism.

3.2.2 Stereoisomerism

Isomers having the same connectivity of the atoms (*i.e.*, the same constitution) but different spatial arrangement of their atoms are known as **stereoisomers** and the isomerism exhibited by them is called **stereoisomerism.**

There are two types of stereoisomerism : **configurational isomerism** and **conformational isomerism**.

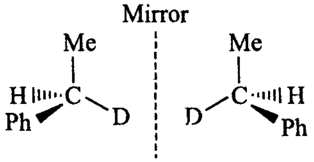
Configurational Isomerism

The different spatial arrangements of atoms in a molecule which are not interconvertible without breaking of bond(s) are called **configurations** or **configurational isomers** and the isomerism exhibited by them is called **configurational isomerism.** Because they cannot interconvert, configurational isomers can be separated. Changing the configuration of a molecule always means that bonds are broken. A different configuration is a different molecule.

There are two kinds of configurational isomerism : **optical isomerism (enantiomerism) and geometrical (*cis-trans*) isomerism.**

Optical Isomerism (Enantiomerism)

Isomers which are nonsuperimposable mirror images of each other are called enantiomers and the isomerism exhibited by them is known as enantiomerism. Enantiomers are also called mirror-image isomers, enantiomorphs or optical antipodes.



Note : Isotopes of an atom behave as different atoms in stereoisomerism.

The stereoisomers which are mirror images of each other are called enantiomers, and stereoisomers which are not mirror images of each other are called diastereoisomers (or diastereomers).

All the optically active compounds exhibit enantiomerism. Consequently, in the older literature the term *optical isomerism* has been used for enantiomerism, but this is not appropriate because sometimes it has also been used for diastereomers having chiral centres. Thus, before further discussing enantiomerism we will have an account of optical activity in the following pages.

3.3 OPTICAL ACTIVITY

Ordinary light is composed of rays of different wavelengths vibrating in all directions perpendicular to the path of its propagation. The same is the case with a light of a single wavelength, *i.e.*, a monochromatic light. These vibrations can be made to occur in a single plane (polarisation) by passing ordinary light through the polarising Nicol prism (made of calcite, a special crystalline form of $CaCO_3$). Such *light whose vibrations occur in only one plane is called* **plane polarized light**. The polarisation of ordinary light transmitted through a Nicol prism is easily detected by viewing through a second Nicol prism called analyser (Fig. 3.1).

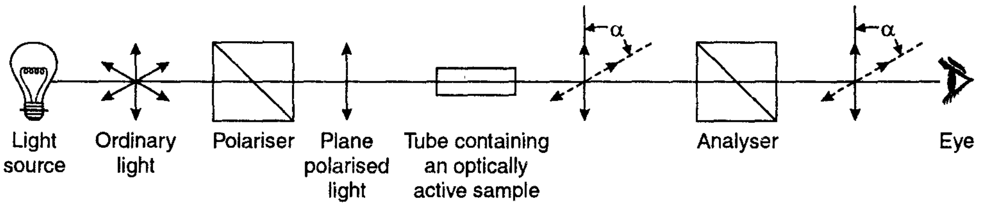


Fig. 3.1. Schematic diagram of a polarimeter. Solid lines : before rotation. Broken lines : after rotation. α is angle of rotation.

Compounds which rotate the plane of polarised light are called **optically active** compounds and this property is known as **optical activity**. If the compound rotates the plane of polarisation to the right (clockwise), it is said to be **dextrorotatory** (Latin : *dexter* = right) and is denoted by (+), or *d*. If the rotation is to the left (anticlockwise), the compound is said to be **laevorotatory** (Latin : *laevus* = left) and is denoted by (–), or *l*. Now the notations *d* and *l* are not used.

The change in the angle of plane of polarisation is known as **optical rotation**. The optical rotation is detected and measured by an instrument called polarimeter (Fig. 3.1). The degree of rotation depends on the nature of the compound, the temperature, the solvent, the concentration of the solution, the length of the polarimeter tube, and on the wavelength of the light used. It is therefore, necessary to introduce some standard by which rotating powers of different compounds may be compared. Thus, the measurement of optical activity is reported in terms of **specific rotation** $[\alpha]$, or molecular rotation $[M]$.

$$[\alpha]_\lambda^t = \frac{\alpha}{lc}$$

Where $[\alpha]$ = specific rotation
t = temperature of the measurement
λ = wavelength of the light used (usually sodium D line, 5893 Å)
α = observed angle of rotation
l = length of sample tube in decimeter
c = concentration of the sample in g/mL of solution

For example, the specific rotation of cane sugar (sucrose) in water is $[\alpha]_D^{20} = +66.4°$.

In most cases, the concentration of the sample g/mL of solution and the solvent used are reported in parantheses after the value of the specific rotation. For example, the specific rotation of camphor is $[\alpha]_D^{20} = -44.2°$ ($c = 0.165$, ethanol).

$$\text{Molecular rotation } [M]_\lambda^t = \frac{[\alpha]_\lambda^t \times \text{mol. wt.}}{100}$$

mol. wt. = the molecular weight of the optically active compound.

The specific and molecular rotations of a compound are its characteristic property similar to m.p., b.p., density, and refractive index.

3.4 CHIRALITY

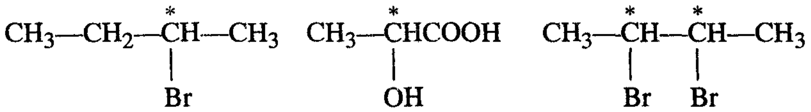
The term chiral (Greek : *cheir* = hand) was first introduced by Kelvin (1884) for those objects which have "handedness", *i.e.*, object and mirror-image relationship of a left and right hand.

***Object or molecules which are not superimposable on their mirror images are* chiral *and are said to possess* chirality**. Chirality (nonsuperimposability on mirror image) is the essential criterion for exhibiting optical activity as well as for enatiomerism. Compounds exhibit enantiomerism only when their molecules are chiral. If a molecule or object is superimposable on its mirror image, it is **achiral** (non-chiral). Achiral molecules are optically inactive and cannot exhibit enantiomerism.

The terms chiral and chirality have been widely accepted, and they have replaced the earlier terms : *dissymmetric, dissymmetry, asymmetric* and *asymmetry.*

3.5 STEREOGENIC CENTRE

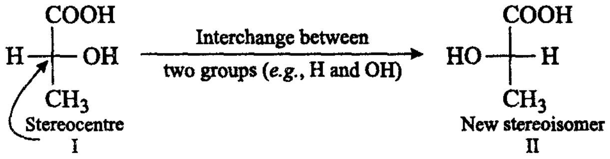
A carbon bonded to four different atoms or groups is called **a chiral centre**. The term **"a chirality centre"** is the most recently IUPAC-approved term for the earlier used terms : a chiral centre, a chiral carbon, or an asymmetric carbon. The chirality centre in each of the following compounds is indicated by an asterisk.



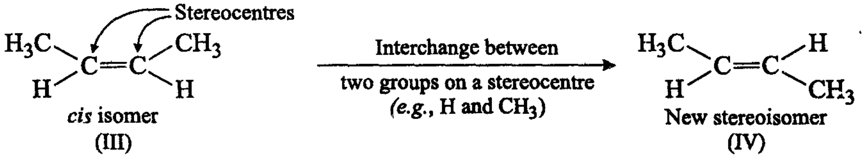
$CH_3—CH_2—\overset{*}{C}H(Br)—CH_3$ $\quad CH_3—\overset{*}{C}H(OH)COOH$ $\quad CH_3—\overset{*}{C}H(Br)—\overset{*}{C}H(Br)—CH_3$

It should be noted that besides carbon, suitably substituted nitrogen, phosphorus, etc. can also be a chirality centre.

A stereogenic centre (stereocentre) is defined as an atom on which an interchange of any two atoms or groups results in a new stereoisomer. When the new stereoisomer is an enantiomer, the stereocentre is called a **chiral centre**. All the stereocentres are not tetrahedral.



I and II are enantiomers, hence the stereocentre is a chiral centre.



III and IV are not enantiomers. They are diastereomers, hence in this case stereocentres are not chiral centres. Also these are not tetrahedral.

Thus, all chiral centres are stereocentres but all stereocentres are not chiral centres.

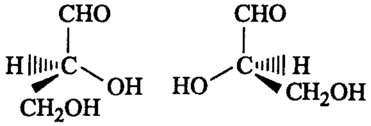
If a molecule contains only one chiral centre, it must be chiral. Molecules containing two or more chiral centres may or may not be chiral, *e.g.*, *meso*-tartaric acid has two chiral centres but it is achiral. Many but not all chiral molecules contain chiral centres, *e.g.*, many biphenyl derivatives are chiral but have no chiral centre. Thus, the presence or absence of a chiral centre is no criterion of chirality. The ultimate test for chirality is that a molecule or object cannot be superimposed on its mirror image.

3.6 REPRESENTATION OF THREE-DIMENSIONAL MOLECULES

If two molecules differ only in three-dimensional terms then we can represent that difference only by using three-dimensional models or by devising systems for representing three-dimensional structures in two-dimensional drawings. Some of (such useful) systems are given below :

3.6.1 Flying-wedge Representation

This is the most commonly used model. In this representation three types of lines are used in a standard way to indicate three-dimensional structures in a two-dimensional picture. A solid wedge, (◄ thick line) represents a bond projecting above the plane of the paper toward the observer. Continuous lines — (solid lines) are bonds in the plane of the paper. A broken wedge, (·ıııl dashed lines) is a bond below the plane (*i.e.*, a bond pointing away from the observer).

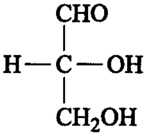


(I) (II)

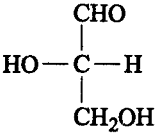
Flying-wedge representation of the two forms of glyceraldehyde.

3.6.2 Fischer Projection Formula

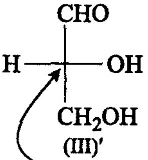
This is also called Fischer projection in which all bonds are drawn as solid lines with the understanding that horizontal bonds (both left and right) point toward the observer (above the plane of the paper) and vertical bonds point away from the observer (below the plane of the paper). The chiral carbon atom lies in the plane of the paper and usually it is omitted (III and IV). For example, the Fischer projections of the two forms of glyceraldehyde are written as (III) and (IV) or (III)′ and (IV)′.



(III)

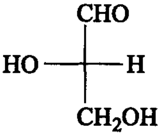


(IV)



(III)′

Cross represents the chiral carbon

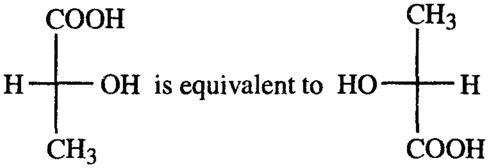


(IV)′

If Fischer projections are to be used certain rules must be obeyed and certain conventions clearly understood, otherwise the structure will be misinterpreted.

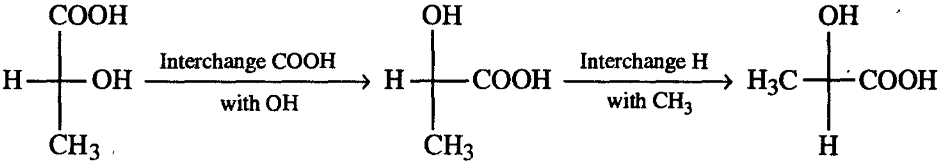
(1) The structure is written in vertical rather than a horizontal form and the carbon atom bearing the lower number in IUPAC nomenclature terms, (*i.e.*, most oxidised carbon) is normally written uppermost. For example, CHO is placed at the top of the Fischer projection of glyceraldehyde because this is C_1 according to the IUPAC nomenclature rules.

(2) For purposes of comparison a Fischer projection may be rotated 180° in the plane of the paper. For example :



R-Lactic acid *R*-Lactic acid

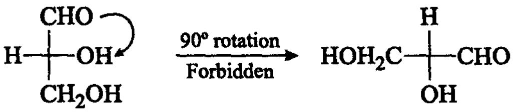
(3) Two or any other even number of interchanges of the ligands at one chiral centre do not change the configuration. For example :



R-Lactic acid *S*-Lactic acid *R*-Lactic acid

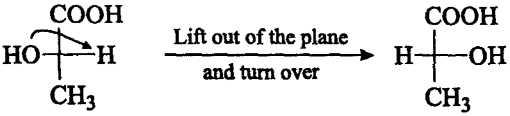
(4) One interchange or any other odd number of interchanges of the ligands at one chiral centre inverts the configuration. As shown above, one interchange changes the configuration of *R*-lactic acid to that of *S*-lactic acid.

(5) A 90° rotation of the projection formula about the chiral centre inverts the configuration in the same way as one interchange of the ligands. For example :



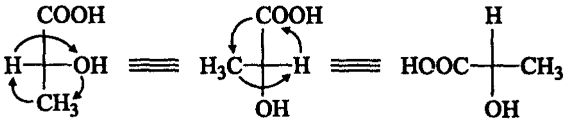
R-Glyceraldehyde *S*-Glyceraldehyde

(6) It is not permitted to lift projection formulae out of the plane of the paper, and turn over, or view them from the opposite side of the paper. For example :



S-Lactic acid *R*-Lactic acid

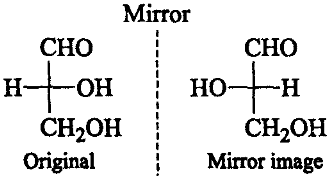
(7) Fischer projections can be manipulated by rotating a group of any three ligands in a clockwise or anticlockwise direction; the fourth ligand does not change its position (such a manipulation is equivalent to two interchanges) :



There are 12 ways of drawing Fischer projection corresponding to each enantiomer with one chiral carbon. Thus the formula, *e.g.*, (III) is only one of 12. It should be noted that all these 12 are equivalent and represent the same enantiomer. The same is the case with each of the flying-wedge representation (I) and (II).

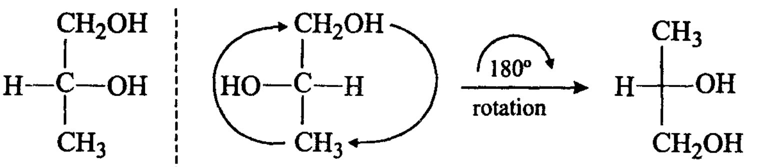
The conformation which is drawn in Fischer projection of any compound containing more than one chiral carbon happens to be least stable, eclipsed conformation of the molecule. Thus, Fischer project does not represent the actual shape of the molecule.

Drawing mirror images of Fischer projection : For drawing mirror image of a Fischer projection interchange the horizontal groups (on left and right sides) on each chiral carbon. For example :



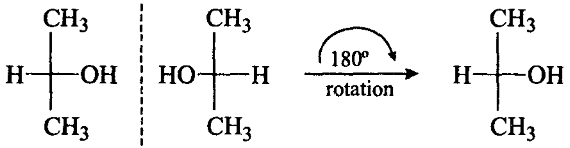
Original Mirror image

Method to know whether mirror image is the same or different : If the mirror image cannot be made to look the same as the original structure (Fischer projection) with a 180° rotation, the mirror image is different from the original structure. In this case the mirror image and the original structure are not superimposable and are enantiomers.



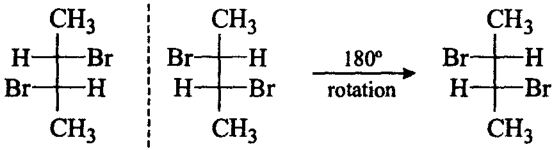
(V) Original (VI) Mirror image Different from the original

Hence, the original (V) and the mirror image (VI) are different and nonsuperimposable.



(VII) Original (VII′) Mirror image Identical to the original

Thus, the original (VII) and the mirror image (VII′) are the same and hence superimposable.

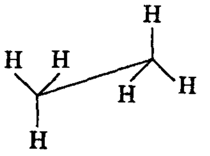


(VIII) Original (IX) Mirror image Different from the original

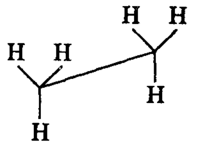
Thus, the mirror image (IX) and the original (VIII) are different, and nonsuperimposable.

3.6.3 Sawhorse Formula

The sawhorse formula indicates the spatial arrangement of all the atoms or groups on two adjacent carbon atoms. The bond between the adjacent carbon atoms is represented by a diagonal line, usually from lower left to upper right, the left hand bottom end representing the atom nearest to the observer and the right hand top end the atom that is farther away. Two of the remaining bonds to the two atoms are drawn vertically and the other four at 120° angles to these two as shown below :



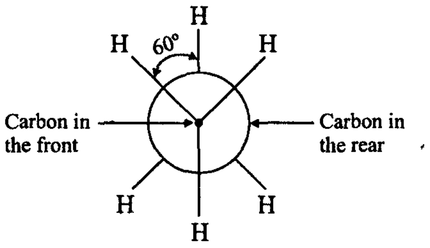
Staggered conformation of ethane



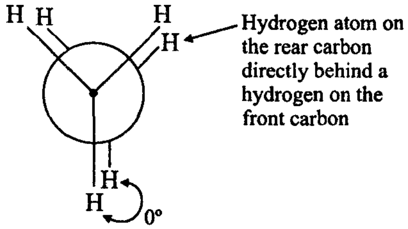
Eclipsed conformation of ethane

3.6.4 Newman Projection

Similar to sawhorse formula, Newman projection represents the spatial arrangement of all the atoms or groups on two adjacent carbon atoms. Here a molecule is viewed along the axis of a carbon-carbon bond. The carbon atom toward the front is represented by a dot and the carbon atom toward the rear by a circle. The atoms or groups on the carbon atoms are shown as being bonded to the dot or circle. For example :



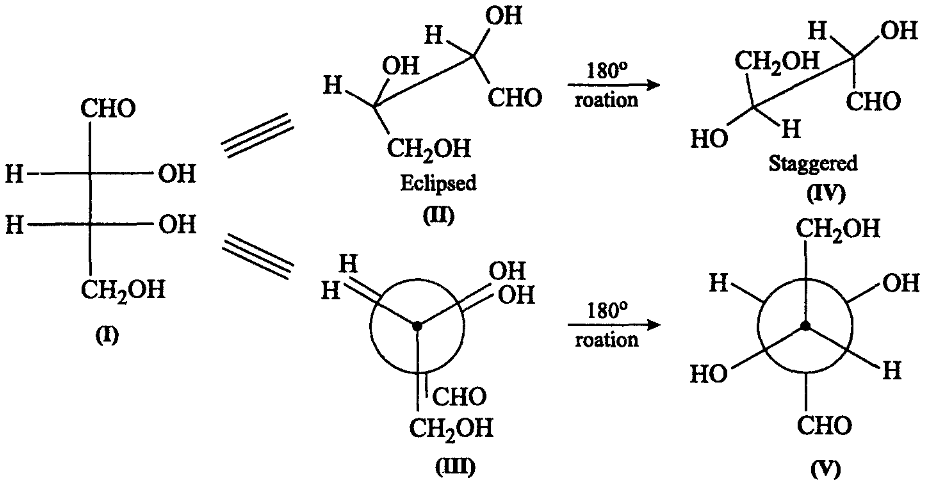
Staggered conformation of ethane



Eclipsed conformation of ethane

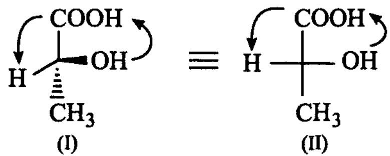
3.6.5 Interconversions of Projection and Perspective Formulae

Conversion of Fisher projection into Sawhorse and Newman formulae and vice-versa : It is desirable that anyone dealing with stereochemical problems be able to translate rapidly one set of formulae into the other. Let us convert the enantiomer of erythrose having Fischer projection (**I**) into Sawhorse and Newman formula. Here the Fischer projection is directly translated into eclipsed sawhorse (II) and Newman (**III**) formula keeping in mind that the Fischer projection represents eclipsed conformation molecule. The front of the II and III is then rotated 180° about the C_2—C_3 bond with respect to rear to give the more stable staggered sawhorse (**IV**) and Newman (**V**) formulae, respectively. Similarly, **IV** or **V** can be converted into I through **II** or **III**.



3.6.6 Simple Method for Converting Wedge Formula into Fischer Projection Formula

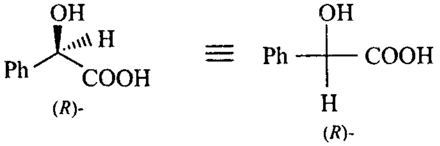
The group which is below the plane of the paper (*i.e.*, connected by … or ·ıııı) is kept at bottom in the Fischer projection formula and the remaining three groups are attached in the same sequer (*i.e.*, clockwise or anticlockwise) as they appear in the flying wedge formula. For example, let us convert the flying wedge formula (I) into the Fischer projection formula (II). In the flying wedge formula (I) CH_3 group is below the plane of the paper thus it is written at the bottom of the Fisher projection formula (II) and the remaining groups $OH \rightarrow COOH \rightarrow H$ are in anticlockwise sequence hence they an attached in the same sequence (anticlockwide) in the Fischer projection formula (II). Both the formula (I) and (II) represent (*R*)-lactic acid.



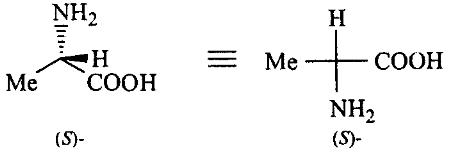
(I) (*R*)-Lactic acid

(II) (*R*)-Lactic acid

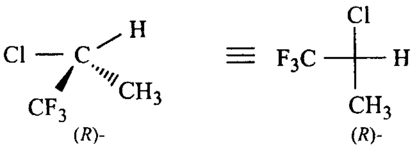
Satisfy yourself with the following conversions of flying wedge formula into the corresponding Fischer projection formulae :



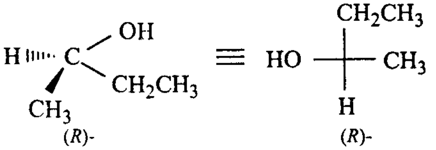
(*R*)- (*R*)-



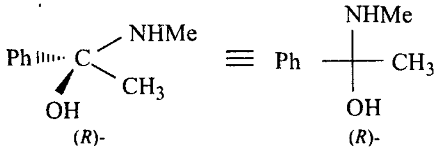
(*S*)- (*S*)-



(*R*)- (*R*)-



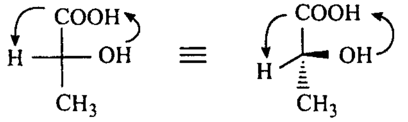
(*R*)- (*R*)-



(*R*)- (*R*)-

3.6.7 Simple Method for Converting Fischer Projection Formula into Flying Wedge Formula

The group which is at the bottom of the Fischer projection formula is kept below the plane of the paper in the flying wedge formula (*i.e.*, connected by ... or ''''' and the remaining three groups are attached in the same sequence (*i.e.*, clockwide or anticlockwise) as they appear in the flying wedge formula. One of the horizontal line groups is kept above the plane of the paper in the flying wedge formula. Thus, the sequence of all the four groups in both the formulae should be the same. For example, let us convert the Fischer projection formula (II) into the flying ewdge formula (I) In the Fischer projection formula (II) the CH_3 group is at the bottom thus it is kept below the plane of the paper in the flying wedge formula (I) and the remaining groups OH → COOH → H are in anticlockwide sequence hence they are attached in the same sequence (anticlockwise) in the flying wedge formula (I). One of the vertical line groups (*e.g.*, OH) is kept above the pane of the paper in the flying wedge formula (I). The sequence of all the four groups in both the formulae (I) and (II) is the same and both of them represent (*R*)-lactic acid.

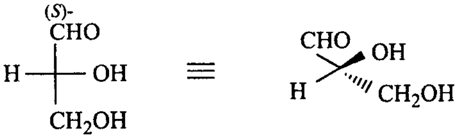


(II) (*R*)-Lactic acid (I) (*R*)-Lactic acid

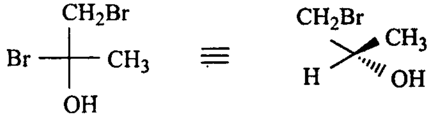
Satisfy yourself with the following conversions of Fischer projection formulae into the corresponding flying wedge formulae :

(*S*)- (*S*)-

(*R*)- (*R*)-



(*R*)- (*R*)-



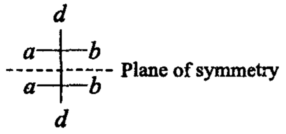
(*R*)- (*R*)-

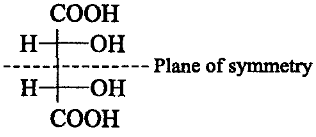
3.7 ELEMENTS OF SYMMETRY

Elements of symmetry offer a simple device to decide whether a molecule (or object) is chiral or not, *i.e.*, whether it is superimposable on its mirror image or not. When a molecule has a *plane of symmetry* or a *centre of symmetry* or an *n*-fold *alternating axis of symmetry*, it is superimposable on its mirror image and is achiral (optically inactive).

3.7.1 Plane of Symmetry

The plane which devides a molecule into two equal halves which are related as object and mirror image is known as plane of symmetry. For example :



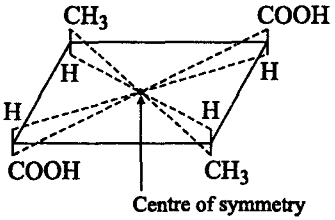


Meso-tartaric acid

The molecules having a plane of symmetry are achiral (optically inactive). For example, *meso*-tartaric acid is optically inactive because the molecule has a plane of symmetry and thus is achiral. All planar molecules have at least one plane of symmetry, identical with the molecular plane. Linear molecules have infinite number of planes of symmetry. Water molecule has two mutually perpendicular planes of symmetry.

3.7.2 Centre of Symmetry

The centre of symmetry is a point in a molecule from which if lines are drawn on one side and extended an equal distance on the other side, will meet the same atoms or groups. For example, 2, 4-dimethylcyclobutane-1, 3-dicarboxylic acid possesses a centre of symmetry which is the centre of the ring. Thus, it is optically inactive.

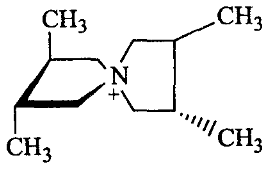


3.7.3 Alternating Axis of Symmetry

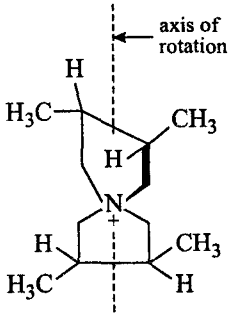
A molecule possesses an *n*-fold **alternating axis of symmetry** if it is rotated through an angle of 360/*n* about this axis and then reflected in a plane perpendicular to the axis, the molecule is the same as it was in the starting position.

A few organic compounds are known in which *n*-fold alternating axis of symmetry is the only symmetry element present. For example, the spiro compound *X* possesses neither a plane nor a centre of symmetry, but it does not exist in enantiomeric forms because it possesses fourfold alternating axis of symmetry. Thus, *X* is superimposable on its mirror image.

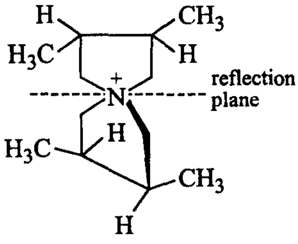
To show that *X* contains a fourfold alternating axis of symmetry, an orientation of *X*, say *X*a, is rotated through 90° about the co-axis of both rings to get *X*b. Reflection of *X*b through the central plane (*i.e.*, through *N* atom) perpendicular to this axis gives a molecule identical to *X*a.



X



Xa

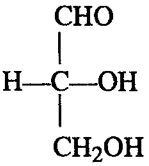


Xb

3.8 NOMENCLATURE

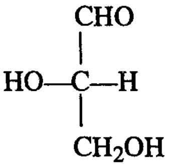
3.8.1 D, L Nomenclature (Relative Configuration)

Actual spatial arrangement of atoms or groups in a molecule is known as its absolute configuration. Before 1951, there was no method for determining the absolute configuration, hence the configuration of molecules were described with respect to glyceraldehyde, which was arbitrarily chosen as a standard by Rosanoff (1906). All the configurations described with respect to glyceraldehyde are called relative configurations. (+)-Glyceraldehyde having the —OH group on the right and hydrogen on the left, the —CHO and —CH_2OH groups being on the top and bottom, respectively was arbitrarily given the configurational symbol D. The mirror image compound (−)-glyceraldehyde was given the configuration L.



$$\begin{array}{c}CHO\\ |\\ H-C-OH\\ |\\ CH_2OH\end{array}$$

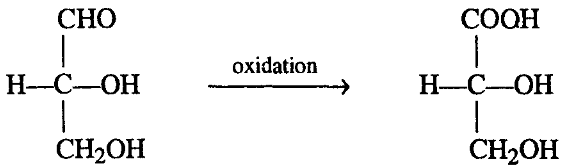
D-(+)-glyceraldehyde



$$\begin{array}{c}CHO\\ |\\ HO-C-H\\ |\\ CH_2OH\end{array}$$

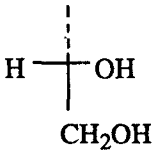
L-(−)-glyceraldehyde

Any compound that can be prepared from, or converted into D-(+)-glyceraldehyde will belong to D series; and similarly any compound that can be prepared from or converted into L-(−)-glyceraldehyde will belong to L series **(relative configuration)**. Thus the relative configurations may be classified as D or L. For example, D-(+)-glyceraldehyde can be converted into glyceric acid by simple oxidation, thus the configuration of glyceric acid obtained must be D. *It should be noted that there is no change in configuration if a reaction does not involve the cleavage of a bond to the chiral centre.*



$$\begin{array}{c}CHO\\ |\\ H-C-OH\\ |\\ CH_2OH\end{array} \xrightarrow{\text{oxidation}} \begin{array}{c}COOH\\ |\\ H-C-OH\\ |\\ CH_2OH\end{array}$$

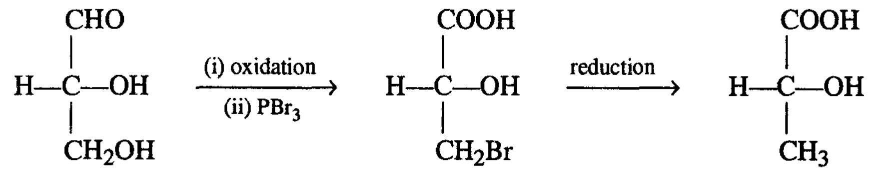
D-(+)-glyceraldehyde D-(−)-glyceric acid



$$\begin{array}{c}\vdots\\ H-\!\!\!-\!\!\!+\!\!\!-\!\!\!-OH\\ |\\ CH_2OH\end{array}$$

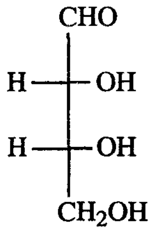
D-series

Similarly, lactic acid obtained from D-(+)-glyceraldehyde in the following way is also assigned D configuration.

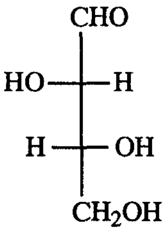


D-(+)-glyceraldehyde D-(−)-lactic acid

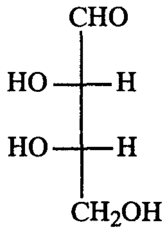
When representing relative configurational relationship of molecules containing more than one chiral carbon, the chiral carbon of glyceraldehyde is always drawn at the bottom. For example, (−)-erythrose and (−)-threose belong to D series, whereas the corresponding (+)-enantiomers belong to L series. Similarly, the natural (+)-glucose is D-(+)-glucose, and (−)-fructose is D-(−)-fructose.



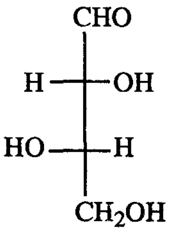
D-(−)-erythrose



D-(−)-threose



L-(+)-erythrose



L-(+)-threose

As it is clear from the above examples, *there is no correlation between the D and L designation and the sign of rotation.*

The D, L system of relating the configuration has a basic defect that sometimes the configuration of the same molecule may be related to both D and L series. Moreover, the D, L system of nomenclature specifies the configuration of only one chiral carbon in the case of compounds having more than one chiral carbon. For example, D-(+)-glucose means that it has the same configuration at its bottom chiral carbon as that of D-(+)-glyceraldehyde, *i.e.*, the —OH group on the right and —H on the left side.

Note : (i) If the OH group is on left side at the bottom chiral carbon when the structure is written in such a way that the most oxidised carbon is kept on the top of the vertical line, it is designated as *L*.

(ii) If the OH group is on right side at the bottom chiral carbon when the structure is written in such a way that the most oxidised cabon is kept on the top of the vertical line, it is designated as *D*.

3.8.2 *R*, *S* Nomenclature (Absolute Configuration)

As we have noted above, there are several drawbacks of D, L nomenclature. Thus, an unambiguous and universally applicable system for specifying the **absolute configuration** (actual spatial arrangement of atoms or groups) of each chiral centre in a molecule was devised by Cahn *et al.* (1956, 1966). It is known as the *R*, *S* nomenclature or the Cahn-Ingold-Prelog (CIP) nomenclature. This system of nomenclature is based on the actual (absolute) configuration.

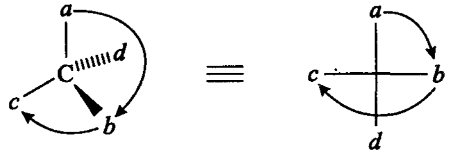
3.8.2.1 *R*, *S* nomenclature system involves two steps

Step 1. The four ligands (atoms or groups) attached to the chiral centre are assigned a sequence of priority according to sequence rules given in Section 3.8.3.

Step 2. After assigning the priorities of ligands attached to the chiral carbon, the molecule is imagined to be oriented so that the group of *lowest*-priority is directed away from the observer. Now the arrangement of the remaining three groups is viewed in the decreasing order of their priorities. If in looking so, the eye travels in clockwise direction, the configuration is specified *R* (Latin : *rectus* = right), while in case the eye travels in the anticlockwise direction, the configuration is specified *S* (Latin : *sinister* = left). *Step 2* is called the ***conversion rule.***

When the molecule contains more than one chiral carbon, the same procedure (*Steps 1 and 2*) is applied to each.

For making the above steps clear, let us take a general example of the compound *Cabcd* in which the sequence of priority is : *a* before *b*; *b* before *c*, and *c* before *d*. Orient the molecule in a way that the ligand of lowest priority (*d*) is away from the observer, *i.e.*, below the plane of the paper in the case of flying-wedge formula, and either at the top or at the bottom (*i.e.*, below the plane of the paper) in the case of Fischer projection. The molecule is then viewed from the opposite to the ligand of lowest priority (*d*) and the arrangement of the rest of the ligands is observed. If the arrangement of ligands *a* to *b* to *c* is in the clockwise direction, the configuration is assigned as *R*; if this arrangement is in anticlockwise direction, the configuration is specified as *S*.



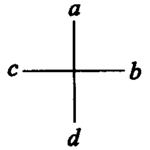
Flying-wedge formula **Fischer projection formula**

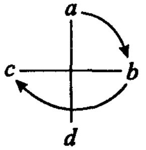
Clockwise arrangement, *R* configuration

Flying-wedge formula **Fischer projection formula**

Anticlockwise arrangement, *S* configuration

While using a Fischer projection formula, if the group of lowest priority (*d*) is not at the top or bottom of the vertical line, then it must be done so by making an even number of interchanges of groups as already described in Section 3.6.2. Let us take a general example of the following compound where the group of lowest priority (*d*) is not at the top or bottom, so we have to make an even number of interchanges to bring it either at the vertical line (bottom or top). Let us interchange the positions of *d* and *c*, and that of *a* and *b*. By carrying out these two interchanges, we get the following Fischer projection of the same enantiomer with the ligand of lowest priority (*d*) at the bottom.





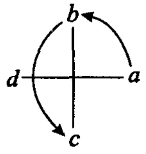
***R*-Configuration**

Now view the molecule from above the plane of the paper, *i.e.*, from the opposite side of the group of the lowest priority (*d*) which is below the plane of the paper (the groups on the top and bottom in a Fischer projection are considered below the plane of the paper). In doing so the arrangement of the remaining groups *a* to *b* to *c* is in clockwise direction, thus the configuration of the above molecule will be *R*.

An alternative, simple and most widely accepted procedure used now (Epling, 1982) to assign *R*, *S* configuration in the case of Fischer projections is as follows :

If in a Fischer projection the group of lowest priority (*d*) is on a vertical line, then the assignment of configuration is *R* for a clockwise sequence of *a* to *b* to *c*, and *S* for anticlockwise sequence.

However, if the ligand of lowest priority is on a horizontal line, then the assignment of configuration is *S* for a clockwise sequence of *a* to *b* to *c*, and *R* for the anticlockwise sequence. Thus, the following structure in which the group of lowest priority (*d*) is on the horizontal line can directly be assigned *R* configuration, as the molecule has an *anti* clockwise sequence of $a \rightarrow b \rightarrow c$.

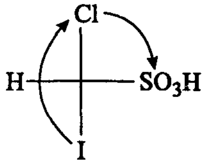


3.8.3 Sequence Rules

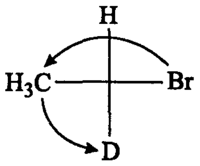
The priorities of the four ligands (atoms or groups) attached to a chiral centre are decided by applying the following sequence rules in trun, as long as necessary to reach a decision. The sequence rules are arbitrary but consistent.

1 If all the four atoms directly attached to the chiral centre are different, sequence of priorities is determined by their atomic numbers, the atom of higher atomic number is given higher priority. If two atoms are isotopes of the same element, the isotope of higher mass number has the higher priority.

For example, in chloroiodomethanesulphonic acid the sequence is I > Cl > S > H, where > denotes "has higher priority;" in α-deuterioethyl bromide it is Br > C > D > H.



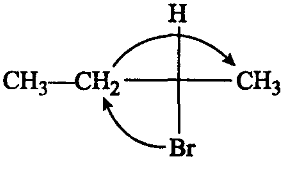
Chloroiodomethanesulphonic acid *S* configuration; (I → Cl → S sequence is clockwise but the group of lowest priority (H) is on the horizontal line, hence the configuration will be *S*)



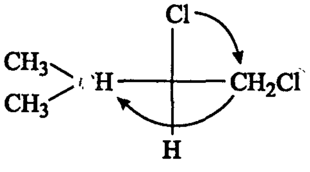
α-deuterioethyl bromide (Br → CH_3 → D sequence is anticlockwise and the group of lowest priority (H) is on the vertical line, hence the configuration will be *S*)

2. If two or more atoms attached to the chiral centre are the same, the priority is decided by applying the sequence rule **1** to the next to the next atoms in the groups and so on, if necessary, working outward from the chiral centre. When a group has branches the branch of highest priority is followed.

For example, in 2-bromobutane two of the atoms directly attached to the chiral centre are carbon. In CH_3 the second atoms are H, H, H; in C_2H_5 they are C, H, H. Since carbon has a higher atomic number than hydrogen, C_2H_5 has the higher priority than CH_3. Therefore, a complete sequence of priority for 2-bromobutane is Br > C_2H_5 > CH_3 > H.



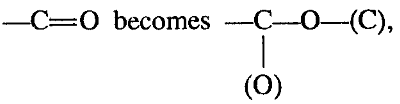
(*R*)-2-Bromobutane



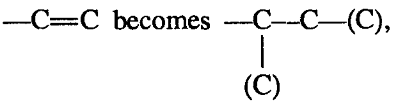
(*R*)-1,2-Dichloro-3-methylbutane

In 1, 2-dichloro-3-methylbutane the Cl, H, H of CH_2Cl has a higher priority than the C, C, H of isopropyl. Chlorine has a higher atomic number than carbon, and the fact that there are two C's and only one Cl does not matter. One higher number is worth than two or three of a lower number.

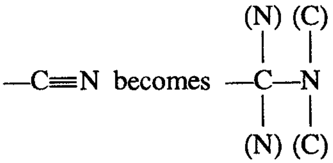
3. If there is a double or triple bond, both double or triple bonded atoms are considered to be duplicated or triplicated. The priority sequence is then, determined by considering the structure containing the duplicated or triplicated atoms. Thus,



$$-\mathrm{C}=\mathrm{O} \text{ becomes } -\underset{\mathrm{(O)}}{\mathrm{C}}-\mathrm{O}-\mathrm{(C)},$$

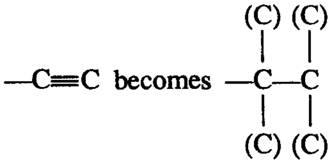


$$-\mathrm{C}=\mathrm{C} \text{ becomes } -\underset{\mathrm{(C)}}{\mathrm{C}}-\mathrm{C}-\mathrm{(C)},$$



$$-\mathrm{C}\equiv\mathrm{N} \text{ becomes } -\overset{\mathrm{(N)}}{\underset{\mathrm{(N)}}{\mathrm{C}}}-\overset{\mathrm{(C)}}{\underset{\mathrm{(C)}}{\mathrm{N}}}$$

and

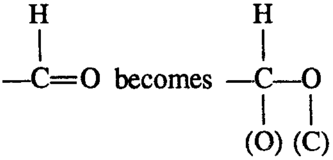


$$-\mathrm{C}\equiv\mathrm{C} \text{ becomes } -\overset{\mathrm{(C)}}{\underset{\mathrm{(C)}}{\mathrm{C}}}-\overset{\mathrm{(C)}}{\underset{\mathrm{(C)}}{\mathrm{C}}}$$

The *phantom (duplicate) atoms* are enclosed in parentheses and bear no further substituents. For example :

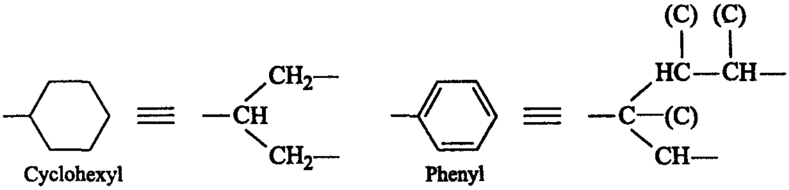
In glyceraldehyde the —OH group has highest priority and the O, O, H of —CHO takes priority over O, H, H of —CH_2OH. Thus, the complete sequence of priority is —OH > —CHO > —CH_2OH > H.

D-(+)-glyceraldehyde is (*R*)-(+)-glyceraldehyde



$$-\overset{\mathrm{H}}{\mathrm{C}}=\mathrm{O} \text{ becomes } -\overset{\mathrm{H}}{\underset{\mathrm{(O)}}{\mathrm{C}}}-\underset{\mathrm{(C)}}{\mathrm{O}}$$

Ring systems are treated as branched chains, and if unsaturated, then duplication is used for a double bond or triplication for a triple bond. Thus, the C, C, C of a phenyl group takes priority over C, C, H of a cyclohexyl group.

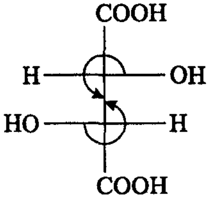


By using the above sequence rules, some common ligands are given the following order of priority sequence :

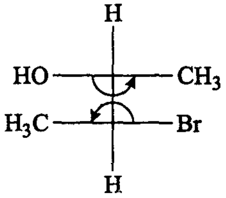
I, Br, Cl, SO_3H, SH, F, OCO*R*, O*R*, OH, NO_2, NR_2, NH*R*, NH_2, COO*R*, COOH, CO*R*, CHO, CH_2OH, CN, Ph, CR_3, CHR_2, CH_2R, CH_3, D, H.

On the basis of the above discussion, the designations *R* and *S* have been assigned to the following absolute configurations of some molecules as examples :

When a molecule contains two chiral centres, each chiral centre is assigned an *R* or *S* configuration according to the sequence and conversion rules. Thus, (+) tartaric acid is (2*R*, 3*R*)-(+)-tartaric acid.

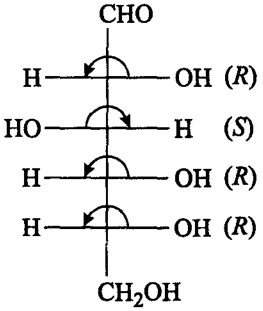


The group of lowest priority, *i.e.*, H is on the horizontal line at both the chiral centres, hence the anticlockwise sequence of the remaining groups shows *R* configuration.



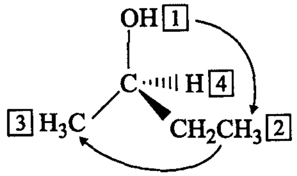
In 3-bromo-2-butanol, H is on the vertical line at the chiral centres, hence the anticlockwise sequence of the remaining groups gives *S* configuration.

Applying the rule that if the group of lowest priority (H) is on the horizontal line then clockwise sequence gives *S* and anticlockwise sequence *R* configuration; the correct designation assigned to D-(+)-glucose is given on the next page :

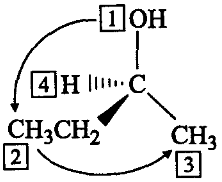


D-(+)-glucose

The assignment of *R* and *S* configuration to both the enantiomers of 2-butanol represented by flying-wedge formula is shown below :

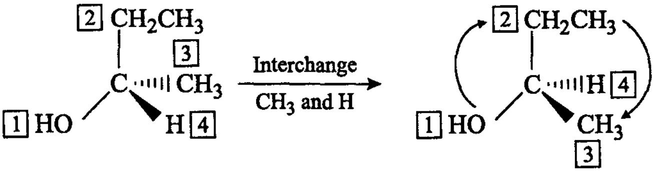


Clockwise sequence
(*R*)-2-butanol



Anticlockwise sequence
(*S*)-2-butanol

1. If the group of the lowest priority is away from the observer (*i.e.*, bonded by dashed line) and the priority sequence (1 → 2 → 3) is clockwise, then the configuration is assigned as *R* as shown above.
2. If the group of the lowest priority is not bonded by dashed line (*i.e.*, not away from the observer) then interchange a pair of groups so that the group with the lowest priority is bonded by dashed line. Now see the sequence (1 → 2 → 3), if it is clockwise then the configuration is assigned as *S*, and if anticlockwise *R*. This is because you have interchange a pair of groups and now you are determining the configuration of enantiomer of the original molecule.



XI

This is *R* configuration, which means that the original compounds XI has the *S* configuration

3.8.4 The Comparison Between D, L And *R*, *S* Nomenclatures

The D, L system of nomenclature is for the nomenclature of **relative configurations**, whereas the *R*, *S* system is for the nomenclature of **absolute configurations**. The *R*, *S* system is used for specifying the configurations of known absolute configurations of the enantiomers and diastereomers. When a compound has been placed in D or L series, its absolute configuration is said to be known, because the absolute configurations of D-(+)-and L-(−)-glyceraldehydes are the same as they were arbitrarily chosen as standard.

It should be noted that there is no relation between D, L and *R*, *S* configurations, *i.e.*, all the D compounds are not necessarily *R* and all the L compounds are not necessarily *S*. Similarly, there is no relationship between the D, L and *R*, *S* configurations and the sign of rotation of the molecules, *i.e.*, all the *R* or D isomers may not have (+) and all the *S* or L isomers may not have (−) sign of rotation.

3.8.5 *Erythro* And *Threo* Nomenclature

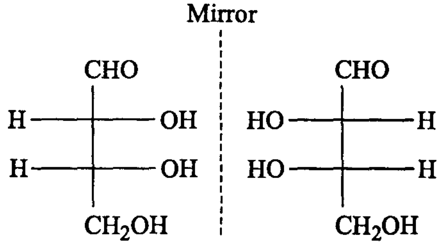
This system of nomenclature is used only in those compounds which have :

(i) only two chiral carbons, and

(ii) the following general structure

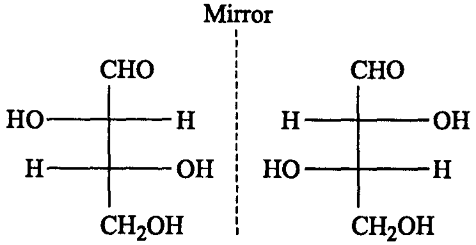
R—Cab—Cab—*R′* or *R*—Cab—Cbc—*R′*

Erythro and *threo* nomenclature is based on aldotetroses, erythrose and threose which exist as two enantiomeric pairs.



(−)-Erythrose (+)-Erythrose

Enantiomeric pair



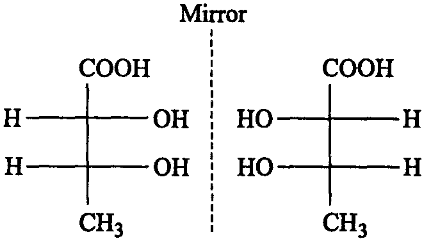
(−)-Threose (+)-Threose

Enantiomeric pair

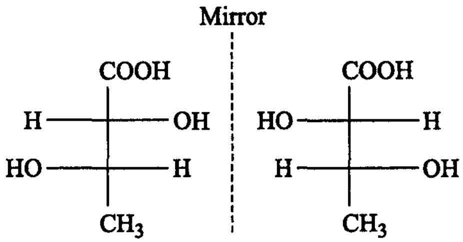
An enamtiomer of one pair is diastereomeric with that of the other pair.

When two similar groups at two adjacent (nonidentical) chiral carbons are on the same side of the vertical line of the Fischer projection, the isomer is called erythro isomer; if the groups are on the opposite sides, the isomer is called threo isomer.

For example :

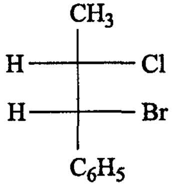


One pair of enantiomers either can be named as *erythro*-2, 3-dihydroxybutanoic acid, and these enantiomers called *erythro* enantiomers.

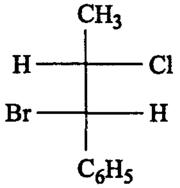


One pair of enantiomers either can be named as *threo*-2, 3-dihydroxybutanoic acid, and these enantiomers called *threo* enantiomers.

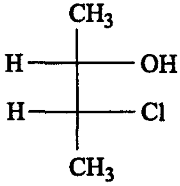
Following are some other examples of *erythro* and *threo* nomenclature.



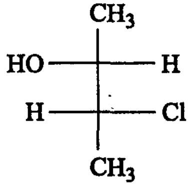
Erythro form



Threo form



Erythro form



Threo form

3.9 MOLECULES WITH ONE CHIRAL (STEREOGENIC) CENTRE

If a molecule contains only one chiral carbon, it must be chiral and will exist in two optically active forms, *i.e.*, as two enantiomers.

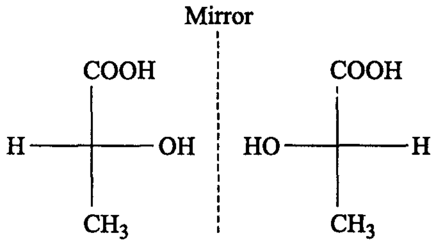
3.9.1 Properties Of Enantiomers

1. Enantiomers have identical physical properties (such as mp, bp, density and refractive index) except their optical rotations which are of equal magnitude but opposite sign. Enantiomers may also have different odours, *e.g.*, (+)-limonene has smell of oranges and (–)-limonene smells like lemons.
2. Enantiomers have identical chemical properties except in the presence of chiral reagents and chiral solvents, when their rate of reactions are different.
3. Enantiomers may also be different physiologically, *e.g.*, (–)-nicotine is more poisonous than (+)-nicotine; (+)-histidine is sweet but (–)-histidine is tasteless; L-(+)-ascorbic acid (vitamin C) is more efficient than D-(–)-ascorbic acid. In many cases one enantiomer of a drug molecule is more efficient and safe than the other.

3.9.2 Racemic Modification

An equimolar mixture of a pair of enantiomers is known as racemic modification. Sometimes the terms racemic mixture and racemate are also used as synonym for racemic modification. Racemic modifications are optically inactive due to external compensation of the two components. Racemic modifications are designated by the prefix (±)- or *RS* or *rac*-. Racemic modifications in the vapour or liquid phase show physical properties (such as bp, density and refractive index) identical to those of pure enantiomers. Racemic mixtures melt above, below, or at the same temperature as the enantiomers depending on the nature of the solid (crystalline) state of the racemic modification. Racemic mixtures can be resolved into their component enantiomers.

Thus, a compound containing only one chiral carbon can exist in three forms, *viz.*, (+), (–) and (±). One of the most common examples of enantiomerism of compounds containing only one carbon atom is that of lactic acid. Lactic acid exists in three forms, *i.e.*, dextrorotatory or (+)-lactic acid, laevorotatory or (−)-lactic acid, and as equimolar mixture (racemic modification) of (+) and (−) lactic acids, which is optically inactive due to mutual compensation (external compensation) of the two enantiomers. The absolute configurations of (−)-and (+)-lactic acids are *R* and *S*, respectively.



R-(−)-Lactic acid *S*-(+)-Lactic acid

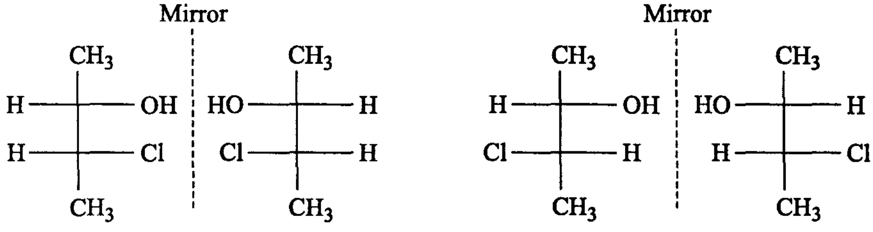
Enantiomers

3.10 MOLECULES WITH TWO CHIRAL (STEREOGENIC) CENTRES

3.10.1 Molecules with Two Dissimilar (Nonidentical) Chiral Centres

In the case of an acyclic molecule with *n* dissimilar (nonidentical) chiral carbons, the number of stereoisomers will be 2^n (all optically active forms). There will be $2^{(n-1)}$ pairs of enantiomers and the same number, $2^{(n-1)}$, of racemic modifications. Any molecule with more than one chiral centre must have diastereomers.

For example, 3-chloro-2-butanol contains two chiral carbons and, as expected, exists as two pairs of enantiomers and $2^2 = 4$ stereoisomers as shown below :



(I) (II) (III) (IV)

Two Enantiomers Two Enantiomers

The configurations I and II are nonsuperimposable mirror images of each other, *i.e.*, they are enantiomers; similar is the case with III and IV. Furthermore, equimolar mixtures of enantiomers I and II; and III and IV constitute two different racemic modifications. Thus, we can say that such compounds exist in six different forms; two enantiomeric pairs and two racemic modifications.

The configurations I and III; I and IV; II and III; and II and IV are not mirror images of each other. Such *stereoisomers which are not mirror images of each other are known as diastereomers, i.e.,* the stereoisomers which are not enantiomers are diastereomers.

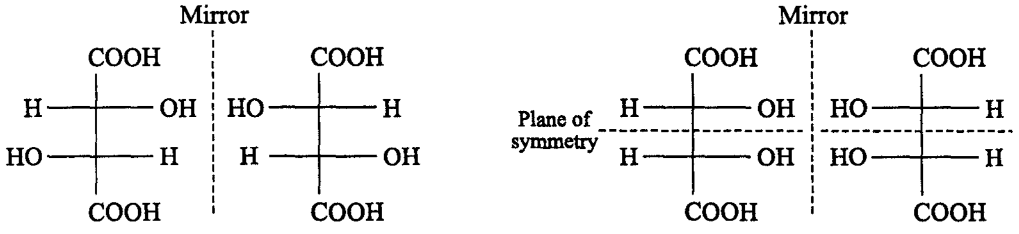
Properties of Diastereomers

1. Diastereomers have different physical properties such as m.p., b.p., density, solubility, refractive index, etc.
2. They may or may not be optically active, *e.g.*, achiral stereoisomers like *meso* forms and geometrical isomers are optically inactive.
3. Diastereomers have similar but not identical chemical properties. Their rate of reactions differs with chiral as well as achiral reagents and solvents.

4. Due to difference in their physical properties, diastereomers can easily be separated through techniques like fractional crystallisation, fractional distillation, chromatography, etc.

3.10.2 Molecules with Two Similar (Identical) Chiral Centres

Identically substituted chiral carbons are called as similar (identical) chiral carbons. The number of stereoisomers in a compound containing n number of similar chiral carbons is always less than 2^n. Let us consider tartaric acid as an example of molecules containing two similar chiral carbons. It can be easily seen that the two chiral carbons in tartaric acid are identically substituted. The following Fischer projections can be written for tartaric acid :



(I) (II) (III) (IV)

Structures I and II, and III and IV are mirror images. I and II are nonsuperimposable mirror images, hence they are enantiomers, and each is diastereomeric with III and IV. Structures III and IV are superimposable mirror images, hence they are the same (identical).

Although III or IV has chiral carbons, the molecule is not chiral because it is superimposable on its mirror image. This molecule has a plane of symmetry, therefore the molecule as a whole is achiral and is optically inactive. Such *a stereoisomer that contains chiral carbons but is achiral and optically inactive is called a meso form.*

Because of the plane of symmetry in *meso*-tartaric acid, there are only three stereoisomers for tartaric acid rather than the four as predicted by the 2^n rule. These three isomers are a pair of enantiomers (I and II) and the *meso* form (III or IV). The stereoisomers I and III; and II and III are not mirror images of each other, hence these are diastereomers. In contrast to racemic modifications *meso* compounds cannot be resolved. It should be noted that tartaric acid will also exist as a racemic form (racemic modification) besides a pair of enantiomers and a *meso* form. The racemic modification is not a stereoisomeric form; actually it is an equimolar mixture of two enantiomeric forms (I and II). The racemic modification is optically inactive because of external compensation, whereas the *meso* form is optically inactive because of internal compensation caused by the presence of a plane of symmetry in the molecule. Physical properties of different forms of tartaric acid are given in Table 3.1.

Table 3.1 Physical properties of different forms of tartaric acid

	(+) form	(–) form	(±) from	*Meso* form
(i) Rotation	+12°	–12°	0°	0°
(ii) Melting point	168–70°C	168–70°C	0	140°C
(iii) Solubility in 100 ml water at 20°	139 g	139 g	139 g	125 g
(iv) *pKa*	2.93	2.93	2.93	3.11
(v) Density	1.7598	1.7598	1.7598	1.666

3.10.3 Calculation of Number of Optical Isomers

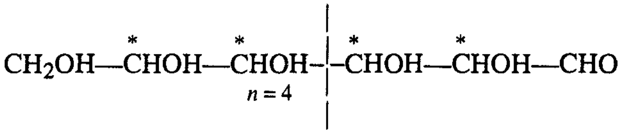
(1) If molecule is not divisible into two identical halves and molecule has n asymmetric carbon atoms then :

Number of optically active forms $= 2^n = a$
Number of enantiomeric pair $= a/2$
Number of racemic mixture $= a/2$
Number of *meso* form $= 0$

Examples :

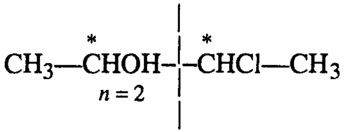
$C_6H_5-\overset{*}{C}HOH-\overset{*}{C}HOH-\overset{*}{C}HOH-CH_3$

This molecule cannot be divided into two identical halves and it has three asymmetric carbons. Hence number of optically active isomers $= a = 2^n = 2^3 = 8$.



$CH_2OH-\overset{*}{C}HOH-\underset{n=4}{\overset{*}{C}HOH}-\,|\,-\overset{*}{C}HOH-\overset{*}{C}HOH-CHO$

Number of optically active forms $= a = 2^4 = 16$



$CH_3-\underset{n=2}{\overset{*}{C}HOH}-\,|\,-\overset{*}{C}HCl-CH_3$

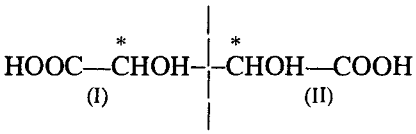
Number of optically active forms $= 2^2 = 4$

(2) If molecule is divisible into two identical halves, then the number of configurational isomers depends on the number of asymmetric carbon atoms.

Case I : When compound has even number of carbon atoms, *i.e.*, $n = 2, 4, 6, 8, 10, 12, \ldots$:

(i) Number of optically active forms $= a = 2^{n-1}$
(ii) Number of enantiomeric pairs $= a/2$
(iii) Number of racemic mixture $= a/2$
(iv) Number of *meso* forms $= m = 2^{(n/2)} - 1$
(v) Total number of configurational isomers $= a + m$

Example :



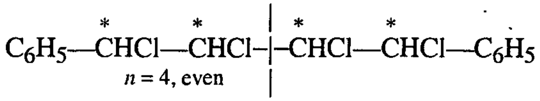
$HOO C-\underset{(I)}{\overset{*}{C}HOH}-\,|\,-\underset{(II)}{\overset{*}{C}HOH-COOH}$

Two identical halves (I) and (II) having $n = 2$.

Thus number of optical isomers $= a = 2^2 - 1 = 2$

Number of *meso* form $= m = 2^{(n/2)} - 1 = 2^{(2/2)} - 1 = 2^0 = 1$

Total number of configurational isomers $= 2 + 1 = 3$



$C_6H_5-\overset{*}{C}HCl-\underset{n=4,\text{ even}}{\overset{*}{C}HCl}-\,|\,-\overset{*}{C}HCl-\overset{*}{C}HCl-C_6H_5$

$$a = 2^{4-1} = 2^3 = 8$$

$$m = 2^{(n/2)} - 1 = 2^1 = 2$$

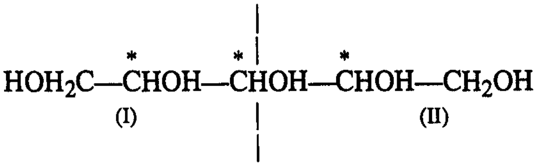
Total number of configurational isomers $= 8 + 2 = 10$

Case II : When compound has odd number of carbon atoms, *i.e.*,

$$n = 3, 5, 7, 9, 11, \ldots :$$

(i) Number of optically active forms $= a = 2^{n-1} - 2^{(n-1)/2}$
(ii) Number of enantiomeric pairs $= a/2$
(iii) Number of racemic mixture $= a/2$
(iv) Number of *meso* forms $= m = 2^{(n-1)/2}$
(v) Total number of configurational isomers $= a + m$

Example :



$$HOH_2C—\overset{*}{C}HOH—\overset{*}{C}HOH—\overset{*}{C}HOH—CH_2OH$$

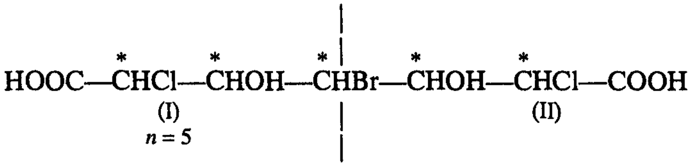
(I) (II)

Compound has two identical halves and has three asymmetric carbons. Thus

$$a = 2^{n-1} - 2^{(n-1)/2} = 2^2 - 2^1 = 4 - 2 = 2$$

$$m = 2^{(n-1)/2} = 2^1 = 2$$

Hence total number of configurational isomers $= 2 + 2 = 4$



$$HOOC—\overset{*}{C}HCl—\overset{*}{C}HOH—\overset{*}{C}HBr—\overset{*}{C}HOH—\overset{*}{C}HCl—COOH$$

(I) (II)

$n = 5$

Compound is divisible in two identical halves. Therefore

$$a = 2^{n-1} - 2^{(n-1)/2} = 2^4 - 2^2$$

$$= 16 - 4 = 12$$

$$m = 2^{(n-1)/2} = 2^2 = 4$$

Therefore, total number of configurational isomers $= 12 + 4 = 16$.

3.11 RESOLUTION OF RACEMIC MODIFICATIONS

The synthesis of optically active compounds using symmetrical (achiral) compounds and conditions always gives racemic modification. Enantiomerically pure compounds are of immense importance in chemical and pharmaceutical fields. Thus, we must have efficient methods for obtaining pure enantiomers. ***The separation of a racemic modification into its constituent enantiomers is known as resolution.***

Methods of Resolution

1. Mechanical separation : Some enantiomeric compounds form left-handed and right-handed (chiral) crystals which allow their separation by hand using a magnifying glass and a small forceps. This method is too tedious for practical purposes and is now of historical importance only because it was the first method of resolution which Pasteur (1848) used for the separation of (±)-sodium ammonium tartrate.

2. Biochemical method : When certain bacteria and moulds are allowed to grow in a solution of a racemic modification, they destroy one enantiomer selectively than the other and are useful in separation. For example, *Penicillium glaucum* (a mould) can be used to remove (+)-ammonium tartrate from a racemic mixture to leave back only the (–) ammonium tartrate (Pasteur, 1858).

This method of resolution has the following main disadvantages :

(i) One enantiomer is always destroyed, *i.e.*, we get one enantiomer at the cost of the other.

(ii) Sometimes it is difficult to find a specific microorganism applicable to a given racemic modification.

3. Chemical method (*via* diastereomers) : This is the best method of resolution and was introduced by Pasteur (1858). In this method a racemic modification is converted into a mixture of diastereomers of its constituent enantiomers by using a pure enantiomer of another compound. The diastereomers have different physical properties (solubility, m.p., b.p., etc.), hence can easily be separated by fractional crystallisation or fractional distillation. After the complete separation of the two diastereomers, each of them is converted back into the individual enantiomer of the racemic mixture by a suitable reaction.

For example, acid-base reactions are often used to resolve racemic acids and bases. A racemic acid reacts with an optically active base to form two diastereomeric salts. Similarly, a racemic base reacts with an optically active acid to form two diastereomeric salts. The salts can be separated by conventional methods (usually fractional crystallisation) and the resolved compounds are liberated by treatment with dilute acid or base.

$$(R)\text{-acid} + (S)\text{-acid} \xrightarrow{(S)\text{-base}} (R, S)\text{-salt} + (S, S)\text{-salt}$$

(Diastereomers, can be separated by, *e.g.*, fractional crystallisation)

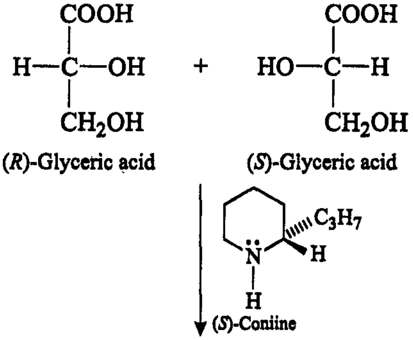
$$(R, S)\text{-salt} \xrightarrow{\text{Dil. HCl}} (R)\text{-acid} + (S)\text{-base-HCl}$$

$$(S, S)\text{-salt} \xrightarrow{\text{Dil. HCl}} (S)\text{-acid} + (S)\text{-base-HCl}$$

Optically active bases used for resolution of (±)-acids are mainly alkaloids, *e.g.*, brucine, quinine, morphine, cinchonine and cinchonidine. Other optically active bases are also used, *e.g.*, coniine, menthylamine, 1-phenylethylamine, etc.

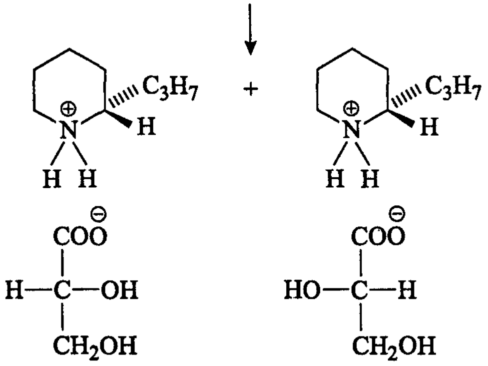
Racemic modifications of bases (amines) may be resolved using various optically active acids such as tartaric acid, malic acid, camphor-β-sulphonic acid and menthoxyacetic acid.

As an specific example let us look how we might resolve the enantiomers of glyceric acid. We need an optical active pure base as resolving agent and this may be (*S*)-coniine.



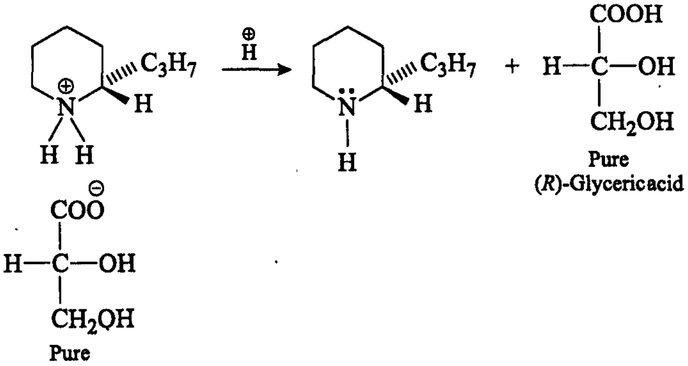
(*R*)-Glyceric acid (*S*)-Glyceric acid

(*S*)-Coniine



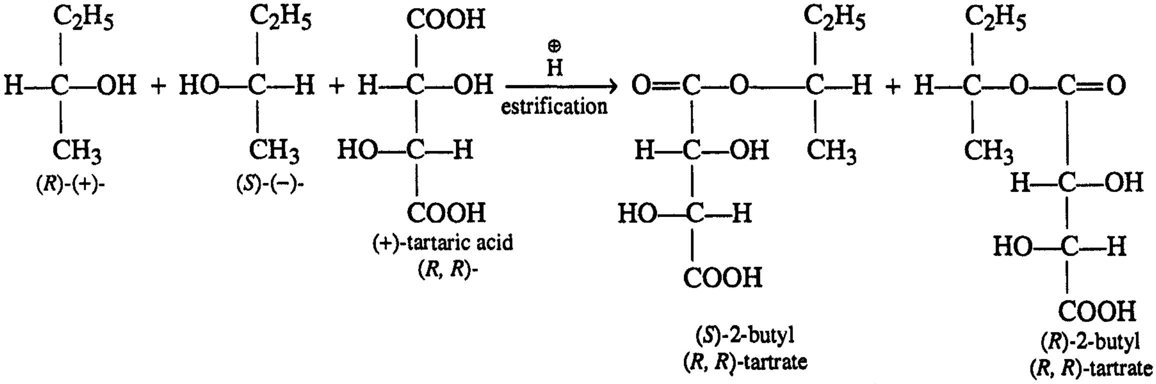
Diastereomeric salts

These salts are diastereomers. They can be separated by recrystallisation. The separated salts are individually treated with HCl to regenerate the resolved enantiomers of glyceric acid.



Racemic modifications of alcohols may be resolved by their esterification with an optically active acid to give diastereomeric esters which can easily be separated, and converted back into the individual enantiomer by hydrolysis.

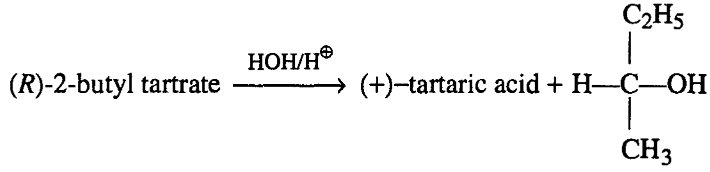
Let us use our racemic mixture of (+)- and (–)-2-butanol as an example of how we might resolve the two enantiomers. We need a resolving agent that reacts with an alcohol and that is readily available in an enantiomerically pure state. This resolving agent can be (+)-tartaric acid. Given scheme shows that diastereomeric esters are formed when (+)- and (–)-2-butanol react with (+)-tartaric acid.



Diastereomers

Hydrolysis of (R)-2-butyl tartrate gives (R)-2-butanol and (+)-tartaric acid, while hydrolysis of (S)-2-butyltartrate gives (S)-2-2butanol and (+)-tartaric aicd.

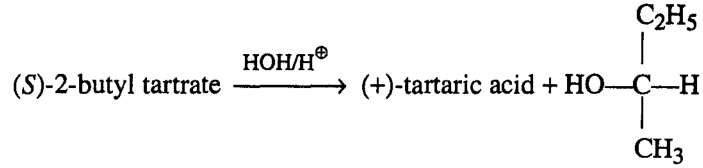
Hydrolysis in one flask



$$(R)\text{-2-butyl tartrate} \xrightarrow{HOH/H^{\oplus}} (+)\text{-tartaric acid} + H-\overset{\displaystyle C_2H_5}{\underset{\displaystyle CH_3}{C}}-OH$$

(*R*)-2-butanol

Hydrolysis in another flask



$$(S)\text{-2-butyl tartrate} \xrightarrow{HOH/H^{\oplus}} (+)\text{-tartaric acid} + HO-\overset{\displaystyle C_2H_5}{\underset{\displaystyle CH_3}{C}}-H$$

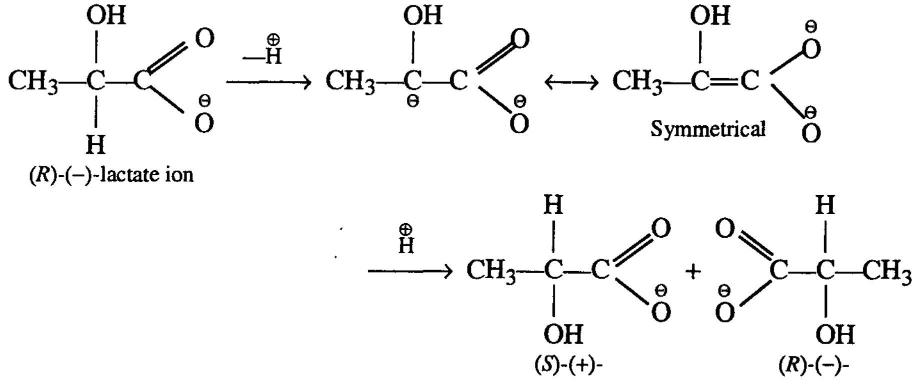
(*S*)-2-butanol

3.12 RACEMISATION

The process of conversion of an optically active compound into the racemic modification is known as racemisation. Racemisation may be brought about by heat, light or chemical reagents. The racemisation which occurs spontaneously at room temperature is known as **autoracemisation**, *e.g.*, dimethyl bromosuccinate autoracemises. Many optically active substances undergo autoracemisation simply by prolonged storage.

Many theories have been proposed to explain racemisation. One of the most widespread is the mechanism of racemisation through a carbanion formation at the chiral carbon *alpha* to a carbonyl group, *e.g.*, in the case of chiral aldelydes, ketones, carboxylic acids, etc., where the chiral carbon is *alpha* to the > C=O group. This is because in such cases the carbanions, as a rule, undergo racemisation.

The carbanion mechanism of racemisation of (–)-lactic acid is given below as an example :



Racemic mixture

In addition to heat, light or chemical reagents, the ease of racemisation also depends on the nature of the chiral compound, for example,

(a) Some compounds racemise so easily that they cannot be isolated in optically active forms.

(b) The majority of compounds have various rates of racemisation under the influence of different reagents.

(c) Only a small number of compounds cannot be racemised at all, *e.g.*, Ph—CH(Me)—Et (*sec.* butylbenzene).

When a molecule contains two or more chiral carbons and the configuration of one or more (but not all) of these is inverted by some reaction, the process is called **epimerisation.**

OPTICAL PURITY

Optical purity tells us whether a particular compound consists a single enantiomer or a mixture of enantiomers. Optical purity of a compound can be determined by its observed specific rotation. Optical purity is also called optical yield.

$$\%\text{ optical purity } (\%\text{ o.p.}) = \frac{\text{observed specific rotation}}{\text{specific rotation of the pure enantiomer}} \times 100$$

Usually, *the % optical purity is equal to the % excess of one enantiomer over the other.*

$$\%\text{ o.p.} = \%\text{ enantiomeric excess } (\%\text{ ee}) = \%R - \%S$$

For a racemic modification, the optical purity is zero.

If a sample of 2-bromobutane has 40% ee of (*S*)-(+)-bromobutane then what is the % of *S* and *R* enantiomers in the sample?

$$\%R + \%S = 100$$

$$\%S - \%R = 40 \quad (S\text{ isomer is in 40\% excess})$$

$$\%2S = 140$$

$$\%S = 70$$

$$\therefore \quad \%R = 100 - 70 = 30$$

Thus, the sample contains 70% of the *S* and 30% of the *R* enantiomers.

3.13 INVERSION, RETENTION AND RACEMISATION

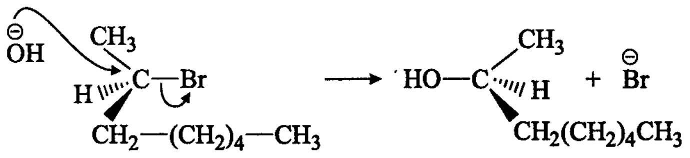
One of the most interesting and useful aspects of stereochemistry is the study of what happens to optically active molecules when they react. The products isolated from the reaction of a chiral starting material can tell us a great deal about the reaction mechanism.

We divide our discussion on the reactions of chiral compounds into the following parts :

Reaction that Takes Place at the Chiral Carbon Atom

3.13.1 Inversion of Configuration

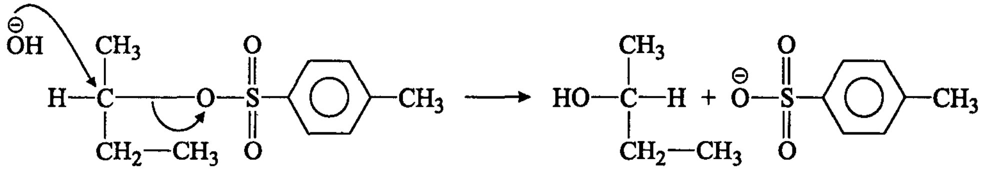
When a reaction takes place at a chiral carbon atom, it may change the configuration of the chiral carbon. For example, the SN2 mechanism involves an **inversion** of configuration of the carbon atom under attack by the nucleophile. An inversion of the configuration gives a product whose stereochemistry is opposite to that of the reactant. The reaction of hydroxide ion with optically active 2-bromooctane proceeds with inversion of configuration :



S-2-bromooctane

R-2-octanol
(Inversion of configuration)

Similarly, the reaction of hydroxide ion with optically active 2-butyl tosylate proceeds with inversion of configuraton :


S-2-butyl tosylate

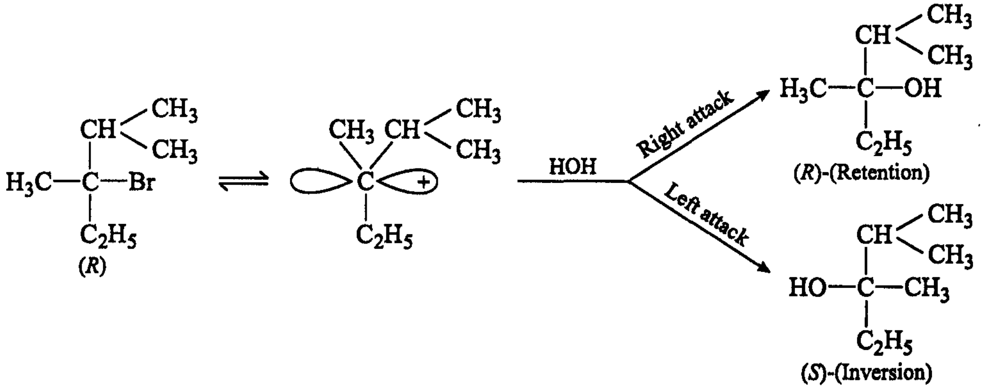
R-2-butanol
(Inversion of configuration)

P. Walden first proved that a substitution reaction had inverted configuration of a chiral carbon. In his honour, a substitution that inverts the configuration at a chiral carbon is called a **Walden inversion.** The SN2 family of reactions are common examples of Walden inversions since the backside attack of the nucleophile inverts the configuration of the electrophilic carbon atom.

3.13.2 Racemisation

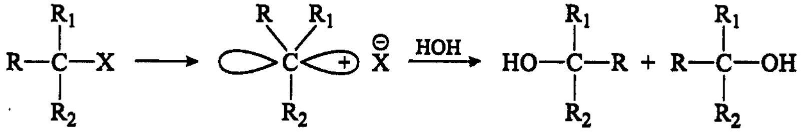
Some reactions of optically active compounds show neither clean inversion of configuration nor clean retention of configuration. This result is called **racemisation.** If the product is a racemic mixture (optically inactive) we say that the reaction proceeds with *complete racemisation.* If some optical activity remains, the compound has undergone *partial racemisation.* In the case of partial racemisation, we say that the reaction has produced predominant retention or predominant inversion, depending on whether the retention product or the inversion product predominates in the reaction mixture.

An example of a mechanism that usually proceeds with racemisation is the SN1 reaction. Since a flat achiral carbocation is formed as an intermediate, the product is found to be racemic. The following reaction shows the first-order hydrolysis of a tertiary alkyl halide, (*R*)-3-bromo-2, 3-dimethylpentane.



Although the starting material is optically active, the intermediate carbocation is planar and achiral. Water can attack the carbocation on either face leading to racemisation.

The racemisation is not complete, however, because the leaving bromide ion partially blocks the side of the carbocation it leaves. Thus, water can attack more easily from the back, giving predominant inversion of configuration.

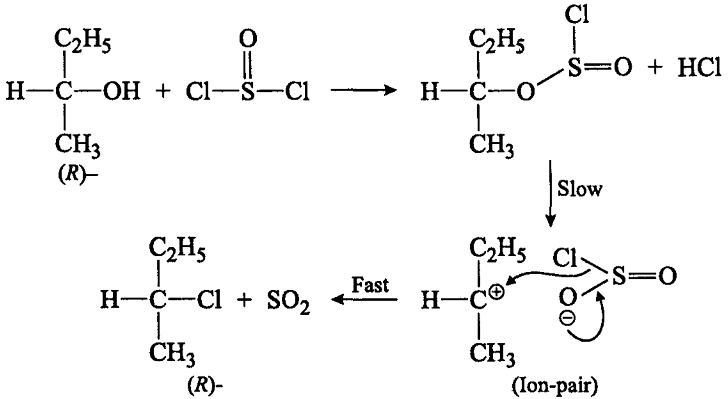


Ion-pair (Major) (Minor)

This result shows that the leaving group in the SN1 reaction does not always have time to diffuse away from the carbocation before attack by the nucleophile occurs.

3.13.3 Retention of Configuration

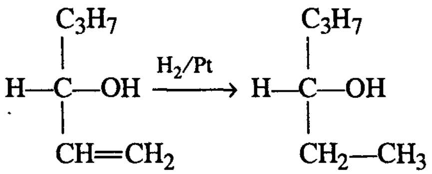
Inversion of configuration and racemisation are the most common stereochemical results of reactions that take place at a chiral carbon atom. A few reactions at chiral carbon atoms give products that have the same configuration as the starting material; this result is called retention of configuration. An example is the reaction of an alcohol with thionyl chloride. This reaction provides a method for converting alcohols to alkyl chlorides with retention of configuration.



Retention of configurtion

The product formation takes place *via* the formation of ion-pair. Ion-pair formation in SN1 reaction gives racemic mixture. Then the question arises why do not we get a racemised product as we do in the standard SN1 reaction? The difference lies in the source of the nucleophile. In the SN1 reaction the nucleophile is randomly distributed throughout the solution. In the thionyl chloride reaction the nucleophile is a part of the leaving group. The carbocation and the leaving group form a **closely associated ion-pair**, and the chloride ion immediately attacks the nearby face of the carbocation.

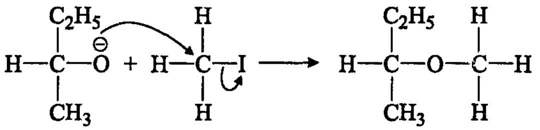
In most of the cases, the term "retention of configuration" refers to reactions that actually take place at the chiral carbon atom, yet give products with retention of configuration. When a reaction does not involve the chiral carbon atom, it is generally assumed that the stereochemistry of the chiral carbon is not affected.



$$\begin{array}{c} C_3H_7 \\ | \\ H{-}C{-}OH \\ | \\ CH{=}CH_2 \end{array} \xrightarrow{H_2/Pt} \begin{array}{c} C_3H_7 \\ | \\ H{-}C{-}OH \\ | \\ CH_2{-}CH_3 \end{array}$$

Retention of configuration

Even the SN2 reaction can take place with retention of configuration, provided that the chiral carbon atom is not the carbon being attacked by the nucleophile. For example, in the following SN2 reaction, the chiral carbon atom is a part of the nucleophile, and its four bonds are never broken. It is the iodomethane that is attacked and undergoes inversion of configuration. Since the iodomethane is not chiral, however, its inversion of configuration is unnoticed in the product.



3.14 GEOMETRICAL (*CIS-TRANS*) ISOMERISM

The isomerism which arises due to restricted (frozen) rotation about a bond in a molecule is known as **geometrical** or ***cis-trans*** **isomerism**. The rotation either about a double bond or about a single bond incorporated in a ring is restricted. Also, there may be restricted rotation about a single bond due to steric hindraince, *e.g.*, as in biphenyls. Compounds having restricted rotation about a bond exhibit geometrical isomerism if they are suitably substituted.

Geometrical (*cis-trans*) isomerism is exhibited by a variety of compounds which may be classified as follows :

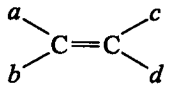
(i) Compounds containing a double bond; C=C, C=N, N=N.
(ii) Compounds containing cyclic structure; homocyclic, heterocyclic and fused-ring, ring systems.
(iii) Compounds having restricted rotation about a single bond due to steric hindrance; some biphenyls.

No stereoisomerism can result from triply bonded tetravalent or trivalent atoms because such systems display cylindrical symmetry.

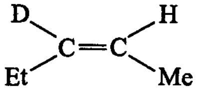
Conditions for geometrical isomerism : A compound will show geometrical isomerism if it fulfils the following two conditions :

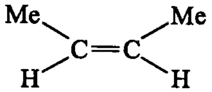
1. There should be restricted (frozen) rotation about a bond in the molecule.
2. Both substituents on each carbon about which rotation is frozen (restricted) should be different.

Examples :



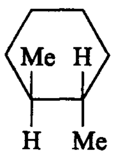
$a \neq b, c \neq d$

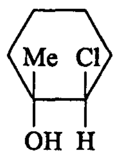


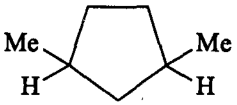


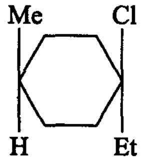
$a \neq b, c \neq d$

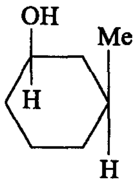
PhCH=CHCOOH
(Two isomers)
HOOCCH=CHCOOH
(Two isomers)

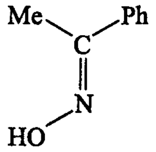


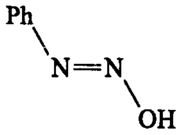


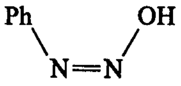












Geometrical isomers are not related as object and mirror image, hence they are diastereomers (according to the definition : stereoisomers which are not mirror images of each other are called diastereomers).

3.14.1 Geometrical Isomerism Due To $>C=C<$ Bond

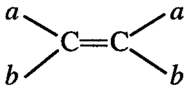
Double bonds consist of a σ- and a π-bond perpendicular to each other. If there is rotation about the double bond, the π-bond will break, thus there is no free rotation about a double bond, *i.e.*, the rotation about a double bond is frozen.

The energy barrier for rotation about $>C=C<$ bond in simple alkenes is about 62–65 kcal/mole. For example, the energy barrier of (*E*)-1, 2-dideuterioethylene was found to be 65 kcal/mole. Steric and electronic contributions of substituents greatly influence the magnitude of energy barrier. If the rotation barrier values are down to about 10 kcal/mole then these result in conformers but not geometrical isomers. Geometrical isomers are configurational isomers; they can be isolated in a pure form and they exist as individual stable of compounds. For their interconversion an energy of not less than 30 kcal/mole is usually required.

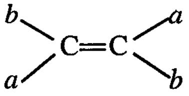
Compounds containing $>C=C<$ bond with frozen rotation exhibit geometrical isomerism if they are suitably substituted, *i.e.*, the ligands attached to the same double bonded carbon are different.

3.14.2 Nomenclature of Geometrical Isomers

I. *cis-trans* nomenclature : Compounds of the type *ab*C=C*ab* can exist in the following two forms due to frozen rotation about carbon-carbon double bond.



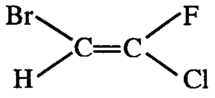
cis-form



trans-form

The isomer in which the identical groups are on the same side of the double bond is called *cis* and the isomer in which the identical groups are on the opposite sides is called *trans*.

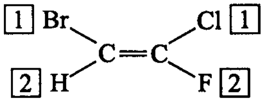
cis-trans nomenclature can be used only in those compounds in which only two or three types of ligands are attached to both the double bonded carbons. When all the four ligands are different, this nomenclature cannot be used, *e.g.*,



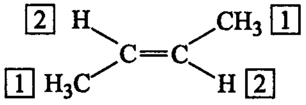
(*E*)

II. *E* – *Z* system of nomenclature : This nomenclature of geometrical isomers is more general and can be applied to all compounds. *E* – *Z* nomenclature is based on the Cahn-Ingold-Prelog system. In the *E* – *Z* system the group of highest priority on each carbon atom is identified by using the sequence rules (Section 3.8.3). If the highest priority groups are on the same side of the double bond, the configuration is *Z* (German : *zusammen* = together), and if they are on the opposite sides, the configuration is *E* (German : *entgegen* = opposite).

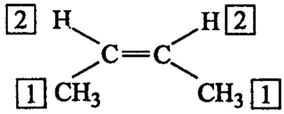
For example :



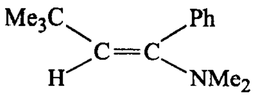
(*Z*)-isomer

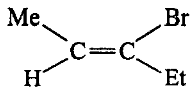


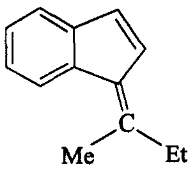
(*E*)-2-butene



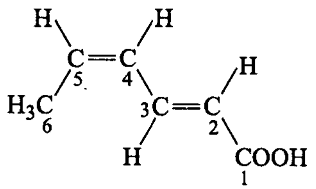
(*Z*)-2-butene

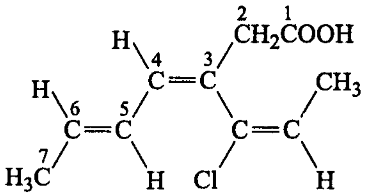

E


Z


E

If geometrical isomers contain two or more double bonds, the compound is considered as a derivative of the longest chain which contains the maximum number of double bonds and the prefixes *Z* and *E* are placed before the numbers indicating the positions of the double bonds in the main chain. For example :


(2*E*, 4*Z*)-2, 4-hexadienoic acid


3-[*E*-1-chloropropenyl]-
(3*Z*, 5*E*)-3, 5-heptenedioic acid

It should be noted that there is no relation between cis, trans and E, Z configurations, i.e., all the cis compounds may not be Z and all the trans may not be E.

3.14.3 Number of Geometrical Isomers in Polyenes

(a) When a compound has n double bonds and ends of a polyene are different, the number of geometrical isomers $= 2^n$. For example :
$\text{Ph CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}CHCl}$ has four double bonds and the ends are different, hence it will have $2^4 = 16$ geometrical isomers.

(b) When the ends of a polyene are identical :

(i) If the number of double bonds (n) is even then the number of geometrical isomers

$$= 2^{n-1} + 2^{n/2-1}$$

For example :

$$\text{ClCH{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}CHCl}$$

Ends identical; $n = 4$, even

$$\text{Number of geometrical isomers} \quad = 2^3 + 2^1 = 8 + 2 = 10$$

(ii) If the number of double bonds (n) is odd then the number of geometrical isomers $= 2^{n-1} + 2^{(n+1)/2-1}$.

For example :

$$\text{Ph CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}CHPh}$$

Ends indentical, $n = 3$, odd

$$\text{Number of geometrical isomers} = 2^2 + 2^{2-1} = 2^2 + 2^1 = 4 + 2 = 6$$

3.14.4 Determination of The Configuration of Geometrical Isomers

There is no general method for determining the configuration of geometrical isomers. There are a number of methods and one uses one or more of them depending on the nature of the compound in question.

1. Physical Methods

(i) The melting point and intensity of absorption of the *cis*-isomer are *lower* than those of the *trans*.

(ii) The boiling point, solubility, heat of combustion, heat of hydrogenation, density, refractive index, dipole moment and dissociation constant (if the compound is an acid) of the *cis*-isomer are *greater* than those of the *trans*.

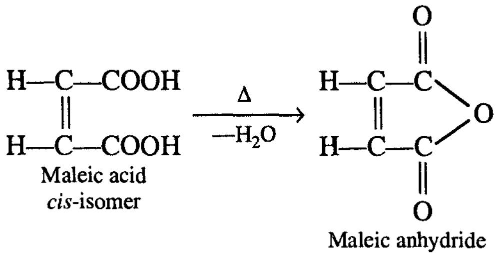
X-ray analysis and spectroscopy have also been used for determining the configuration of geometrical isomers.

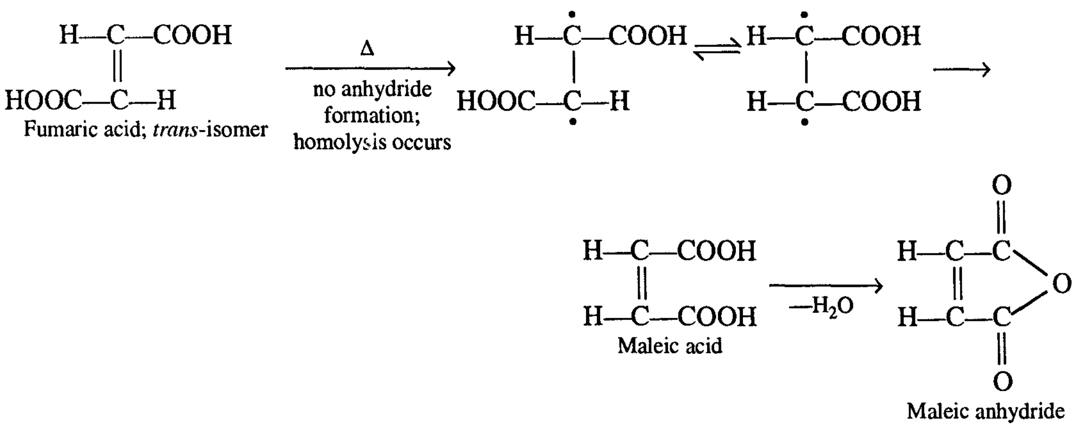
2. Method of Cyclisation

Intramolecular reactions are more likely to occur the closer together the reacting groups are in the molecule (Wislicenus). Thus, a *cis* isomer is expected to undergo cyclisation much more readily than the *trans*. For example :

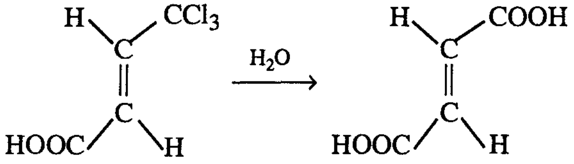
Maleic acid forms a cyclic anhydride when heated, whereas fumaric acid does not form fumaric anhydride. Thus, maleic acid is the *cis*-isomer and fumaric acid *trans*. However, on strong heating fumaric acid gives maleic anhydride because the hydrolysis of the anhydride obtained from fumaric acid gives only maleic acid.

Fumaric acid forms maleic anhydride *via* the formation of maleic acid, because high temperature ruptures π-bond and rotation of the carboxyl groups toward each other occurs followed by formation of the π-bond and loss of water.





3. Method of conversion into compound of known configuration : In a number of cases it is possible to determine the configuration of geometrical isomers by converting them into compounds of known configuration. For example, there are two trichlorocrotonic acids one of which can be hydrolysed to fumaric acid, hence it must be the *trans*-isomer, and the other is *cis*.

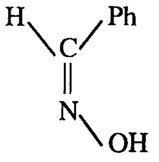


trans-isomer of trichlorocrotonic acid

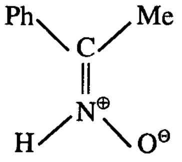
Fumaric acid

3.15 GEOMETRICAL ISOMERISM OF OXIMES

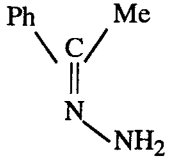
Nitrogen compounds containing >C=N— as well as —N=N— bond exhibit geometrical isomerism. The important classes of compounds exhibiting geometrical isomerism due to C=N— bond are : (i) oximes (ii) nitrones (iii) hydrazones and (iv) semicarbazones.



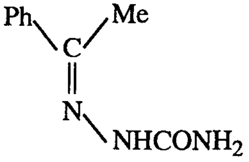
anti (*Z*)
(Benzaldoxime)



(*E*)
Nitrone

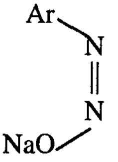


(*E*)
Hydrazone

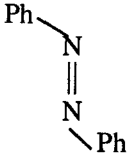


(*E*)
Semicarbazone

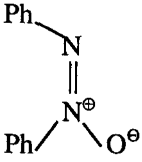
Examples of compounds exhibiting geometrical isomerism due to —N=N— bond are :



syn (*Z*)
Diazoate



anti (*E*)
Azobenzene

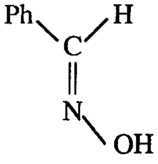


syn (*E*)
Azoxybenzene

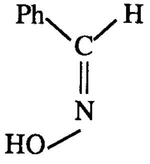
Oximes are the most common compounds and we will discuss their geometrical isomerism in detail.

Both the carbon and nitrogen atoms in oximes are sp^2 hybridised. The C=N bond in oximes consists of one σ and one π-bond. There is no free rotation about C=N, hence oximes of aldehydes and unsymmetrical ketones exhibit geometrical isomerism.

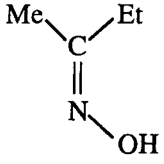
Nomenclature : The prefixes *syn* and *anti* are used instead of *cis* and *trans*. In the *syn* oxime the hydroxyl group on nitrogen, and hydrogen or the first-named of the two groups on the carbon are on the same side, while in the *anti*-isomer they are on the opposite sides. The *E* – *Z* system of nomenclature is also applied to oximes and it is more convenient. **If the group with greater priority and the hydroxyl group are on the same side of the double bond, the configuration is *Z*, if on the opposite sides it is *E*.** For example :



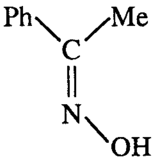
syn- or (*E*)-benzaldoxime



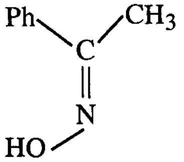
anti- or (*Z*)-benzaldoxime



syn- or (*Z*)-ethylmethylketoxime



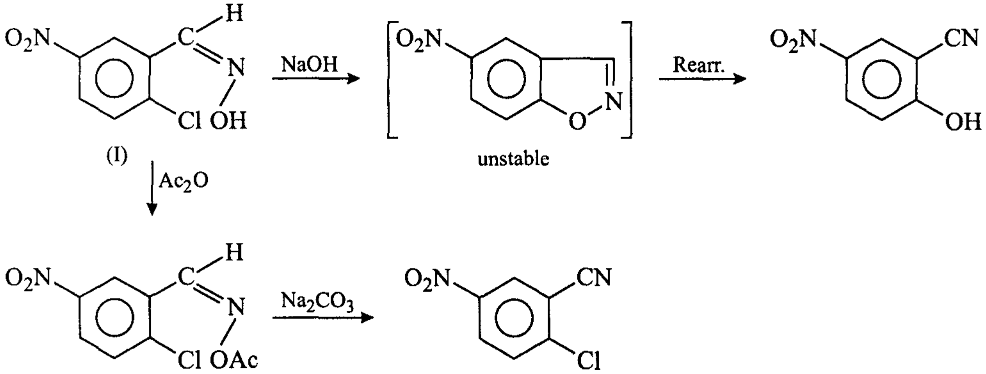
syn- or (*E*)-methylphenylketoxime



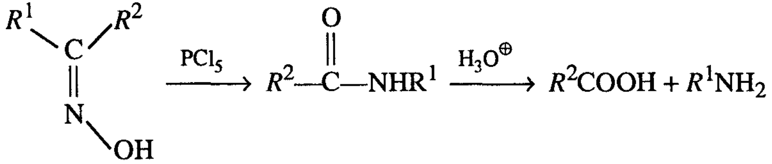
anti- or (*Z*)-methylphenylketoxime

Determination of the Configuraton of Oximes

The configurations of geometrical isomers of **aldoximes** are determined by their relative ease of dehydration. For example, the *anti*-aldoxime **I** (*anti*-2-chloro-5- nitrobenzaldoxime) readily undergoes cyclisaton, hence this form is *anti*-isomer. This isomer gives cyanide on treatment with acetic anhydride followed by aqueous sodium carbonate. Thus, *anti*-elimination must have occured. On the other hand, the *syn*-aldoxime does not give cyanide. Hence, using *anti*-elimination as the criterion for these reactions, the configurations of *syn*- and *anti*-forms can be determined.

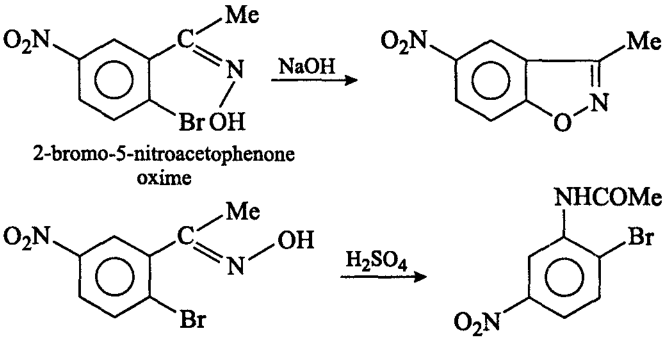


The configurations of **ketoximes** have been determined by *Beckmann rearrangement.* When treated with acidic reagents such as H_2SO_4, acid chlorides, acid anhydride, PCl_5, P_2O_5, etc. ketoximes undergo Beckmann rearrangement to give a substituted amide by migration of the group which is *anti* to the hydroxyl group. The structure of the amide obtained is determined by their hydrolysis to the corresponding carboxylic acid and amine which indicates the configuration of the parent oxime because the group R incorporated in the amine must be *anti* to the hydroxyl group in the oxime.



$$R^1R^2C{=}NOH \xrightarrow{PCl_5} R^2{-}\overset{O}{\overset{\|}{C}}{-}NHR^1 \xrightarrow{H_3O^{\oplus}} R^2COOH + R^1NH_2$$

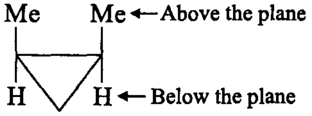
That the group *anti* to the hydroxyl group actually migrates was shown by the following reaction :



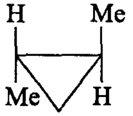
Out of the two isomeric ketoximes of 2-bromo-5-nitroacetophenone, one undergoes cyclisation with NaOH, hence it must be *syn*-methyl isomer. The other isomer is unaffected by NaOH, but on treatment with H_2SO_4 it undergoes Beckmann rearrangement to give *N*-substituted acetamide; thus group *anti* to the hydroxyl group migrates.

3.16 GEOMETRICAL ISOMERISM OF ALICYCLIC COMPOUNDS

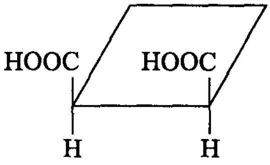
We have noted that geometrical isomerism is due to frozen rotation about a bond. Since there is no rotation about the ring-carbons, suitably substituted cycloalkanes, *e.g.*, cyclopropane, cyclobutane, cyclopentane, cyclohexane, etc. also exhibit *cis-trans* isomerism. Thus, in disubstituted cycloalkanes where the two substituents are located on different carbons two geometrical isomers are possible in each case. The isomer in which the two substituents are located on the same face or side of the ring is called the ***cis*-isomer**, and in which the two substituents are on the opposite sides is called the *trans*-isomer. For example :



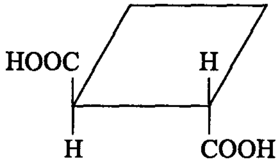
cis-1, 2-dimethyl-cyclopropane



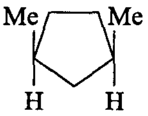
trans-1, 2-dimethyl-cyclopropane



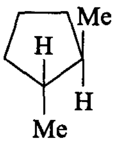
cis-cyclobutane-1, 2-dicarboxylic acid



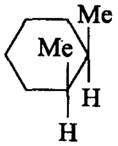
trans-cyclobutane-1, 2-dicarboxylic acid



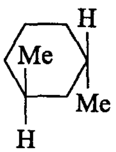
cis-1, 3-dimethyl-cyclopentane



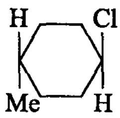
trans-1, 2-dimethyl-cyclopentane



cis-1, 2-dimethyl-cyclohexane



trans-1, 3-dimethyl-cyclohexane



trans-1-chloro-4-methyl-cyclohexane

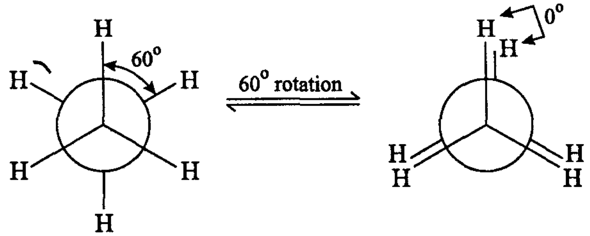
3.17 CONFORMATIONAL ANALYSIS

The different spatial arrangements of atoms in a molecule which are readily interconvertible by rotation about single bonds are called ***conformations;*** if not, *configurations.* Conformations represent *conformers* which are readily interconvertible and thus nonseparable. The terms **conformational isomers** and **rotamers** are also used for **conformers**. Sometimes different conformations corresponding to energy minima are called **conformers**. The terms conformation and configuration are related to energy barrier for interconversions of different spatial arrangements of atoms in a molecule. If the energy barrier for conversion of different spatial arrangements is between > 0.6 and < 16 kcal/mole they are conformations (*i.e.*, conformers), and if it is $\geq$ 16 kcals/mole, they are configurations (*i.e.*, stereoisomers). If the energy barrier is 0.6 kcal/mole or less at room temperature, the rotation would be free because this amount of energy can be readily provided by the thermal energy of the molecule.

The study of the existence of preferred conformations in molecules, and the relating of physical and chemical properties of a molecule to its preferred conformation is known as conformational analysis.

3.17.1 Conformations of Acyclic Systems

Conformations of ethane : When an ethane molecule rotates about its carbon-carbon single bond, two extreme conformations can result : the **staggered conformation** and the **eclipsed conformation**. An infinite number of conformations between these two extreme conformations is also possible. These are called skew conformations. There are various ways to represent the three-dimensional conformations on the paper, as discussed in Section 3.6. Here we will use **Newman projections** Section 3.6.4 to discuss the conformations of acyclic compounds. The Newman projections for staggered and eclipsed conformations are given below :



Staggered conformation Eclipsed conformation

Newman projections of ethane

Staggered conformation : A conformation with a 60° dihedral (torsional) angle is known as staggered conformation. The angle between the atoms attached to the front and the rear carbon atoms is called the torsional angle.

Eclipsed conformation : A conformation with a 0° torsional angle is known as eclipsed conformation.

The electrons in a carbon-hydrogen bond will repel the electrons in another carbon-hydrogen bond if the bonds get too close to each other. This is called torsional or bond opposition strain. Therefore, the staggered conformation is the most stable conformation because the carbon-hydrogen bonds are as far away from each other as possible, *i.e.*, it has least torsional strain. The eclipsed conformation is the least stable conformation because the carbon-hydrogen bonds are closest. In staggered conformation the distance between the hydrogen nuclei is 2.55 Å, but they are only 2.29 Å apart in the eclipsed conformation. The rotational energy barrier in ethane is 2.9 kcal/mole. This rotational barrier can be described in terms of the change in potential energy of the molecule as a function of the change in torsional angle as shown in Fig. 3.2.

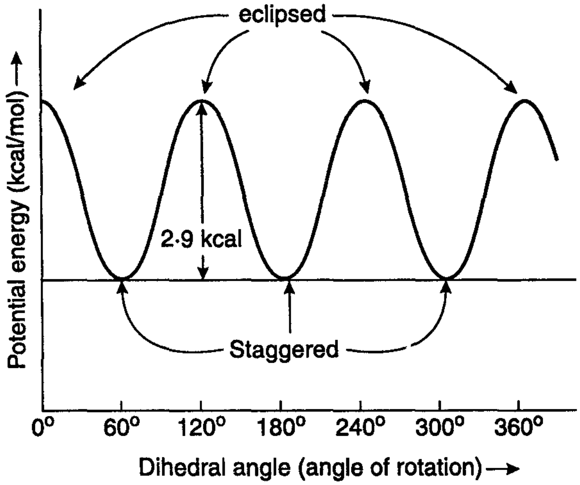
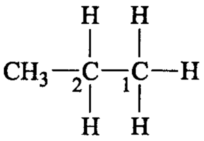


Fig. 3.2.

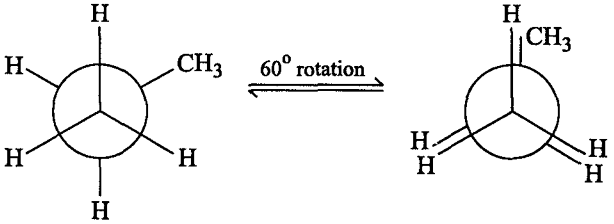
The extra energy of the eclipsed conformation is called **torsional strain.** Torsional strain is the name given to the repulsion felt by bonding electrons of one substituent as they pass close the bonding electrons of another substituent. The energy barrier between staggered and eclipsed conformation in ethane molecule is 2.9 kcal/mole. This barrier is more than *RT* (≈ 0.6 kcal/mole) at room temperature (energy for free rotation) and less than 16–20 kcal/mole (energy barrier for complete restricted rotation, *i.e.*, frozen rotation). Thus, the rotation about the carbon-carbon single bond is neither completely free nor frozen (completely restricted) but only restricted by 2.9 kcal/mole.

Conformations of Propane

Similar to ethane, propane also has the following two extreme conformations :



$$CH_3-\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{_2C}}-\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{_1C}}-H$$

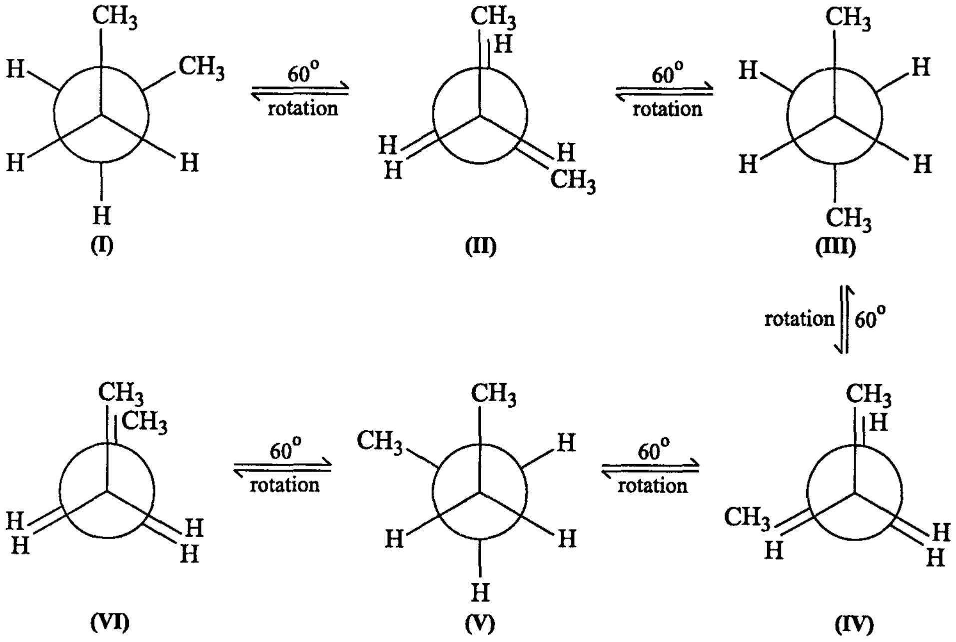


Staggered **Eclipsed**

Conformations of *n*-butane : Butane has three carbon-carbon single bonds and the molecule can rotate about each of them. If the rotation will be about C_2 and C_3 bond

$$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{CH_3}$$

then conformations will be symmetrical. For conformational analysis butane may be treated as the derivative of ethane where one hydrogen on each carbon is replaced by a methyl group. Different



conformations of butane can be obtained by rotation about its middle carbon-carbon bond (*i.e.*, between C_2 and C_3 bond) as shown below :

Butane has three staggered conformers (I, III and V). Conformer III, in which the two methyl groups are as far apart as possible is more stable than the other two staggered conformers I and V. The most stable of the staggered conformers (III) is called the ***anti conformer*** and the other two staggered conformers (I and V) are called ***gauche conformers*** (*anti* is Greek for "opposite of", gauche is French for "left.")

In the *anti* conformer the largest substituents are opposite to each other; in the gauche conformer, they are adjacent. The two gauche conformers have the same energy but each is 0.9 kcal/mole less stable than the *anti* conformer.

Anti and gauche conformers do not have the same energy because of the **steric strain. Steric strain or steric hindrance** is the strain put on a molecule when its atoms or groups are large in size and due to this they are too close to each other, which causes repulsion between the electrons of atoms or groups. There is more steric strain in the gauche conformer than in the *anti* because the two methyl groups are closer together in the gauche conformer. Steric strain in gauche conformer is called **gauche interaction.**

The eclipsed conformer in which the two methyl groups are closest to each other (VI) is less stable than the other eclipsed conformers (II and IV). All these eclipsed conformers have both torsional and steric strain. Torsional strain is due to bond-bond repulsion and steric strain is due to the closeness of the eclipsing groups. In general, steric strain in the molecule is directly proportional to the size of the eclipsing groups. Eclipsed conformer VI is called the fully eclipsed conformer, while II and IV are called eclipsed conformers. The energy diagram for rotation about the $C_2—C_3$ bond of butane is shown in Fig. 3.3.

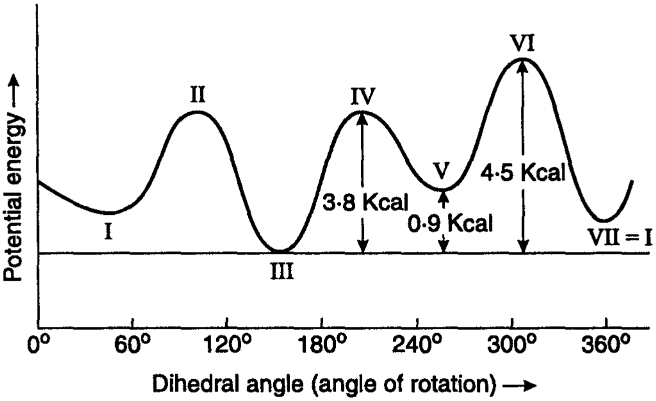


Fig. 3.3.

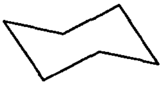
Thus, the relative stabilities of the six conformers of *n*-butane in decreasing order is as follows :

$$\underset{\text{III}}{\textit{Anti}} > \underset{\text{I and V}}{\text{gauche}} > \underset{\text{II and IV}}{\text{eclipsed}} > \underset{\text{VI}}{\text{fully eclipsed}}$$

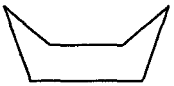
Molecules with carbon-carbon single bonds have many interconvertible conformers. Conformers cannot be separated because they rapidly interconvert.

3.17.2 Conformation of Cyclohexane

Sachse (1890) and Mohr (1931) assumed three dimentional structure of alicyclic compounds. They pointed out that two forms are possible for cyclohexane if it has puckered conformation. These two forms are the chair and boat conformations of cyclohexane which are free from angle strain. Both forms are interconvertible into each other.



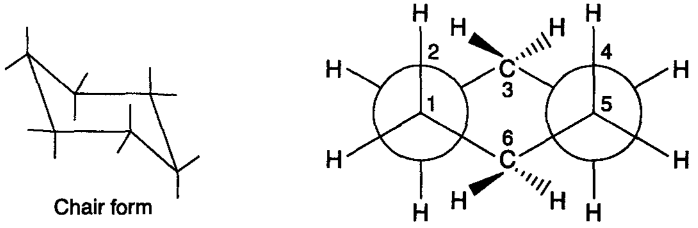
Chair conformation
(1)



Boat conformation
(2)

The chair form is rigid (in the sense that it resists distortion) and when it is transformed into the boat form some angular deformation is necessary. The energy barrier in this process is about 9–11 kcal/mole. This value is large enough for each conformation to retain its identity, but is not large enough to prevent their rapid interconversion at room temperature. Thus it is not possible to isolate each conformation. In 1947 Hassel established by means of electron diffraction studies that cyclohexane exists predominantly in the chair conformation.

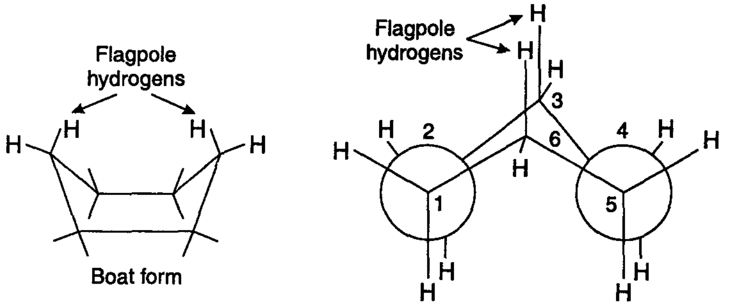
The chair and boat forms are free from angle strain, (The angle between the carbon-carbon bonds are all 111° which is very close to tetrahedral angle 109·5°) but because of differences in the steric strain and bond opposition strain, the two forms differ in energy content. Fig. 3.4(a) and 3.4(b) represent the chair and boat conformations and the direction of the C—H bonds.



Chair form

Newman projection

Fig. 3.4 (a)



Boat form

Newman projection

Fig. 3.4 (b)

In the chair form Fig. 3.4(a) all the C—H bonds on adjacent carbons are in the skew position (The arrangement is skew as in the gauche form of *n*-butane). On the other hand, in the boat conformation there are four skew interactions (2, 3; 3, 4; 5, 6 and 6, 1) and two eclipsed interactions (1, 2 and 4, 5) Fig. 3.4(b).

Based on these conditions, one can calculate the difference between internal energies (E) of the boat and chair forms in the following manner :

$E_{\text{boat}} - E_{\text{chair}} =$ Energy of two eclipsed butane type structures + energy of four skew butane type structures in boat form − Energy of six skew butane type structures in chair form.

= Energy of two eclipsed butane type structures − energy of two skew butane type structures

$= 5 \times 2 - 2 \times 0.80 = 10 - 1.60 = 8.40$ kcal/mole

Here 5 kcal/mole is the approximate value of the energy of interaction between two eclipsed carbon atoms and 0.80 kcal/mole is the energy of interaction between two skew carbon atoms.

Apart from the factor mentioned above there is one more factor which makes the boat conformation less stable. It is the repulsion between hydrogen atoms which are at the top of the boat. These

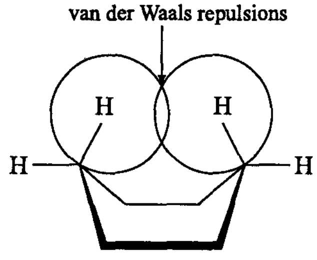


Fig. 3.4(c)

hydrogens are known as flagpole hydrogens. The distance between their centres is only 1.83 Å while the sum of the van der Waals radii of the two hydrogen atoms is 2.5 Å. This repulsion is called ***bow-sprint repulsion*** van der Waals or and contributes to increase the energy of the boat form [Fig. 3.4 (c)].

Thus the total strain in the boat conformation is larger than that in the chair conformation and consequently the former is less stable than the latter. The boat form is however flexible and can readily be distorted into many shapes (Fig. 3.5).

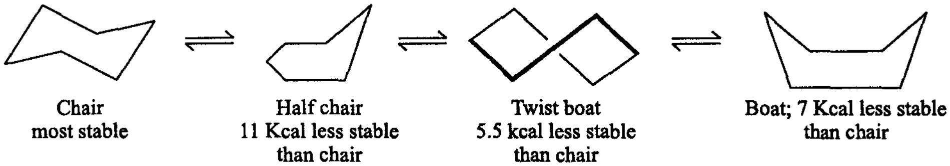


Fig. 3.5. Interconversion of chair and boat forms.

The twist boat conformation contains 1.5 kcal/mole less energy than the classical boat form. Due to this reason when someone refers to the "boat conformation", the twist boat is often intended. At

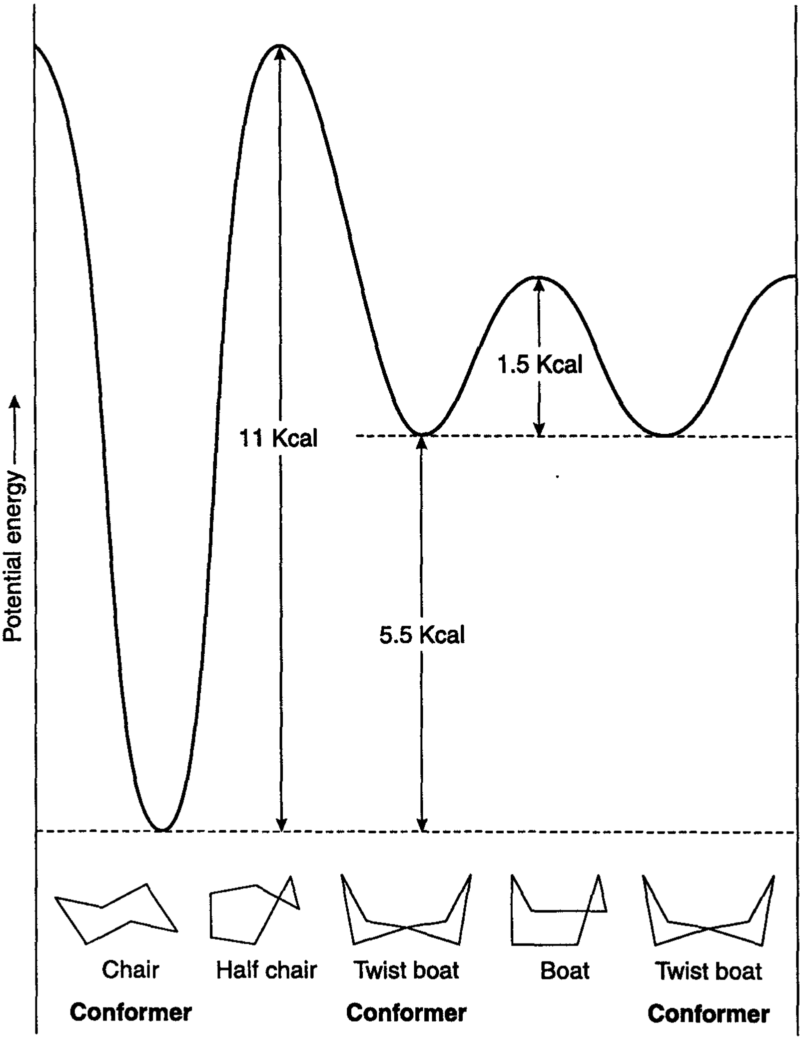
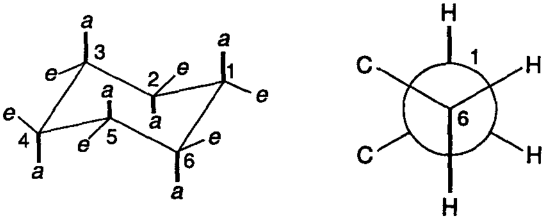


Fig. 3.6. Potential energy relationships among conformations of cyclohexane.

room temperature most of cyclohexane molecules (99.9%) exist in the most stable chair conformation. The twist boat form occurs as an intermediate stage in the conversion of one chair form to another (Fig. 3.6). There is one molecule in the flexible boat form per thousand molecules in the chair conformation. Thus, we shall confine our attention to the chair conformation, which is preferred conformation in most of the cases. Fig. 3.6 shows how the energy of cyclohexane varies as it interconverts between boat and chair forms.

3.17.3 Axial and Equatorial Bonds

The carbon atoms of the chair form of cyclohexane roughly form a plane. Notice first that opposite sides of the chair are parallel. That is if we numbered the carbons around the ring 1 through 6, the C_1-C_2 bond is parallel to the C_4-C_5 bond; the C_2-C_3 bond is parallel to the C_5-C_6 bond; and C_3-C_4 bond is parallel to the C_6-C_1 bond. Let us now look carefully at the hydrogens on the cyclohexane ring. If we place the chair form of the cyclohexane model on a table top, we find that six C—H bonds are perpendicular to the plane of the table. These hydrogens, shown in bold lines in Fig. 3.7(a), are called **axial** (*a*) **hydrogens**. The remaining six C—H bonds point **outward** from the ring along its periphery. These hydrogens show in thin line, are called **equatorial** (*e*) hydrogens. Notice that each bond to an equatorial hydrogen is parallel to two carbon-carbon bonds of the ring. For example, the C_1—H equatorial bond is parallel to the C_2-C_3 and C_5-C_6 bonds.



(a) (b)

Fig. 3.7. (a) Chair conformation of cyclohexane. The axial hydrogens are shown in bold line and the equotrial hydrogen in thin.

(b) Newmann projection from C_6 to C_1. Notice that all bonds are staggered.

Notice that three of the axial hydrogens are up (C-1, C-3, C-5 axial hydrogens); the other three are down (C-2, C-4, C-6 axial hydrogens) Likewise, three of the equatorial hydrogens are down (C_1, C_3, C_5 equatorial hydrogens) and three are up (C_2, C_4 and C_6 equatorial hydrogens) as shown in Fig. 3.8. All the six axial hydrogens are completely equivalent. Similarly, all the six equatorial hydrogens are also completely equivalent.

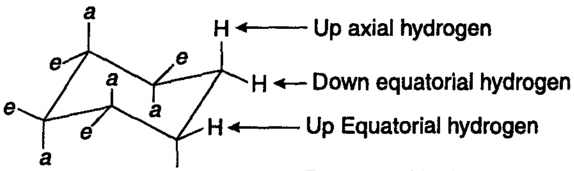


Fig. 3.8.

The rigid cyclohexane ring can change its conformation by flipping to another chair conformation as shown in Fig. 3.9. In this transformation the axial bonds of one chair conformation become equatorial and the equatorial bonds become axial in the other conformation. The standard free energy of activation for flipping is the energy difference between the chair and half chair forms (*i.e.*, 11 kcal/mole). Although this barrier is larger than that for internal rotation in butane, the

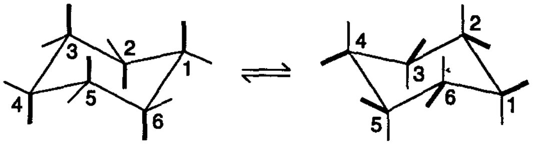


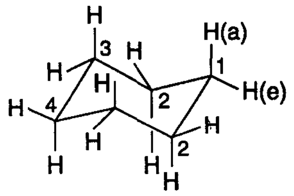
Fig. 3.9. Flipping of one chair form to another.

chair-chair interconversion is neverthless very rapid at room temperature. The axial and equatorial hydrogens are different and distinguishable in any one chair form, but the high rate of the chair-chair interconversion causes the axial and equatorial hydrogens overtime to average out to be equivalent and indistinguishable. Hence only one cyclohexane is known.

It is also important to note that 1, 2-axial bonds are always *trans* to each other; 1, 2-equatorial bonds are also *trans* to each other. Similarly, 1, 3-axial bonds are always *cis* to each other and 1, 3-equatorial bonds are also *cis* to each other (Fig. 3.10).

Note : (i) 1, 2- or 1, 4-diaxial and 1, 2- or 1, 4-diequatorial bonds of cyclohexane are always *trans* to each other.

(ii) Similarly, 1, 3,- or 1, 5-diaxial and 1, 3- or 1, 5-diequatorial bonds of cyclohexane are always *cis* to each other.



1*a*, 2*a* — *trans* to each other
1*e*, 2*e* — *trans* to each other
1*a*, 3*a* — *cis* to each other
1*e*, 3*e* — *cis* to each other
1*a*, 4*a* — *trans* to each other
1*e*, 4*e* — *trans* to each other
1*a*, 2*e* — *cis* to each other
1*a*, 3*e* — *trans* to each other
1*a*, 4*e* — *cis* to each other

Fig. 3.10. Various *cis* and *trans* bonds in cyclohexane.

3.17.4 Conformations of Monosubstituted Cyclohexanes

Unlike cyclohexane, which has two identical chair conformers, the two chair conformers of a monosubstituted cyclohexane such as methylcyclohexane are not identical. Because the methyl substituent in an equatorial position is one conformer and in an axial in the other conformer (Fig. 3.11), the two chair conformers do not have the same stability.

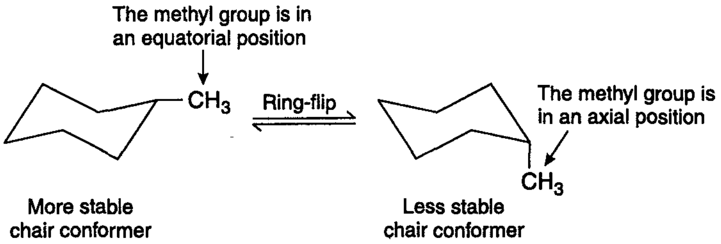
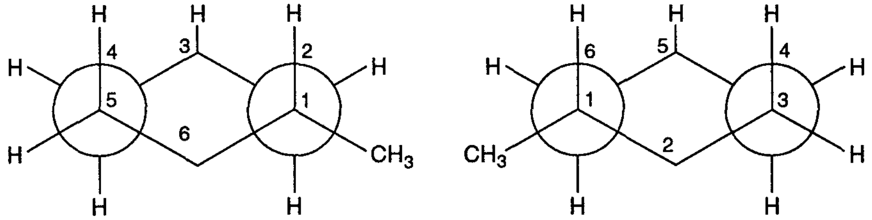


Fig. 3.11. A substituent in the equatorial positionin one chair conformation and in the axial position in the other chair conformation. The conformation with the substitutent in the equatorial position is more stable.

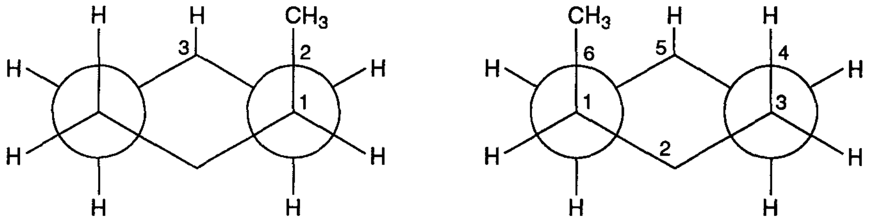
The chair conformer with the substituent in the equatorial position is more stable than the chair conformer with the substituent in the axial position. The reason is the same as the reason that an *anti* conformer is more stable than a gauche conformer because the gauche interaction causes steric strain. Gauche interactions also make a cyclohexane with a substituent in the axial position less stable than a cyclohexane with a substituent in the equatorial position. When the methyl group is in the equatorial position, it is *anti* to the C-3 and C-5 carbons, and it extends into space away from the rest of the molecule (Fig. 3.12).



Methyl is *anti* to C-3 Methyl is *anti* to C-5

Fig. 3.12. An equatorial substitutent on the C-1 carbon is *anti* to C-3 and C-5 carbons.

When the methyl group is in the axial position, it is gauche to both the C-3 and C-5 carbons (Fig. 3.13). Recall that the gauche conformation of *n*-butane has 0.9 kcal/mole more energy than the *anti* conformation. In methyl cyclohexane there are two such interaction in axial methylcyclohexane between the CH_3 group and the C_2-C_3 bond and C_5-C_6 bond. This makes axial methylcyclohexane to be less stable than equatorial methylcyclohexane by $2 \times 0.9 = 1.80$ kcal/mole. In fact this value is quite close to the experimental value of 1.7 kcal/mole.



Methyl is *gauche* to C-3 Methyl is *gauche* to C-5

Fig. 3.13. An axial substitutent on the C-1 carbo is gauche to C-3 and C-5 carbons.

There is one more factor which makes axial methyl cyclohexane less stable. This is called 1, 3-diaxial interaction. When the methyl group (or any other larger group at C-1) is in axial position it faces repulsion from the other two axial hydrogens (or other substituents) on C-3 and C-5 due to steric problem. The repulsion results from the distance between them because the distance between them is less than the van der Waals radii of the two hydrogen atoms. (Fig. 3.14). 1, 3-diaxial repulsion increases strain of the conformer. The strain due to the 1, 3-Diaxial repulsion is known as transannular strain.

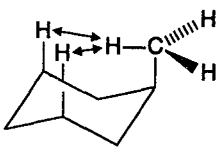


Fig. 3.14. 1, 3-diaxial interactions.

Thus conformer with equatorial methyl dominates because it has less energy. An axial substituent has a less favourable spacial orientation than its equatorial mate because it is more crowded—a fact attributed to either

(i) 1, 3-interaction and

(ii) Gauche interaction.

When methyl group is in equatorial position, it is far apart from other hydrogens and there are practically no steric repulsions.

Thus the axial conformations of substituted cyclohexanes are generally less stable than the corresponding equatorial conformations.

As the size of the substituent increases, 1, 3-diaxial repulsive interaction will also increase. Indeed the repulsion between an axial tertiary-butyl group and the axial hydrogen is so severe that the *tert*-butyl group is never axial (Fig. 3.15). *Tert*-butyl cyclohexane is said to be "Frozen" in the conformation in which the *tert*-butyl group occupies equatorial position.

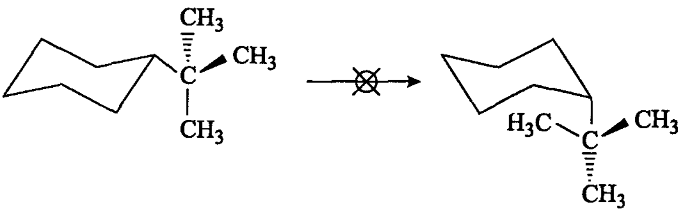
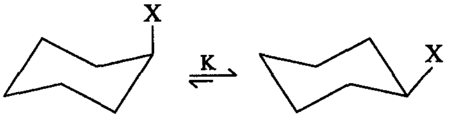


Fig. 3.15.

In conformational analysis relative energies can be calculated either by the use of 1, 3-interaction or by the use of gauche interaction but not by the both. Each CH_3/H 1, 3-interaction imparts 3.75

kJ/mole (0.9 kcal/mole) of instability to a compound. Similarly, each CH_3/CH_3 1, 3-interaction imparts 15 kJ/mole (≈ 4 kcal/mole) of instability of a compound.

Table 3.2 shows the preference of a number of monosubstituted cyclohexanes for the equatorially substituted conformer over the axially substituted conformer.



$$K = \frac{\text{concentration of equatorial conformer}}{\text{concentration of axial conformer}}$$

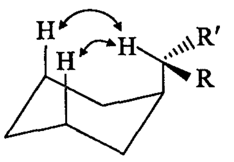
Table 3.2 ***Preferences for the equatorially substituted conformers over axially substituted conformers***

X	Equilibrium constant, *K*	Energy difference between axial and equatorial conformers, kJ/mole	% of equatorially substituted conformer
H	1	0	50
Me	19	7.3	95
Et	20	7.5	95
i-Pr	42	9.3	98
t-Bu	>3000	>20	>99.9
OMe	2.7	2.5	73
Ph	110	11.7	99

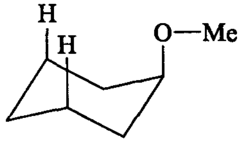
The three colums in Table 3.2 are three different ways of expressing the same information. However, just looking at the % column, it is not clear to see how much more of the equatorial conformer there is, because the % of equatorial conformer for methyl, ethyl, isoprophy, *t*-butyl, and phenyl-cyclohexanes are all 95% or more. Looking at the equilibrium constants gives a clearer picture.

The amount of equatorial conformer does increase in the order Me < Et < *i*-Pr < *t*-Bu, but the increase in the proportion of the equatorial conformer on going from Me to *i*-Pr is up to only 42 as compared to about 3000 for the *t*-butyl equatorial conformer. Similarly, there is much greater proportion of the conformer with an axial methoxy group than with an axial methyl group although the methoxy group is larger in size than a methyl group.

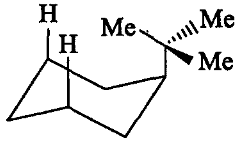
The equilibrium constant does not depend on the actual size of the substituent, but it depends on the interaction of the substituent with the neighbouring axial hydrogens. In the case of the methoxy group, the oxygen acts as link and removes the methyl group away from the ring, lessening the interaction. The groups Me, Et, *i*-Pr, and *t*-Bu a methyl group must be pointing straight at the axial



When a methyl (R=R'=H), ethyl (R=H, R'=CH_3) or *i*-propyl (R=R'=CH_3) is axial, only a hydrogen atom need lie directly over the ring



In methoxycyclohexane, the methyl group is removed away from the ring



On putting a *t*-butyl group axial, there is a severe steric interaction between a methyl group and the axial hydrogens

hydrogens, so *t*-Bu has a much larger preference for the equatorial position than the other alkyl groups. Actually, the interactions between an axial *t*-butyl group and the axial hydrogen atoms are so severe that the *t*-Bu group virtually always stays in the equatorial position.

3.18 DIFFERENCE BETWEEN CONFORMATION AND CONFIGURATION

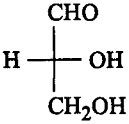
Conformation	Configuration
(i) Conformations of a molecule are the different spatial arrangements of its atoms and groups that arise due to the rotation of a part of the molecule about a single bond.	(i) Configuration of a molecule is the spatial arrangement of atoms and groups about a rigid part of the molecule, *i.e.*, about a double bond or ring and about a dissymmetric part of the molecule.
(ii) Conformations have low energy barrier, which varies from 4.2 to 46 kJ per mole.	(ii) Difference of energy between two configurations is more than 84 kJ/mole.
(iii) Conformers are non-isolable.	(iii) configurations are isolable.
(iv) Conformations are easily interconvertible, they get converted even at room temperature.	(iv) Configurations are not easily interconvertible.
(v) Interconversions of conformations involve rotation of a part of a molecule about a single bond.	(v) Interconversions of configurations involve bond breaking and bond reforming processes.
(vi) A molecule could have an infinite number of conformations.	(vi) A molecule can have only one configuration, *i.e.*, a different configuration is a different molecule.

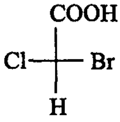
VERY SHORT ANSWER QUESTIONS

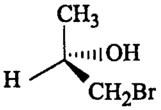
1. What is essential criterion for exhibiting enantiomerism?
2. What is a chiral molecule?
3. Which of the following are true of false statements?
   (a) Any compound cntaining an asymmetric carbon will be optically active.
   (b) Any compound containing a chiral carbon will be optically active.
   (c) All chiral centres are stereocentres.
   (d) All stereocentres are chiral centres.
   (e) A molecule can have only one configuration.
4. Write the structure of the *mose*-form of 2,3-dibromobutance.
5. Give an example of a reaction which proceeds with retention of configuration.
6. Give an example of reaction which proceeds with inversion of configuration.
7. Which of the following statements are true or false?
   (a) All the molecues with D configuration are dextrorotatory.
   (b) There is no relation between D, L and *R*, *S* configuration.
   (c) All the *cis* configurations are Z configurations.
   (d) Maleic and fumaric acids are diastereomers.
   (e) A molecule can have an infinite number of conformations.
8. Give the *R* configuration (Fischer projection) of the lowest molecular weight chiral alcohol.
9. A carboxylic acid having the molecular formula $C_3H_5O_2$ is optically active. Draw its *R* and *S* configuration in Fischer projection.

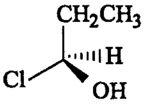
10. A primary alcohol having the molecular formula $C_5H_{12}O$ is optically active. Draw the flying-wedge formula of its *R* configuration.

11. Assign *R* or *S* configuration to each of the following compounds :

(a) 

(b) 

(c) 

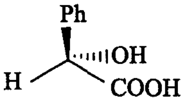
(d) 

12. Draw the Fischer projections of *R* and *S* configurations of an optically active diol with molecular fomula $C_3H_8O_2$.

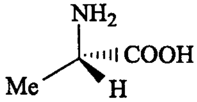
13. Draw the flying-wedge formula of *R* and *S* configurationsof a chiral acid with molecular formula $C_5H_{10}O_2$.

14. Draw the Fisher projection of (*R*)-2-iodobutane and convert it into the flying-wedge formula.

15. Covert the following flying-wedge formulae into the corresponding Fisher projection and assign *R* or *S* configuration.



(I)



(II)

PROBLEMS WITH SOLUTIONS

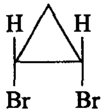
1. Draw configurations for all optical and geometrical isomers for each of the following and indicate which is which :

(i) CH_3—CHOH—CHOH—CH_3

(ii) CH_3—CHCl—CHOH—CH_3

(iii) CH_3—CH=CH—CHCl—CH_3

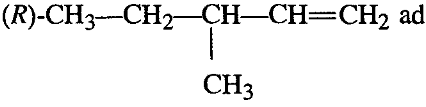
(iv) CH_3—CH=CH—CH_2—CH=CH—CH_3

(v) 

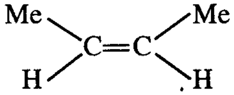
2. (*R*)-1-chloro-1-phenylethane racemises in the presence of $SbCl_5$; what type of reaction intermediate do you expect?

3. What is a stereocentre? Is it related to a chiral centre?

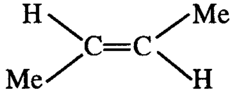
4. Draw Fisher structures for (*R*)- and (*S*)-2-butanol.

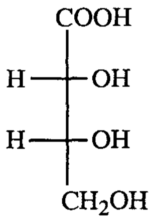
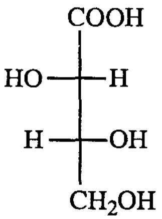
5.  $(R)\text{-}CH_3\text{—}CH_2\text{—}\underset{\underset{CH_3}{|}}{CH}\text{—}CH\text{=}CH_2$ adds D_2 in the presence of a catalyst. Draw the structure of the reactant and all the products. Give *R*/*S* designations.

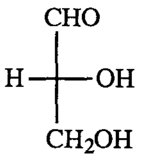
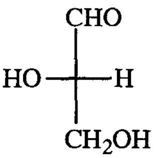
6. Which among the following pairs are diastereomers :

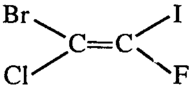
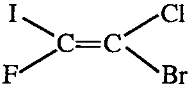
(1) 

and



(2)  and 

(3)  and 

(4)  and 

Select the correct answer from the codes given below :

(a) only 2 (b) only 1 (c) 1 and 2 (d) 1, 2 and 4

7. The number of configurational isomers of 2, 3-dibromocinnamic acid is :

(a) 4 (b) 3 (c) 2 (d) 1

8. The number of configurational isomers of the compound $HOCH_2\,(CHOH)_3\,CH_2OH$ is :

(a) 8 (b) 2 (c) 6 (d) 4

9. The number of geometrical isomers of the compound

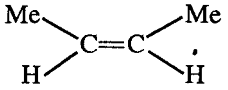
$$Ph—CH{=}CH—CH{=}CH—COOH \text{ is :}$$

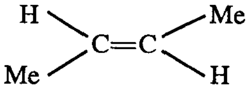
(a) 1 (b) 2 (c) 6 (d) 4

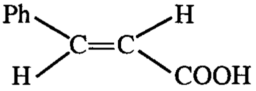
10. The number of optically active isomers of $HOCH_2(CHOH)_4CHO$ is :

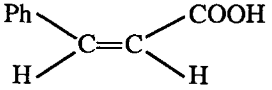
(a) 4 (b) 8 (c) 16 (d) 24

11. Which one of the following will give *meso* form with Br_2 :

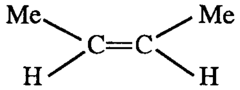
(a) 

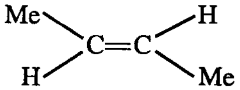
(b) 

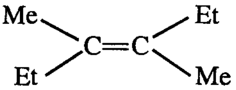
(c) 

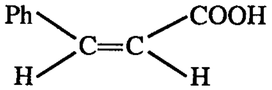
(d) 

12. Which one of the following will give *meso* form with Baeyer's reagent :

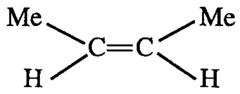
(a) 

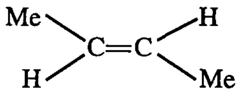
(b) 

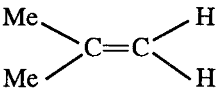
(c) 

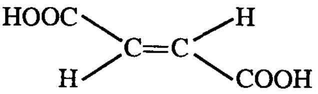
(d) 

13. Which of the following will form (±)-mixture with Br_2 :

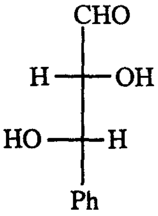
(a) 

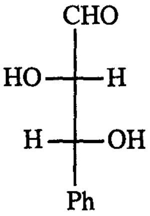
(b) 

(c) 

(d) 

14. Consider the following pair of compounds :


(I)


(II)

Using the given codes, indicate which of the following statements is correct :

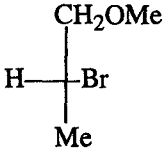
(1) Both are enantiomers (2) Both are *threo* form

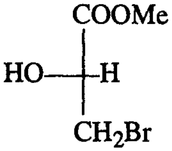
(3) Both are diastereomers (4) Both are D, L pair

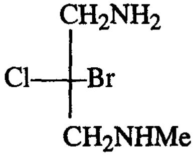
Codes :

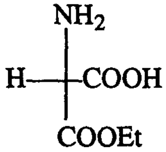
(a) 1 and 2 (b) 1, 2 and 4 (c) 2 and 3 (d) 3 and 4

15. Designate structures I–IV as *R* or *S* :


(I)

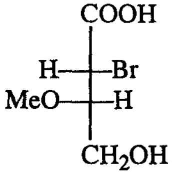

(II)

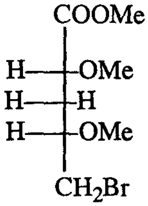

(III)

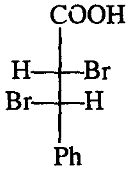

(IV)

16. Draw the configurations and specify the *R* and *S* enantiomers of 2-chloropentane.

17. Which prefix, *threo* or *erythro* is correctly applied to the following structures :

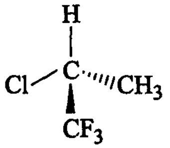

(I)

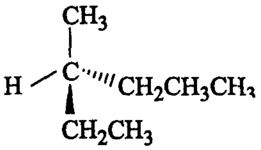

(II)

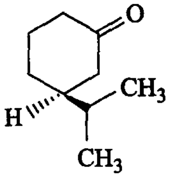

(III)

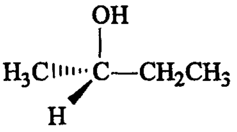
18. Arrange the isomeric butyl groups in decreasing order of priority.

19. Assign *R* or *S* configuration to the following compounds :

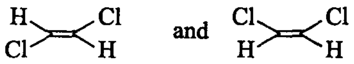
(a) 

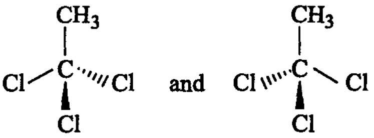
(b) 

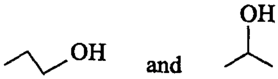
(c) 

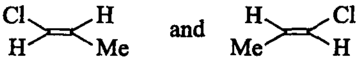
(d) 

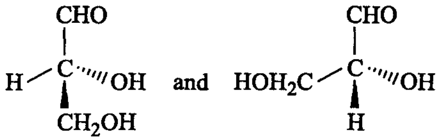
20. Label the following pairs of compounds as homomers, constitutional isomers, enantiomers or diastereomers :

(a) 

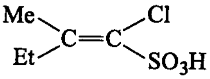
(b) 

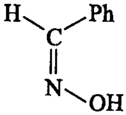
(c) 

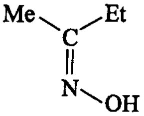
(d) 

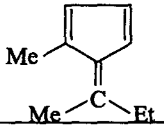
(e) 

21. Assign *E* or *Z* configuration to the following :

(a) 

(b) 

(c) 

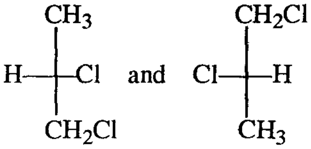
(d) 

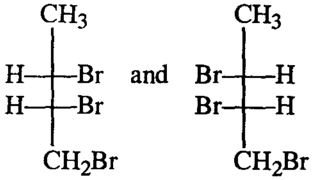
PROBLEMS FOR SELF ASSESSMENT

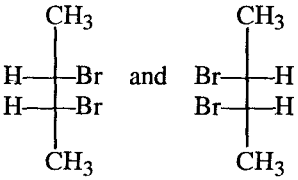
1. Define each of the following terms, or indicate what is meant by them :
   (a) optical activity
   (b) specific rotation
   (c) Fisher projection formula
   (d) Stereocentre
   (e) Asymmetric or chiral molecule
   (f) Enantiomers
   (g) Diastereomers
   (h) *Meso* form

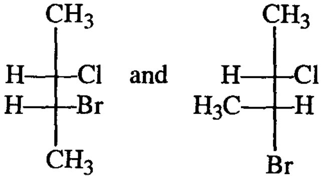
2. Compare the physical and chemical properties of :
   (i) Enantiomers and
   (ii) Diastereomers

3. Consider the following five pairs of stereoisomers. For each pair, state whether they are identical structures, enantiomers or diastereomers. Which structures are optically active? Which are *meso* compounds?

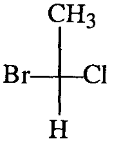
(a) 

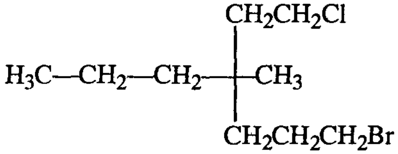
(b) 

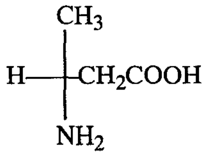
(c) 

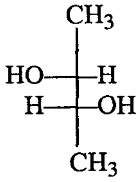
(d) 

4. Using the designations *R/S*, specify the configuration of each of the following :

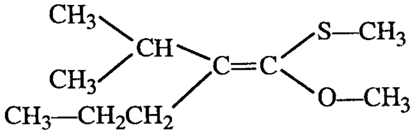
(a) 

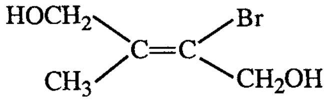
(b) 

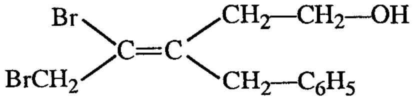
(c) 

(d) 

5. Assign *E*/*Z* designation to each of the following :

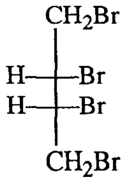
(a) 

(b) 

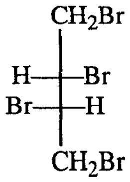
(c) 

6. Write configurations of the given compounds :
   (a) (2*R*, 3*S*)-2, 3-dibromohexane
   (b) (2*S*, 3*S*)-2, 3-dibromohexane
   (c) (2*R*, 3*R*)-2, 3-dibromohexane

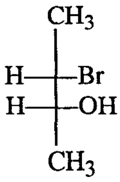
7. For each of the following structures
   (i) Star any chiral carbon atom
   (ii) Label each chiral carbon as (*R*) or (*S*)
   (iii) Draw if any internal mirror plane of symmetry
   (iv) Label the structure as chiral or achiral.
   (v) Label any *meso* structures.



(a)



(b)



(c)

8. Write an explanatory note on chemical method for resolution of racemic modification.

9. Taking suitable examples, discuss inversion, retention and racemisation.

10. Give a comparison between configuration and conformation.

11. Explain why the chair conformation of cyclohexane is more stable than the boat conformation?

12. What is conformational analysis. Discuss the various conformations and their relative stabilities by taking the example of *n*-butane.

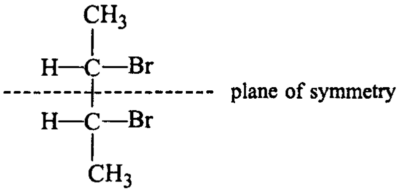
13. Write notes on the following :
    (a) Elements of symmetry
    (b) Molecular chirality
    (c) *Erythro* and *threo* nomenclature

14. Draw Newman projections of various conformations of *n*-butane and arrange them according to their decreasing stability.

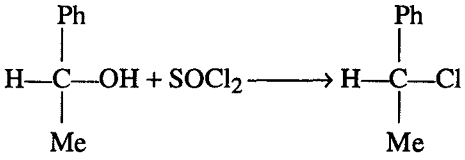
15. Draw the preferred conformation of methylcyclohexane and give reason for your choice.

16. Distinguish between the following terms :
    (a) Observed rotation and specific rotation
    (b) Enantiomers and diastereomers
    (c) Absolute and relative configuration
    (d) *Meso* and racemic forms
    (e) Configuration and conformation

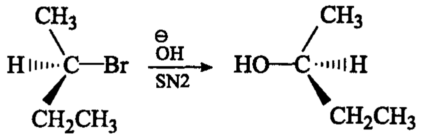
ANSWER TO VERY SHORT ANSWER QUESTIONS

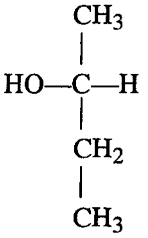
1. The molecule should be chiral.
2. A molecule which is not superimposable on its mirror image is a chiral molecule.
3. (a), (b) and (d) are false; (c) and (e) are true.
4. 

meso-2,3-dibromobutane

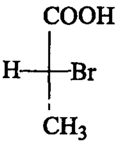
5. 

(For mechanism see the text)

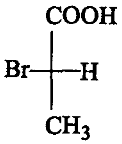
6. 

7. (a) and (c) false; (b), (d) and (e) are true.
8. 

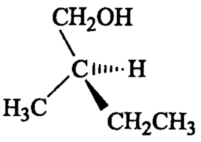
(*R*-2-butanol)

9. 

(*R*)-2-bromopropanoic acid



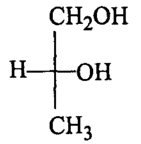
(*S*)-2-bromopropanoic acid

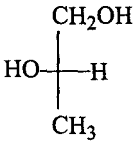
10. 

(*R*)-2-methyl-1-butanol

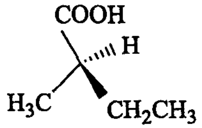
11. (a) *R* (b) *R* (c) *R* (d) *S*

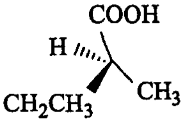
12.


(*R*)-1, 2-propanediol

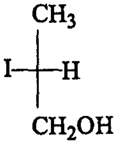

(*S*)-1, 2-propanediol

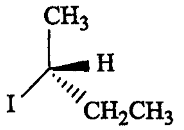
13.


(*R*)-2-methylbutanoic acid

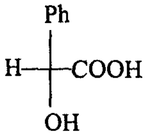

(*S*)-2-methylbutanoic acid

14.

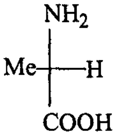

Fisher projection
(*R*)-2-iodobutane


Flying-wedge formula
(*R*)-2-iodobutane

15. (I)


(*R*)-

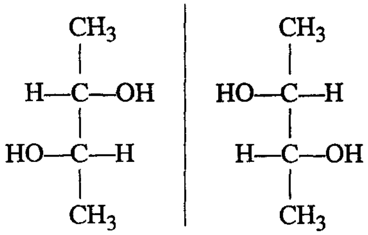
(II)

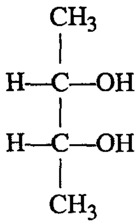

(*S*)-

SOLUTIONS OF PROBLEMS

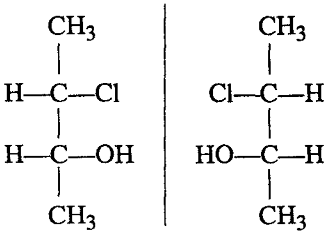
1. (i) The given compound has two alike chiral carbons; hence configuration of three optical isomers can be drawn. Out of three isomers, two are enantiomers and one is *meso* form.

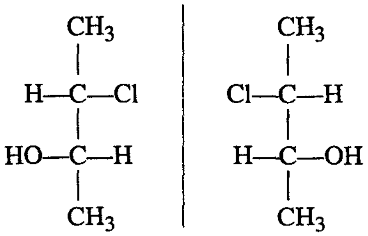
$$a = 2^{n-1} = 2\ ;\ m = 2^{\frac{n}{2}-1} = 2^{0} = 1$$


A pair of enantiomers

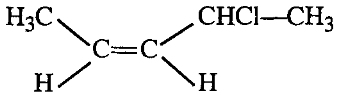

Meso form

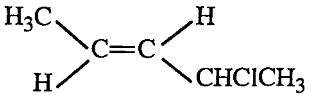
(ii) It has two unlike chiral carbons; hence $2^n = 2^2 = 4$ optical isomers are possible-all are optically active.

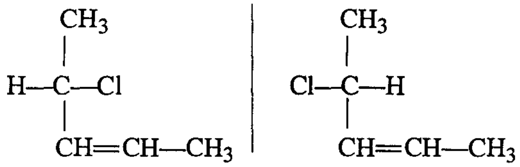

A pair of enantiomers


A pair of enantiomers

(iii) It has one C=C bond, each carbon atom of which contains two different groups and atoms, hence two geometrical isomers are possible. It has one chiral carbon; therefore a pair of enantiomers will be obtained. Thus the compound has four configurational isomers.


cis, optically active

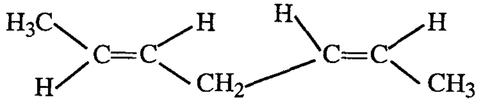

Trans, optically active

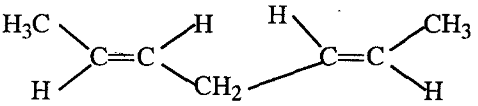

A pair of enantiomers

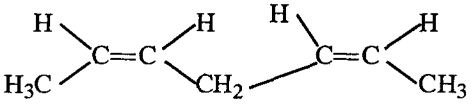
(iv) The ends of the diene are the same and it has even number of double bonds. Therefore, number of geometrical isomers $= 2^{n-1} + 2^{n/2-1}$

$$= 2^1 + 2^{2/2-1}$$

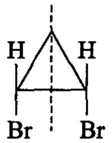
$$= 2 + 1 = 3$$


Trans/cis (I)

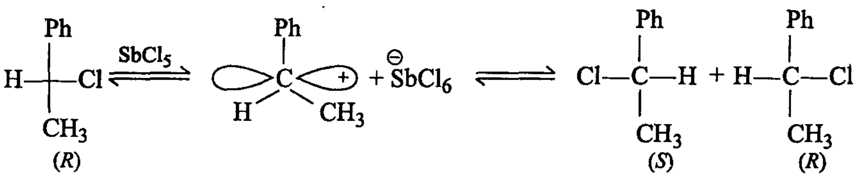

Trans/trans (II)


cis/cis (III)

(v) In this molecule their is frozen rotation about cyclopropane ring; thus *cis-trans* isosmers can exist. *cis*-Isomer has a plane of symmetry, hence this isomer is optically inactive.

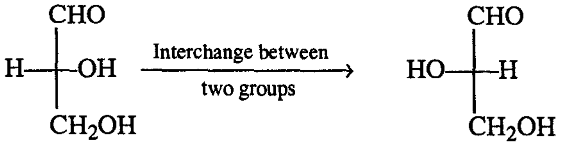


2. The reaction takes place *via* carbocation formation. A carbocation is generated by removal of an anion $Cl^{\ominus}$ from the chiral carbon. This anion is temporarily accepted by the Lewis acid $SbCl_5$ to form $Sb^{\ominus}Cl_6$. The sp^2 hybridised carbocation so formed has a planar structure and the anion (from the $Sb^{\ominus}Cl_6$) then attacks the carbocation from either side which gives rise to the racemised product.



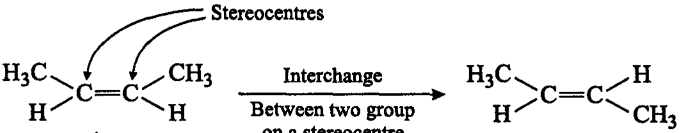
Racemised product

3. A stereocentre is an atom on which an interchange of any two groups will result in a new stereoisomer. When the new stereoisomer is an enantiomer, the stereocentre is often called a chiral centre. Not all stereocentres are tetrahedral.



Stereocentre (I) New stereoisomer (II)

I and II are enantiomers, hence stereocentre is chiral centre.

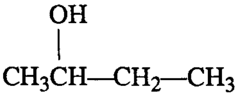


cis-isomer III New stereoisomer IV

III and IV are not enantiomers. They are diastereomers, hence in this case stereocentres are not chiral centres.

Thus all chiral centres are stereocentres but all stereocentres are not chiral centres.

4. **2-Butanol** has the structure :

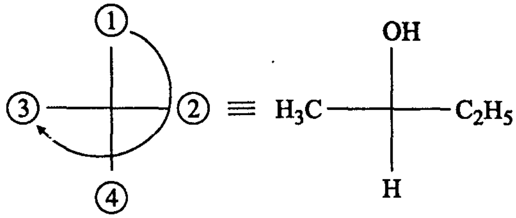


$$CH_3\underset{}{\overset{OH}{\overset{|}{C}}}H—CH_2—CH_3$$

The four groups present on chiral carbon are : H, OH, CH_3 and C_2H_5. The priority order of these four groups is :

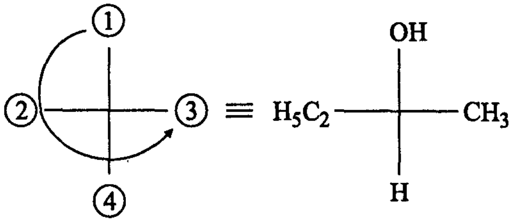
$$\underset{(1)}{HO} > \underset{(2)}{C_2H_5} > \underset{(3)}{CH_3} > \underset{(4)}{H}$$

For (*R*)-configuration arrangements is as follows :



R-Configuration

For (*S*)-configuration arrangements of the groups is as follows :

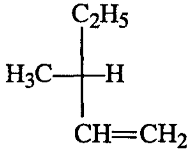


S-Configuration

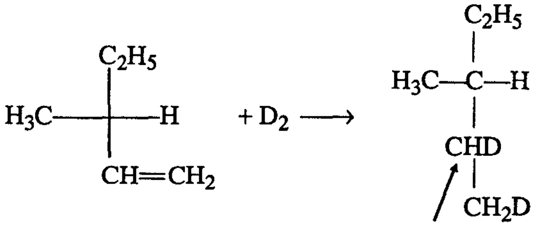
5. The priority order of four groups is :

$$CH{=}CH_2 > C_2H_5 > CH_3 > H.$$

Thus (*R*)-configuration of the reactant is as follows :

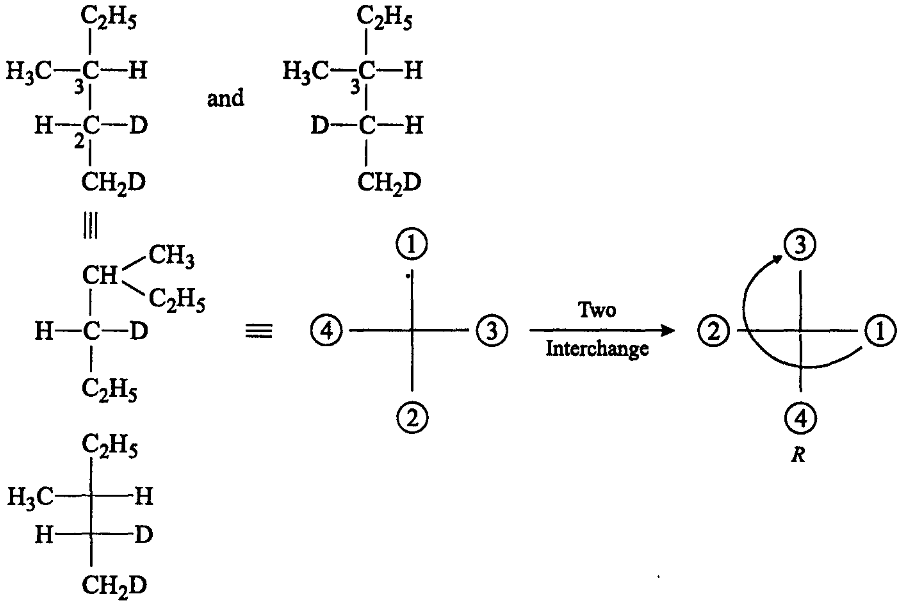


The addition reaction takes place as follows :



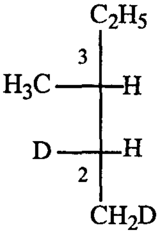
New chiral carbon, hence two stereoisomers

These two stereoisomers are :



2*R*,3*R*

Similarly, configuration of the other product is 2*S*, 3*R*.

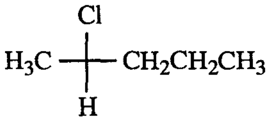


2*S*, 3*R*

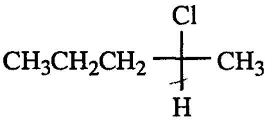
6. (d) **7.** (a) **8.** (d) **9.** (d) **10.** (c) **11.** (b) **12.** (a) **13.** (a)

14. (b) **15. I,** *R*; **II,** *R*; **III,** *S*; **IV,** *R*

16.



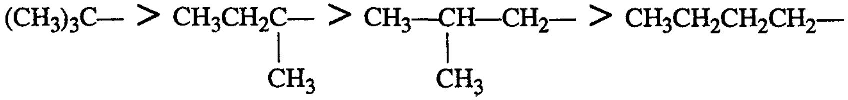
(*R*)-



(*S*)-

17. **I,** *threo*; **II,** *erythro*; **III,** *threo*

18.

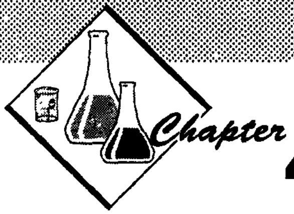


$(CH_3)_3C— > CH_3CH_2\underset{\underset{CH_3}{|}}{C}— > CH_3—\underset{\underset{CH_3}{|}}{C}H—CH_2— > CH_3CH_2CH_2CH_2—$

19. (a) *R* (b) *R* (c) *S* (d) *S*

20. (a) diastereomers
(b) homomers (molecules that are superimposable on each other are called homomers)
(c) constitutional isomers (d) homomers
(e) enantiomers

21. (a) *E* (b) *Z* (c) *Z* (d) *E*



Chapter 4

ALKANES AND CYCLOALKANES

4.0 ALKANES

Carbon is unique among the elements as regards the number of compounds which it can form. The chemistry of carbon compounds owes its wonderful unity and variety to the remarkable stability of the C—C single bond. Saturated hydrocarbons, composed only of carbon and hydrogen atoms which bond together by σ bonds, form the structural backbone of many organic compounds. The generic name of acyclic saturated hydrocarbons, linear or branched, is **alkane**. The general formula of alkanes is C_nH_{2n+2}.

The simplest **alkane, methane,** has been known for a long time in the form of **'marsh gas'** which is produced by the bacterial decomposition of organic matter under **anaerobic** conditions. Methane is also present in coal seams; when released during mining operation, it can accumulate in sufficient amount to form an explosive mixture with air (fire damp). Petroleum is the principal source of alkanes.

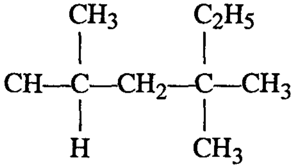
The hydrogen atoms in CH_4 are arranged about a carbon atom in a tetrahedral fashion. The alkanes are all derivable from methane by the successive replacement of hydrogen atoms by methyl groups. They are thus all built on a skeleton in which the valence angles are near to the tetrahedral value of 109·5° and the distances between two linked carbon atoms are 154 picometers (or 1·54 Å). The homologous series has the general formula C_nH_{2n+2}, each member differing from the next by a $—CH_2—$ unit. Alkanes are classified into the following two groups :

1. Unbranched or straight chain alkanes : All the carbon atoms in the chain are linked to no more than two carbon atoms. Such compounds are specified by suffixing *n* (meaning normal) before their names.

$$CH_3—CH_2—CH_2—CH_2—CH_3$$

Straight cahin or normal (*n*) alkane

2. Branched chain alkanes : One or more carbon atoms are linked to more than two other carbon atoms.



$$\begin{array}{ccccccccc} & & CH_3 & & & & C_2H_5 & & \\ & & | & & & & | & & \\ CH & — & C & — & CH_2 & — & C & — & CH_3 \\ & & | & & & & | & & \\ & & H & & & & CH_3 & & \end{array}$$

Branched chain alkane

The first four straight chain (normal) alkanes are known by their **common** or *trivial names* which are generally based on their sources or some other facts, *e.g.*,

CH_4	$CH_3—CH_3$	$CH_3—CH_2—CH_3$	$CH_3—CH_2—CH_2—CH_3$
Methane	Ethane	Propane	Butane

The higher members are named by prefixing Greek numerals, indicating the number of carbon atoms in the molecule, the suffix **'ane'**. Examples are listed in Table 4.1.

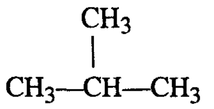
Table 4.1 ***Alkanes*** C_nH_{2n+2}

n	Name	Molecular forkula	*n*	Name	Molecular formula
1	Methane	CH_4	20	Eicosane	$C_{20}H_{42}$
2	Ethane	C_2H_6	21	Heneicosane	$C_{21}H_{44}$
3	Propane	C_3H_8	22	Docosane	$C_{22}H_{46}$
4	Butane	C_4H_{10}	23	Tricosane	$C_{23}H_{48}$
5	Pentane	C_5H_{12}	24	Tetracosane	$C_{24}H_{50}$
6	Hexane	C_6H_{14}	30	Triacontane	$C_{30}H_{62}$
7	Heptane	C_7H_{16}	31	Hentriacontane	$C_{31}H_{64}$
8	Octane	C_8H_{18}	33	Tritriacontane	$C_{33}H_{68}$
9	Nonane	C_9H_{20}	40	Tetracontane	$C_{40}H_{82}$
10	Decane	$C_{10}H_{22}$	50	Pentacontane	$C_{50}H_{102}$
11	Undecane	$C_{11}H_{24}$	60	Hexacontane	$C_{60}H_{122}$
12	Dodecane	$C_{12}H_{26}$	70	Heptacontane	$C_{70}H_{142}$
13	Tridecane	$C_{13}H_{28}$	80	Octacontane	$C_{80}H_{162}$
14	Tetradecane	$C_{14}H_{30}$	90	Nonacontane	$C_{90}H_{182}$
19	Nonadecane	$C_{19}H_{40}$	100	Hectane	$C_{100}H_{202}$

The names in Table 4.1 are common to both normal and branched chain alkanes. The possibility of branched chain alkanes begins with butane.

$CH_3—CH_2—CH_2—CH_3$

n-butane or butane



$CH_3—\overset{\overset{\displaystyle CH_3}{|}}{C}H—CH_3$

Iso-butane or 2-methylpropane

4.1 ISOMERISM IN ALKANES

Butane and isobutane are constitutional isomers. Isobutane has branched chain constitution whereas butane has a continuous—chain constitution. This butane is the first alkane to exhibit constitutional isomerism. This is an example of *chain* (or *nuclear*) isomerism which arises due to the difference in the constitution of the carbon chain.

The number of theoretically possible isomers (constitutional isomers—having the same moelcular formula) increases sharply as the homologous series expands (Table 4.2).

Table 4.2 ***Constitutional isomers for*** C_nH_{2n+2}

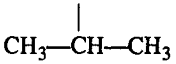
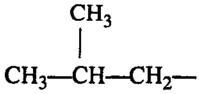
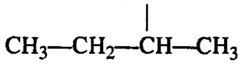
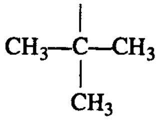
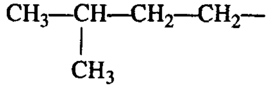
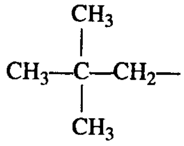
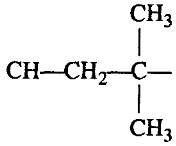
n	Isomer number	*n*	Isomer number
5	3	8	18
6	5	9	35
7	9	10	75
		20	366319

All alkanes up to including the 75 decanes have been synthesised but beyond C_{10} only a minute fraction of the total isomers represented in Table 4.2 are known substances.

4.2 THE ALKYL GROUP

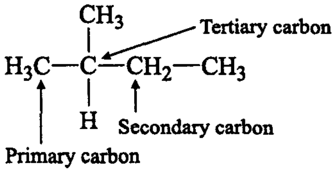
Univalent groups that are formed by the removal of one hydrogen atom from an alkane are known as alkyl groups. The name of each individual group is obtained by replacing the suffix *ane* of the parent hydrocarbon by *yl* (Table 4.3).

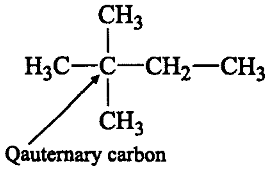
Table 4.3

Alkane	Alkyl Group	Shorthand notation
CH_4	$CH_3—$ Methyl	Me
C_2H_6	$C_2H_5—$ Ethyl	Et
Propane	$CH_3—CH_2—CH_2—$ *n*-propyl	*n*-Pr or Pr
	 $CH_3—\overset{\vert}{C}H—CH_3$ *iso*-propyl	*iso*-Pr or Pr^i
Butane	$CH_3—CH_2—CH_2—CH_2—$ *n*-butyl	*n*-Bu or Bu
	 $CH_3—\overset{\overset{CH_3}{\vert}}{C}H—CH_2—$ *iso*-butyl	*Iso*-Bu
	 $CH_3—CH_2—\overset{\vert}{C}H—CH_3$ *sec*-butyl	*s*-Bu
	 $CH_3—\overset{\vert}{\underset{\underset{CH_3}{\vert}}{C}}—CH_3$ *tert*-butyl (*t*-butyl)	*t*-Bu or Bu^t
Pentane	$CH_3—CH_2—CH_2—CH_2—CH_2—$ *n*-pentyl	*n*-pen
	 $CH_3—\underset{\underset{CH_3}{\vert}}{C}H—CH_2—CH_2—$ *iso*-pentyl	*iso*-pen
	 $CH_3—\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}—CH_2—$ *neo*-pentyl	*neo*-pen
	 $CH—CH_2—\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}—$ *tert*-pentyl	*t*-pen

4.3 CLASSIFICATION OF CARBON ATOMS IN ALKANES

The carbon atoms in alkanes are designated as *primary*, *secondary* or *tertiary* depending on their positions in molecules. A carbon (methyl carbon) which is directly linked to only one carbon is called *primary carbon* and if a carbon is directly linked to two carbon atoms it is called a *secondary carbon.* A carbon is called a *tertiary carbon* or *quaternary carbon* when it is directly attached to three or four other carbon atoms respectively. This classification is very useful in the study of alkanes as well as various other classes of compounds. Hydrogen atoms attached to primary, secondary and tertiary carbon atoms are called primary, secondary and tertiary hydrogen atoms, respectively.





4.4 IUPAC NOMENCLATURE OF ALKANES

The common or trivial naming system (Section 4.0) is not suitable for naming the higher branched chain alkanes. The more scientific **IUPAC** (International Union of Pure and Applied Chemistry) system is quite satisfactory for the nomenclature of organic compounds. This is often called the systematic nomenclature because in this system the names are systematically derived. The IUPAC names are logical and highly definite, *i.e.*, a compound has one and only one IUPAC (or systematic) name in terms of principles underlying the IUPAC system of nomenclature.

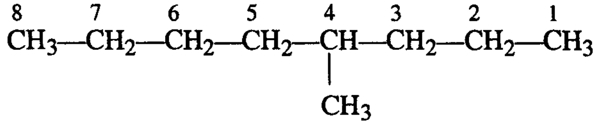
4.4.1 IUPAC Nomenclature of Unbranched Alkanes

The names of unbranched alkanes are derived from the Greek names for the numbers of carbon atoms present in the alkane followed by the suffix *ane*, except in the case of the first four members where the common or trivial names have been retainied in the IUPAC system. For example, the IUPAC names of some unbranched alkanes are given in Table 4.1.

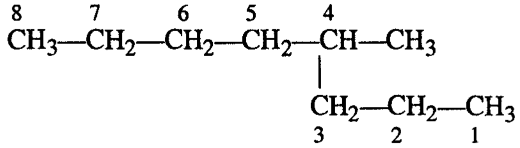
4.4.2 Nomenclature of Branched-Chain Alkanes

Branched-chain alkanes are named according to the following rules :

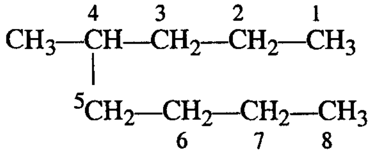
(1) Longest Chain Rule : Locate the longest continuous chain of carbon atoms. This chain determines the parent name of the alkane. Notice that the longest continuous chain is chosen regardless of how the molecule is written.



$$\overset{8}{CH_3}-\overset{7}{CH_2}-\overset{6}{CH_2}-\overset{5}{CH_2}-\underset{\displaystyle CH_3}{\overset{4}{CH}}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{CH_3}$$



$$\overset{8}{CH_3}-\overset{7}{CH_2}-\overset{6}{CH_2}-\overset{5}{CH_2}-\underset{\displaystyle \underset{3}{CH_2}-\underset{2}{CH_2}-\underset{1}{CH_3}}{\overset{4}{CH}}-CH_3$$

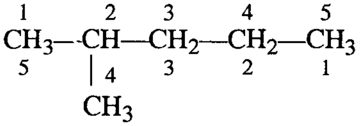


$$CH_3-\underset{\displaystyle {}^{5}CH_2-\underset{6}{CH_2}-\underset{7}{CH_2}-\underset{8}{CH_3}}{\overset{4}{CH}}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{CH_3}$$

The above compounds are designated as an octane because the longest chain contains eight carbon atoms.

(2) Lowest Number Rule or Lowest Sum Rule : The carbon atoms of the longest continuous chain, *i.e.*, parent chain are numbered by arabic numerals 1, 2, 3, 4...... from one end of the chain to the other in such a manner that carbon atom carrying first substituent gets the lowest number. The number that locates the position of the substituent is known as **locant**.

However, if there are two or more substituents, the numbering of parent chain is done in such a way that the sum of the locants is the lowest. This is called the **lowest sum rule.**

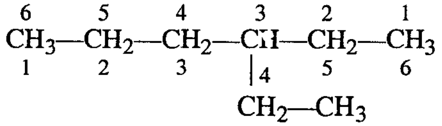


$$\overset{1}{\underset{5}{CH_3}}-\overset{2}{\underset{\underset{\displaystyle CH_3}{|_4}}{CH}}-\overset{3}{\underset{3}{CH_2}}-\overset{4}{\underset{2}{CH_2}}-\overset{5}{\underset{1}{CH_3}}$$

2-Methylheptane

not

4-Methylheptane

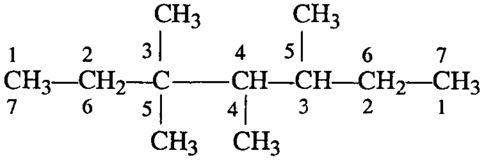


$$\overset{6}{\underset{1}{CH_3}}-\overset{5}{\underset{2}{CH_2}}-\overset{4}{\underset{3}{CH_2}}-\overset{3}{\underset{\underset{\displaystyle CH_2-CH_3}{|_4}}{CH}}-\overset{2}{\underset{5}{CH_2}}-\overset{1}{\underset{6}{CH_3}}$$

3-Ethylhexane

not

4-Ethylhexane



$$\overset{1}{\underset{7}{CH_3}}-\overset{2}{\underset{6}{CH_2}}-\overset{\overset{\displaystyle CH_3}{3|}}{\underset{\underset{\displaystyle CH_3}{5|}}{C}}-\overset{4}{\underset{\underset{\displaystyle CH_3}{4|}}{CH}}-\overset{\overset{\displaystyle CH_3}{5|}}{\underset{3}{CH}}-\overset{6}{\underset{2}{CH_2}}-\overset{7}{\underset{1}{CH_3}}$$

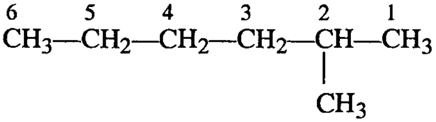
Position of the substituents should be 3, 3, 4 and 5 because

$$3 + 3 + 4 + 5 = 15$$

Position should not be 3, 4, 5 and 5 because

$$3 + 4 + 5 + 5 = 17$$

(3) Name of the Branched Chain Alkane : The substituent name and the parent alkane are joined in one word and there is a hyphen between the number and the substituent name. The whole name is written as one word.



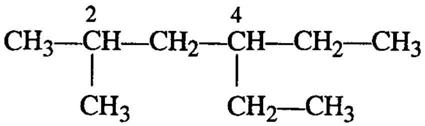
$$\overset{6}{CH_3}-\overset{5}{CH_2}-\overset{4}{CH_2}-\overset{3}{CH_2}-\overset{2}{\underset{\underset{\displaystyle CH_3}{|}}{CH}}-\overset{1}{CH_3}$$

2-Methylhexane

not

2-Methyl hexane

(4) Alphabetical Order of the Side Chains : When two or more substituents are present, give each substituent a number corresponding to its position on the longest chain. The substituent groups should be listed alphabetically.



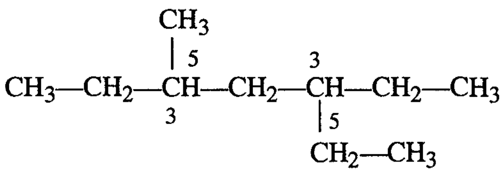
$$CH_3-\overset{2}{\underset{\underset{\displaystyle CH_3}{|}}{CH}}-CH_2-\overset{4}{\underset{\underset{\displaystyle CH_2-CH_3}{|}}{CH}}-CH_2-CH_3$$

4-Ethyl-2-methylhexane

not

2-Methyl-4-ethylhexane

(5) Numbering of Different Alkyl Groups at Equivalent Positions : If two different alkyl groups are present at equivalent positions the numbering of the parent chain is done in such a way that alkyl group which comes first in the alphabetical order gets the lower number. For example :



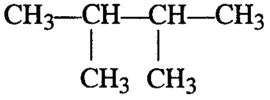
$CH_3-CH_2-\underset{3}{\overset{5}{CH}}(CH_3)-CH_2-\overset{3}{\underset{5}{CH}}(CH_2-CH_3)-CH_2-CH_3$

3-Ethyl-5-methylheptane
not
5-Ethyl-3-methylheptane

Note : In some books it is mentioned that if different alkyl groups are present as substituents on the identical positions then numbering must be done so as to give the smaller alkyl group the minimum number but it is not the case.

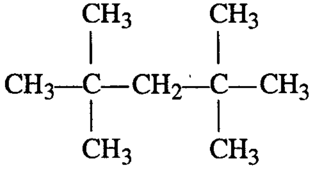
(6) Naming of Same Alkyl Groups at Different Positions : When two or more substituents are identical, indicate this by the use of prefixes *di*, *tri*, *tetra* and so on. Then make certain that each and every substituent has a number. Commas are used to separate numbers from each other.

Note : The prefixes *di, tri, tetra, sec, tert* are ignored in alphabetising substituent groups. The prefixes *iso*, *neo* and *cyclo* are not ignored, For example :



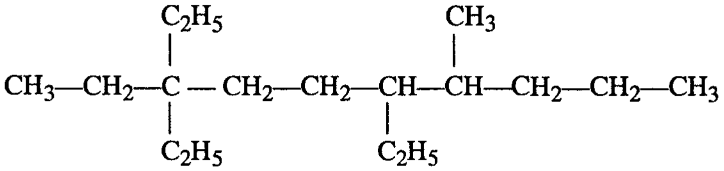
$CH_3-CH(CH_3)-CH(CH_3)-CH_3$

2, 3-Dimethylbutane



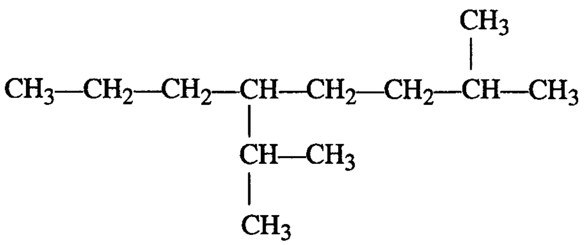
$CH_3-C(CH_3)_2-CH_2-C(CH_3)_2-CH_3$

2, 2, 4, 4-Tetramethylpentane



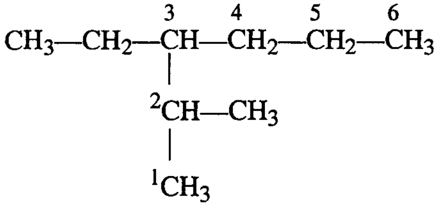
$CH_3-CH_2-C(C_2H_5)_2-CH_2-CH_2-CH(C_2H_5)-CH(CH_3)-CH_2-CH_2-CH_3$

3, 3, 6-Triethyl-7-methyldecane
not
7-Methyl-3, 3,6-triethyldecane

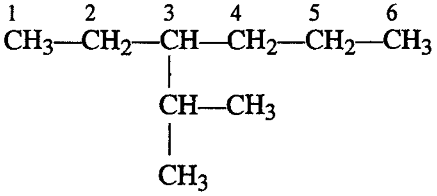


5-Isopropyl-2-methyloctane
not
2-Methyl-5-isopropyloctane

(7) Rule for Larger Number of Substituents : If a compound has two or more chains of the same length, the parent hydrocarbon is the chain with the greater number of substituents.



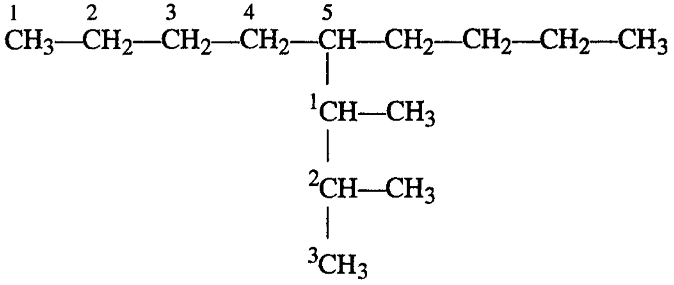
3-Ethyl-2-methyloctane
(two substituents) ⇒ correct name



3-Isopropylhexane
(one substituent) ⇒ wrong name

(8) Numbering the Complex Substituent : Name such as isopropyl, *sec-* butyl and *tert-* butyl are acceptable substituent names in the IUPAC system of nomenclature but systematic substituent names are preferable.

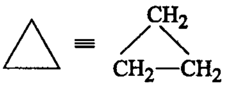
Systematic substituent names are obtained by numbering the substituent starting at the carbon that is attached to the parent hydrocarbon. This means that the carbon that is attached to the parent hydrocarbon is always the number-1 carbon of the substituent. In a compound such as 5-(1, 2-dimethylpropyl)nonane, the complex substituent is in parentheses; the numbers inside the parentheses indicate the positions on the substituent, whereas the number outside the parentheses indicates a position on the parent hydrocarbon.

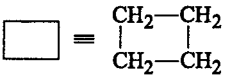


5-(1, 2-dimethylpropyl)nonane

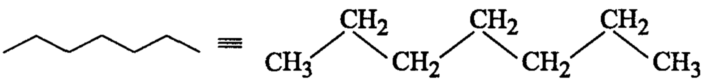
4.5 SKELETAL STRUCTURES (LINE FORMULAE)

(1) Skeletal Structure of Cycloalkanes : Skeletal structures show the carbon-carbon bonds as line but do not show the carbon-hydrogen bonds. Each vertex in a skeletal structure represents a carbon. It is understood that each carbon is bonded to the appropriate number of hydrogens to give it four bonds. For example :

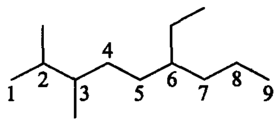




(2) Skeletal Structures of Open Chain Alkanes : In a skeletal structure the carbon chains are represented by *zigzag* lines. In this line each vertex represents a carbon and carbons occupy the ends of the chain.



Heptane



6-Ethyl-2, 3-dimethylnonane

4.6 GENERAL METHODS OF PREPARATION OF ALKANES

Because of the relatively wide differences in boiling points of the lower members of the homologous series methane, ethane, propane, butane, *iso*butane and *iso*meric pentanes may be obained by careful fractional distillation of petroleum. But in general, if a pure alkane is required, it must be synthesised from the functionalised precursor. The alkanes are prepared by the following methods.

1. Reduction of Unsaturated Hydrocarbons : Hydrogenation of olefins is frequently important as the last stage in the synthesis of alkane. Catalytic hydrogenation (homogeneous or heterogeneous catalyst) is the most popular procedure. Most olefins add hydrogen over a hydrogenation catalyst at temperature between 0–300°C. The most commonly used heterogeneous catalysts are platinum, palladium, nickel, rhodium, and copper chromite. The most important and commonly used heterogeneous catalysts are platinum oxide (Adams catalyst) and Raney nickel.

$$R\text{—CH}{=}\text{CH—}R_1 + \text{H}_2 \xrightarrow{\text{Catalyst}} R\text{—CH}_2\text{—CH}_2\text{—}R_1$$

$$R\text{—C}\equiv\text{C—}R_1 + \text{H}_2 \xrightarrow{\text{Catalyst}} R\text{—CH}{=}\text{CH—}R_1 \xrightarrow{\text{H}_2/\text{Catalyst}} R\text{—CH}_2\text{—CH}_2\text{—}R_1$$

When platinum or palladium is used as catalyst the hydrogenation takes place at room temperature but with nickel higher temperature (250°–300°) is required.

$$R\text{—CH}{=}\text{CH—}R_1 + \text{H}_2 \xrightarrow[\text{Ni/300°C}]{\text{Pt or Pd or}} R\text{—CH}_2\text{—CH}_2\text{—}R \quad \textbf{(Sabatier Senderens reaction)}$$

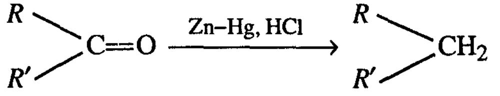
Recently Wilkinson discovered a homogeneous hydrogenation catalyst $(\text{Ph}_3\text{P})_3\text{RhCl}$. This soluble catalyst is effective at room temperature in a variety of solvents. Terminal olefins are hydrogenated more rapidly than are internal olefins.

$$n\text{-C}_8\text{H}_{17}\text{CH}{=}\text{CH}_2 \xrightarrow[\text{H}_2]{(\text{Ph}_3\text{P})_3\text{RhCl}} n\text{-C}_8\text{H}_{17}\text{—CH}_2\text{—CH}_3$$

Amongst reagents that are generally used for the non-catalytic reduction of olefins are di-imide (NH=NH) and sodium dissolved in hexamethyl phosphoric trimide (HMPT)

$$R\text{—CH}{=}\text{CH—}R' \xrightarrow[\text{or HMPT/Na}]{\text{NH=NH}} R\text{—CH}_2\text{—CH}_2\text{—}R'$$

2. From Aldehydes and Ketones : The carbonyl group of aldehydes and ketones can be converted into a methylene group by **Clemmensen** and **Wolff-Kishner reductions** :

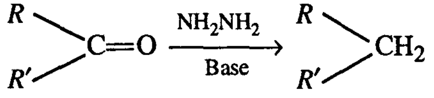


$$\begin{matrix}R\\R'\end{matrix}\!\!>\!\text{C=O} \xrightarrow{\text{Zn–Hg, HCl}} \begin{matrix}R\\R'\end{matrix}\!\!>\!\text{CH}_2$$

Clemmensen reduction

R = alkyl, R' = H (aldehyde)

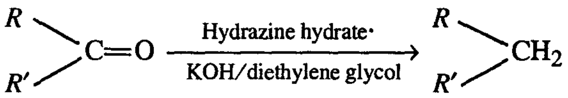
R and R′ = alkyl (ketone)



$$\begin{matrix}R\\R'\end{matrix}\!\!>\!\text{C=O} \xrightarrow[\text{Base}]{\text{NH}_2\text{NH}_2} \begin{matrix}R\\R'\end{matrix}\!\!>\!\text{CH}_2$$

Wolff-Kishner reduction

Now Wolff-Kishner procedure has been replaced by the **Huang-Minlon** modification in which carbonyl compound is heated with hydrazine hydrate, KOH and diethylene glycol under reflux and then at 200°C.



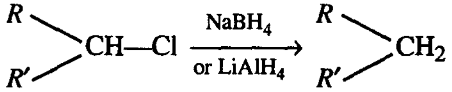
$$R(R')C{=}O \xrightarrow[\text{KOH/diethylene glycol}]{\text{Hydrazine hydrate}\cdot} R(R')CH_2$$

3. Reduction of Alkyl Halides : (1) Alkyl halides when reduced with tri-*n*-butyltin hydride, and triphenyltin hydride are converted to corresponding alkanes. Order of reactivity of halides is $RI > RBr > RCl > RF$:

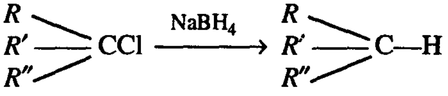
$$R{-}X \xrightarrow[\text{Ph}_3\text{SnH}]{\text{Bu}_3\text{SnH or}} R{-}H$$

Primary and secondary alkyl halides are readily reduced to alkanes by $LiAlH_4$. (Tertiary alkyl halide gives elimination reaction) on the other hand, sodium borohydride reduces secondary and tertiary alkyl halides to corresponding alkanes.

$$R{-}CH_2{-}Cl \xrightarrow{\text{LiAlH}_4} R{-}H$$



$$R(R')CH{-}Cl \xrightarrow[\text{or LiAlH}_4]{\text{NaBH}_4} R(R')CH_2$$



$$R(R')(R'')CCl \xrightarrow{\text{NaBH}_4} R(R')(R'')C{-}H$$

Older direct methods which have been largely replaced by the above methods involved the use of reducing agents such as sodium, aluminium amalgam, zinc dust, zinc-copper couple and magnesium.

Alkyl iodides undergo reduction with hydriodic acid.

$$R{-}I + HI \xrightarrow[\text{red P}]{150^\circ C} RH + I_2$$

4. Wurtz Reaction : Alkyl halides (generally primary) when heated with sodium metal in ether solution give rise to higher alkanes. The reaction is known as **Wurtz reaction.** The reaction works best with primary alkyl iodides. The yields are generally poor, however, and the desired product may be contaminated with alkene.

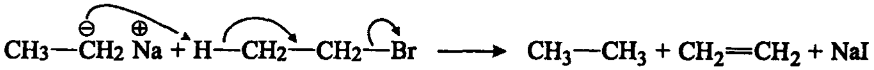
Two mechanisms depending on the conditions of the reaction have been suggested for the Wurtz reaction.

(i) The intermediate formation of organo-metallic compound operates when the reaction is carried out in solution.

$$CH_3{-}CH_2{-}I + 2\overset{\bullet}{Na} \longrightarrow CH_3{-}\overset{\ominus}{C}H_2\overset{\oplus}{Na} + NaI$$

$$CH_3{-}\overset{\ominus}{C}H_2\overset{\oplus}{Na} + CH_3{-}CH_2{-}I \longrightarrow C_2H_5{-}C_2H_5 + NaI$$

This mechanism also accounts for the presence of ethane and ethylene in the products.



$$CH_3{-}\overset{\ominus}{C}H_2\ \overset{\oplus}{Na} + H{-}CH_2{-}CH_2{-}Br \longrightarrow CH_3{-}CH_3 + CH_2{=}CH_2 + NaI$$

(ii) *Via* the formation of free radical as an intermediate—This mechanism operates when the reaction is carried out in the vapour phase (a condition suitable for the generation of free radicals).

$$C_2H_5{-}I + \overset{\bullet}{Na} \longrightarrow \overset{\bullet}{C}_2H_5 + NaI$$

$$\dot{C}_2H_5 + \dot{C}_2H_5 \xrightarrow{\text{Combination}} C_2H_5—C_2H_5$$

The presence of ethane and ethylene in products is explained by the disproportionation of ethyl free radical.

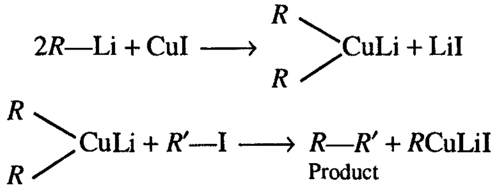
$$\dot{C}_2H_5 + \dot{C}_2H_5 \longrightarrow C_2H_6 + CH_2{=}CH_2$$

Limitation

The coupling of two different alkyl halides by the Wurtz procedure is impractical because the organosodium intermediates (or free radicals) are very reactive and couple as soon as they are formed and three coupled products are obtained in addition to the usual by-products.

$$R—X + R'—X + 2Na \longrightarrow R—R + R'—R' + R—R' + \text{by-products}$$

5. Corey-House Synthesis : A very versatile method for unsymmetrical coupling of two alkyl groups involves the use of lithium dialkylcopper reagent, also called *Gilman reagent* (R_2CuLi). The reaction is known as **Corey-House** synthesis. It is a very good method for preparing pure alkanes from alkyl halides.



$$2R—Li + CuI \longrightarrow R_2CuLi + LiI$$

$$R_2CuLi + R'—I \longrightarrow \underset{\text{Product}}{R—R'} + RCuLiI$$

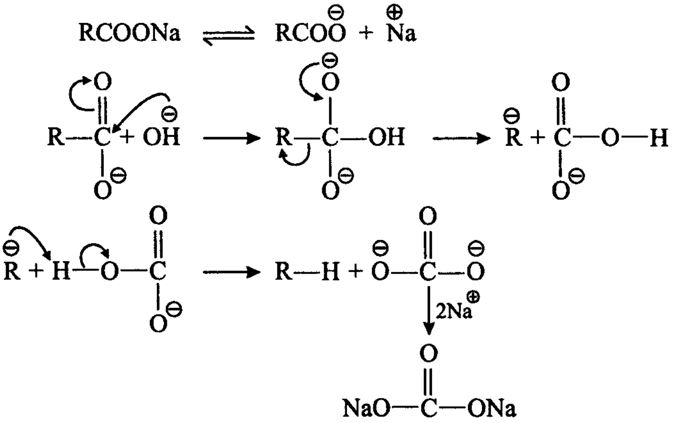
In this reaction $R'—X$ may be CH_3X, prim-alkyl halide or *sec*-alkyl halide. The alkyl group of R_2CuLi may be methyl, primary, secondary or tertiary.

6. From Carboxylic Acid

(i) When sodium salts of monocarboxylic acids are heated with sodalime, they form alkanes. However, the yield in this case is poor.

$$RCOONa + NaOH\ (CaO) \longrightarrow RH + Na_2CO_3$$

Mechanism :



$$RCOONa \rightleftharpoons RCO\overset{\ominus}{O} + \overset{\oplus}{Na}$$

(ii) Good yields of alkanes have been obtained from the photochemical decarboxylation of primary carboxylic acids by lead tetraacetate in chloroform.

$$R—COOH \xrightarrow[CHCl_3]{Pb(OAc)_4} RH + CO_2$$

Decarboxylation of acids provide a route to alkanes containing one less carbon atom than the original acid.

7. Kolbe's Electrolytic Method : Electrolysis of the alkali metal salt of a carboxylic acid gives CO_2 and an alkane which contains twice as many carbon atoms as the alkyl radical of the acid used. The reaction involves the formation of the carboxylate radical. Decarboxylation of this radical gives an alkyl radical which forms the alkane on dimerization.

$$RCOONa \longrightarrow RCO\overset{\ominus}{O} + \overset{\oplus}{Na}$$

At anode

$$2RCO\overset{\ominus}{O} \longrightarrow 2RCO\dot{O} + 2e^-$$

$$\downarrow$$

$$2\dot{R} + 2CO_2$$

$$\dot{R} + \dot{R} \longrightarrow R\text{—}R$$

At cathode

$$2Na + 2e^- \longrightarrow 2\dot{Na} \xrightarrow{2H_2O} 2NaOH + H_2$$

Formation of by-products (alkene and lower alkane) because of disproportionation favours the free radical mechanism.

8. From Grignard Reagents : Grignard reagents when treated with compounds containing active hydrogen yield pure alkane :

$$RMgX + HOH \longrightarrow RH + Mg(OH)X$$

$$RMgX + R\text{—}OH \longrightarrow R\text{—}H + Mg(OR)X$$

$$RMgX + RNH_2 \longrightarrow R\text{—}H + Mg(RNH)X$$

9. Hydroboration of Alkenes : Diborane (B_2H_6), which behaves as its monomer (BH_3), adds to an olefinic bond to give mono-, di-, and trialkylboranes. These on treatment with acetic acid or propionic acid yield alkanes.

$$3R\text{—}CH{=}CH_2 \xrightarrow{B_2H_6} (R\text{—}CH_2\text{—}CH_2)_3B \xrightarrow{CH_3COOH} 3R\text{—}CH_2\text{—}CH_3$$

4.7 PHYSICAL PROPERTIES OF ALKANES

Because alkanes are relatively unreactive they are used primarily as solvents, fuels and lubricants. Natural gas, gasoline, kerosene, heating oil, lubricating oil, and paraffin "wax" are all composed primarily of alkanes, with different physical properties resulting from their different structures.

Solubilities : Alkanes are nonpolar, so they dissolve in nonpolar or weakly polar organic solvents. Alkanes are said to be hydrophobic (water hating) because they do not dissolve in water. Their hydrophobic nature makes alkanes good lubricants and preservatives for metal, because they keep water away from reaching the metal surface and causing corrosion.

Density : Alkanes have densities of approximately 0·7 g/ml (Table 4.4), compared with a density of 1·0 g/ml for water. Because alkane are less dense than water and insoluble in water, a mixture of an alkane and water quickly separates into two phases, with the alkane on top.

Boiling point : Table 4.4. shows boiling points of the straight chain alkanes. The boiling points increase smoothly with the increasing number of carbon atoms and the increasing molecular weight of the alkanes. Larger molecules have larger surface areas, resulting in increased intermolecular van der Waals attractions. These increased attractions must be broken for vaporization and boiling to occur.

A large molecule with greater surface area and greater van der Waals attractions, boils at a higher temperature.

A graph of *n*-alkane boiling point (Fig. 4.1) versus the number of carbon atoms shows the increase in boiling point with increasing molecular weight. The addition of a CH_2 group increases the boiling point by about 30°C up to about ten carbons, and by about 20°C in the higher alkanes.

In general, a branched chain alkane boils at lower temperature than the corresponding isomeric *n*-alkane (Fig. 4.1). This difference in boiling points is also explained by intermolecular van der Waals forces. For any given number of carbon atoms, a straight-chain alkane has more surface area. Branched alkanes are more compact with less surface area for van der Waals interactions.

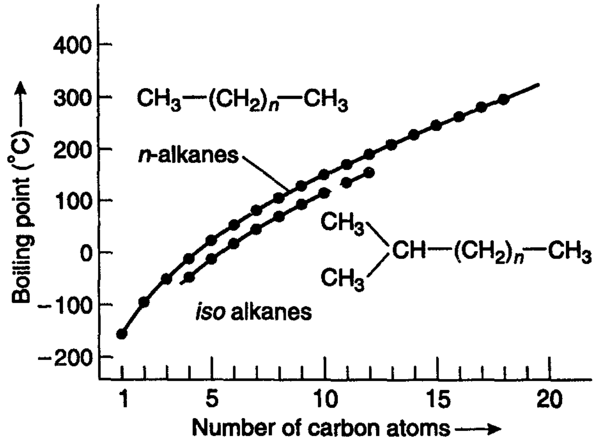


Fig. 4.1. Boiling points of straight chain and branched chain alkanes.

Tale 4.4 ***Physical Properties of n-alkanes***

Alkanes	bp (°C)	mp (°C)	Density
Methane	−162	−183	0.47
Ethane	−89	−183	0.57
Propane	−42	−188	0.50
Butane	0	−138	0.58
Pentane	36	−130	0.56
Hexane	69	−95	0.66
Heptane	98	−91	0.68
Octane	126	−57	0.70
Nonane	151	−54	0.72
Decane	174	−30	0.74
Undecane	196	−26	0.75
Dodecane	216	−10	0.76
Tridecane	235	−5	0.76
Tetradecane	254	6	0.77

Melting Points of Alkanes : Like the boiling points, the melting points generally increase with increasing molecular weight (Fig. 4.2). The melting point graph is not smooth. Alkanes with even numbers of carbon atoms pack better into a solid structure and higher temperatures are needed to melt them. Alkanes with odd numbers of carbon atoms do not pack as well and melt at lower temperature than their just higher or lower homologue with even numbers of carbon atoms. The sawtooth shaped graph of melting points is smoothed by drawing separate lines (thin lines) for the alkanes with even and odd number of carbon atoms.

Branching of the alkane chain also affects its melting point. A branched alkane generally melts at a higher temperature than the *n*-alkane with the same number of carbon atoms. Branching of an

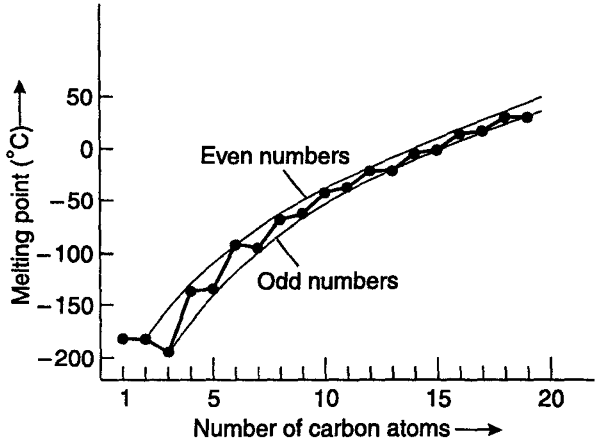
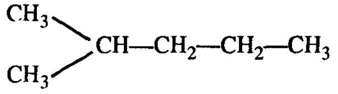
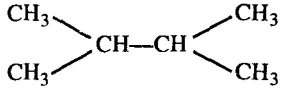
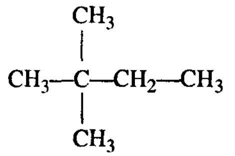


Fig. 4.2. The melting points of *n*-alkanes with even numbers of carbon atoms are slightly higher than those with odd numbers of carbons.

alkane gives it a more compact three-dimensional structure, which packs more easily into a solid structure and increases its melting point (Table 4.5).

Table 4.5 ***Boiling and melting points of some branched-chain isomers***

Isomer	Boiling point	Melting point
	60	−154
	58	−135
 $CH_3-C(CH_3)_2-CH_2-CH_3$	50	−98

4.8 REACTIONS OF ALKANES

The name saturated hydrocarbon or **paraffin** (which means too little affinity) was originally introduced to indicate that the chemical affinity of this class of compounds for most common reagents may be regarded as saturated or satisfied. Alkanes are among the least reactive organic compounds but they are by no means chemically inert. Under suitable reaction conditions they undergo a wide variety of reactions. The processes which involve reactions such as halogenation, oxidation, nitration, dehydrogenation, aromatization and isomerization will be discussed here.

4.8.1 Halogenation

Alkanes are important starting materials for the synthesis of alkyl halides. Flourine, chlorine and bromine readily react with alkanes to form mono- and polyhalogenated products.

$$R\text{—}CH_3 + X_2 \longrightarrow \underset{\text{Monohalogenated}}{R\text{—}CH_2\text{—}X}$$

$$R\text{—}CH_3 + X_2 \longrightarrow \underset{\text{Polyhalogenated}}{R\text{—}CHX_2 + RCX_3}$$

The reactivity of halogens are in the following order :

Fluorine > Chlorine > Bromine

Iodine is generally unreactive.

No halogenation occurs in dark at ordinary temperature except with fluorine. But with UV light or at higher temperature reaction occurs with chlorine and bromine. This type of halogenation occurs by a **radical chain mechanism.** The important steps in free radical chain mechanism are (i) Initiation (ii) Propogation and (iii) Termination.

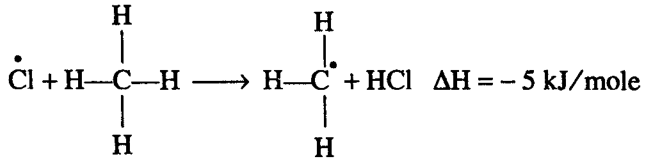
(I) Chlorination

(i) Initiation : For the reaction to occur a C—H and Cl—Cl bond must be broken and a C—Cl and H—Cl bond must be formed. The Cl—Cl bond (bond energy = 58 kcal/mole) is weaker than C—H bond (bond energy = 102 kcal/mole) and is cleaved in a homolytic fashion by UV light or heat.

$$Cl\text{—}Cl \xrightarrow[\text{or } \Delta\ (200\text{–}400°C)]{h\nu\ (\text{UV light})} \dot{C}l + \dot{C}l \quad \Delta H = +244\ \text{kJ/mole} \qquad \ldots(1)$$

This process is endothermic and known as initiation process. Once the reaction is initiated, it will proceed in the absence of light of heat. In chlorination reaction chlorinating agent may also be SO_2Cl_2 and $(CH_3)_3C\text{—}O\text{—}Cl$.

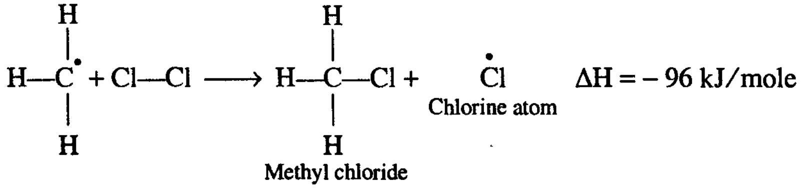
(ii) Propogation : After some chlorine free radicals have been produced, two steps are possible. Firstly, a chlorine free radical can abstract a hydrogen atom from the methane producing a molecule of HCl and methyl radical.



$$\dot{C}l + H\text{—}\overset{H}{\underset{H}{C}}\text{—}H \longrightarrow H\text{—}\overset{H}{\underset{H}{\dot{C}}} + HCl \quad \Delta H = -5\ \text{kJ/mole} \qquad \ldots(2)$$

ΔH suggest that the energy change is favourable though small.

Secondly, the methyl radical can then remove a chlorine atom from a chlorine molecule forming methyl chloride and a new chlorine atom (chlorine atom means chlorine free radical).



$$H\text{—}\overset{H}{\underset{H}{\dot{C}}} + Cl\text{—}Cl \longrightarrow \underset{\text{Methyl chloride}}{H\text{—}\overset{H}{\underset{H}{C}}\text{—}Cl} + \underset{\text{Chlorine atom}}{\dot{C}l} \quad \Delta H = -96\ \text{kJ/mole} \qquad \ldots(3)$$

Another chlorine free radical is formed in this step and the step is exothermic. Thus an important feature of the mechanism is that the chlorine free radical consumed in the first step is replaced by another free radical in the second step. This type of behaviour is typical of a chain process. This free radical can attack yet another methane molecule thus continuing the process. In practice the chain length is limited by recombination reactions which terminate the chain.

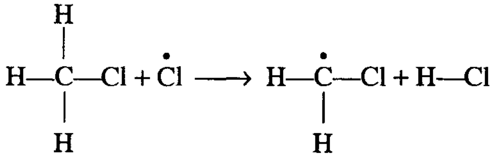
(iii) Termination : Chain termination occurs when chlorine free radicals and methyl radicals combine as follows :

$$\dot{\mathrm{Cl}} + \dot{\mathrm{Cl}} \longrightarrow \mathrm{Cl_2}$$

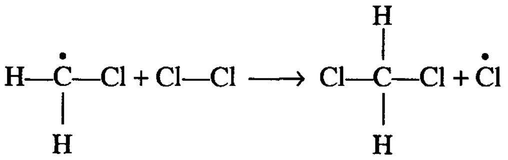
$$\dot{\mathrm{C}}\mathrm{H_3} + \dot{\mathrm{C}}\mathrm{H_3} \longrightarrow \mathrm{CH_3{-}CH_3}$$

$$\dot{\mathrm{C}}\mathrm{H_3} + \dot{\mathrm{Cl}} \longrightarrow \mathrm{CH_3{-}Cl}$$

The halogen free radical generated in step (3) can also abstract hydrogen atom from the methyl chloride formed in that step and lead to the formation of a new substituted alkyl radical. The new alkyl radical can then react with another molecule of chlorine to form a dichloromethane and a chlorine atom (Setps (4) and (5)).

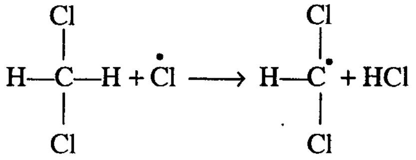


$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}Cl} + \dot{\mathrm{Cl}} \longrightarrow \mathrm{H{-}\underset{H}{\dot{C}}{-}Cl + H{-}Cl} \qquad ...(4)$$

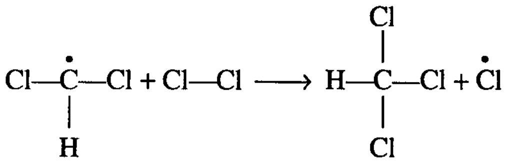


$$\mathrm{H{-}\underset{H}{\dot{C}}{-}Cl + Cl{-}Cl} \longrightarrow \mathrm{Cl{-}\overset{H}{\underset{H}{C}}{-}Cl} + \dot{\mathrm{Cl}} \qquad ...(5)$$

This process can go on till all the replaceable hydrogens in the methane are replaced by chlorine.

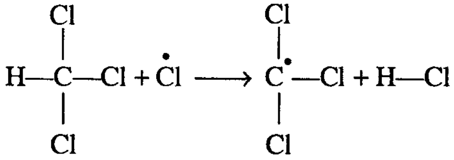


$$\mathrm{H{-}\overset{Cl}{\underset{Cl}{C}}{-}H} + \dot{\mathrm{Cl}} \longrightarrow \mathrm{H{-}\overset{Cl}{\underset{Cl}{\dot{C}}} + HCl} \qquad ...(6)$$

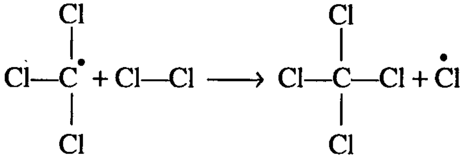


$$\mathrm{Cl{-}\underset{H}{\dot{C}}{-}Cl + Cl{-}Cl} \longrightarrow \mathrm{H{-}\overset{Cl}{\underset{Cl}{C}}{-}Cl} + \dot{\mathrm{Cl}} \qquad ...(7)$$

Chloroform

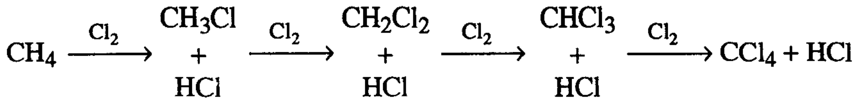


$$\mathrm{H{-}\overset{Cl}{\underset{Cl}{C}}{-}Cl} + \dot{\mathrm{Cl}} \longrightarrow \mathrm{\overset{Cl}{\underset{Cl}{\dot{C}}}{-}Cl + H{-}Cl} \qquad ...(8)$$



$$\mathrm{Cl{-}\overset{Cl}{\underset{Cl}{\dot{C}}} + Cl{-}Cl} \longrightarrow \mathrm{Cl{-}\overset{Cl}{\underset{Cl}{C}}{-}Cl} + \dot{\mathrm{Cl}} \qquad ...(9)$$

Carbon tetrachloride

or 

$$CH_4 \xrightarrow{Cl_2} \begin{matrix} CH_3Cl \\ + \\ HCl \end{matrix} \xrightarrow{Cl_2} \begin{matrix} CH_2Cl_2 \\ + \\ HCl \end{matrix} \xrightarrow{Cl_2} \begin{matrix} CHCl_3 \\ + \\ HCl \end{matrix} \xrightarrow{Cl_2} CCl_4 + HCl$$

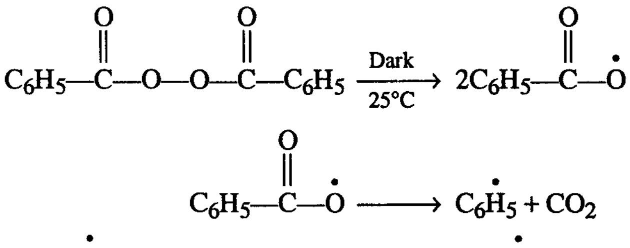
The conversion of methane into alkyl halide is generally controlled by the ratio of chlorine to methane.

$$CH_4 + \underset{\text{Excess}}{4Cl_2} \longrightarrow CCl_4 + 4HCl$$

$$\underset{\text{Excess}}{CH_4} + Cl_2 \longrightarrow CH_3Cl + HCl$$

Evidence for a free radical mechanism

(i) If the reaction actually followed the above mechanism, then the addition of initiator should initiate the reaction even in the absence of light at room temperature. This is actually so. For example, there is practically no reaction between Cl_2 and C_2H_6 at 120°. However, in the presence of dibenzoyl peroxide Cl_2 reacts with C_2H_6 very vigorously.



$$C_6H_5—\overset{\overset{O}{\|}}{C}—O—O—\overset{\overset{O}{\|}}{C}—C_6H_5 \xrightarrow[25°C]{\text{Dark}} 2C_6H_5—\overset{\overset{O}{\|}}{C}—\dot{O}$$

$$C_6H_5—\overset{\overset{O}{\|}}{C}—\dot{O} \longrightarrow \dot{C_6}H_5 + CO_2$$

$$\dot{C_6}H_5 + Cl—Cl \longrightarrow C_6H_5Cl + \underset{\text{Chlorine free radical}}{\dot{Cl}}$$

Once the chlorine free radicals are produced the reaction can proceed in the manner described above.

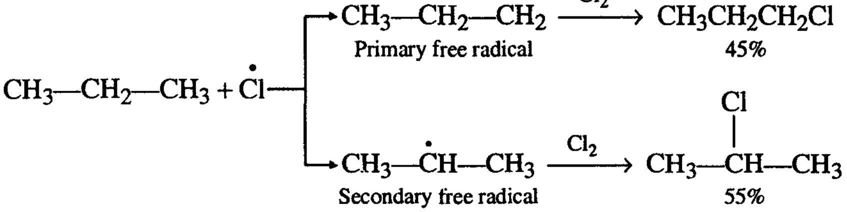
(ii) The reaction is inhibited by oxygen. Even a very small amount of oxygen is enough to slow down the reaction considerably. Oxygen is known to exist as a diradical ($\dot{O}–\dot{O}$) in the ground state. It may act as a free radical inhibitor. Its combination with alkyl radical yields peroxy radical which is much less reactive than the alkyl radical and thereby the chain is broken

$$\dot{R} + \dot{O}—\dot{O} \longrightarrow \underset{\text{Peroxy raidcal}}{R—O—\dot{O}}$$

(iii) The reaction has a high quantum yield.

$$\text{The quantum yield } \Phi = \frac{\text{Number of molecules reacting or produced}}{\text{Number of quanta aborbed}}$$

Chlorination of ethane gives a single monochloro product, C_2H_5Cl, but with propane and the higher alkane, mixtures of products are usually obtained.



Propane contains two types of hydrogens (primary and secondary). Therefore, it gives two monosubstituted products. It has been observed that the reactivity of a hydrogen in an alkane depends mainly on its class (primary, secondary or tertiary) and not on the alkane in which it is present. Thus the ease of substitution at various carbon atoms is of the order Tertiary > Secondary > Primary. This observation is due to the stability of free radicals.

Table 4.6 ***The values ΔH (kJ/mole) for the steps i–iv and the overall reaction leading to CH_3X***

Reaction	F	Cl	Br	I
(i) $X_2 \longrightarrow 2\dot{X}$	+155	+244	+193	+152
(ii) $\dot{X} + CH_4 \longrightarrow \dot{C}H_3 + HX$	−138	−5	+63	+130
(iii) $\dot{C}H_3 + X_2 \longrightarrow CH_3X + \dot{X}$	−298	−96	−88	−71
(iv) $\dot{X} + \dot{X} \longrightarrow X_2$	−155	−244	−193	−152
ΔH	−436	−101	−25	+59

(II) Fluorination

Fluorination of alkanes is so violent that it results in the clevage of C—C and C—H bonds. This can be understood by a consideration of bond dissociation energies of various species involved in the reaction (Table 4.6).

Although direct fluorination of alkanes is not useful, fluorine can be substituted for hydrogen *via* the use of less reactive fluorinating agent, such as cobaltic fluoride (CoF_3). CoF_3 is prepared by the reaction of cobaltous fluoride with fluorine.

$$2CoF_2 + F_2 \longrightarrow 2CoF_3$$

$$CH_4 + 2CoF_3 \longrightarrow CH_3F + 2CoF_2 + HF$$

$$CH_4 + 8CoF_3 \longrightarrow CF_4 + 8CoF_2 + 4HF$$

(III) Bromination

Bromination of alkane has close similarity to chlorination except for the fact that the rate of reaction in slow. This is due to the ΔH value of the reaction (Table 4.6). Brominating agent of the bromination reaction is Br_2 ($h\nu$).

(IV) Iodination

Iodine is unreactive although the chain initiation process is the easiest of all the halogenation process (ΔH = + 152 kJ/mole) but the first propogation step is endothermic and so the overall reaction is endothermic (ΔH = + 59). Furthermore, the reaction is reversible resulting in the generation of the alkane.

$$R\text{—}H + I_2 \rightleftharpoons R\text{—}I + HI$$

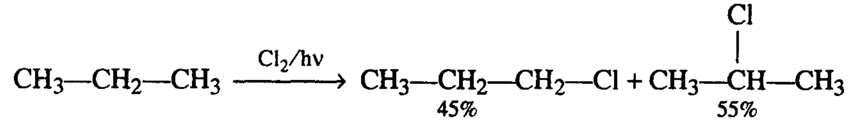
But in the presence of an oxidising agent such as iodic acid, iodination occurs as follows :

$$R\text{—}H + I_2 \rightleftharpoons R\text{—}I + HI$$

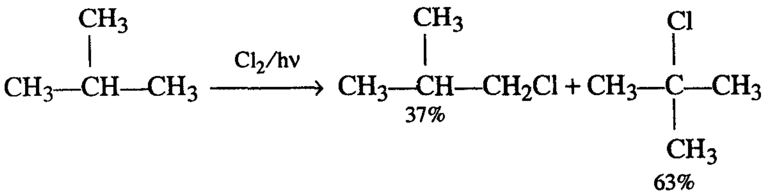
$$5HI + HIO_3 \longrightarrow 3I_2 + H_2O$$

Selectivity in Halogenation

Selectivity of chlorine : A chlorine free radical is so reactive that it makes primary, secondary and tertiary radicals with almost equal ease. According to reactivity selectivity principle **the greater the reactivity of a species, less will be selectivity,** chlorination reaction is not selective reaction.

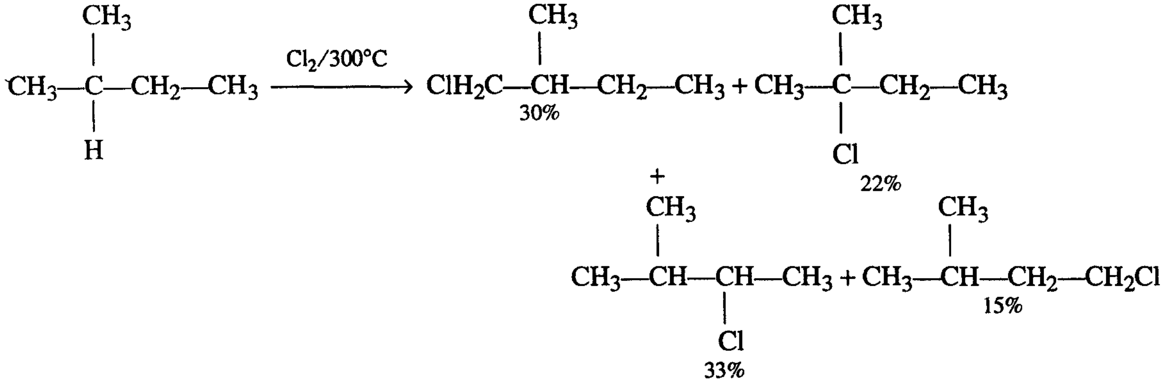


$$CH_3\text{—}CH_2\text{—}CH_3 \xrightarrow{Cl_2/h\nu} \underset{45\%}{CH_3\text{—}CH_2\text{—}CH_2\text{—}Cl} + \underset{55\%}{CH_3\text{—}\overset{\overset{Cl}{|}}{C}H\text{—}CH_3}$$



$$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-CH_3 \xrightarrow{Cl_2/hv} CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2Cl + CH_3-\underset{\underset{CH_3}{|}}{\overset{Cl}{\overset{|}{C}}}-CH_3$$

37% 63%



$$CH_3-\underset{\underset{H}{|}}{\overset{CH_3}{\overset{|}{C}}}-CH_2-CH_3 \xrightarrow{Cl_2/300°C} ClH_2C-\overset{CH_3}{\overset{|}{C}H}-CH_2-CH_3 + CH_3-\underset{\underset{Cl}{|}}{\overset{CH_3}{\overset{|}{C}}}-CH_2-CH_3$$

30% 22%

$$+\ CH_3-\overset{CH_3}{\overset{|}{C}H}-\underset{\underset{Cl}{|}}{CH}-CH_3 + CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2-CH_2Cl$$

33% 15%

The ratios of products that we obtain from chlorination reaction of higher alkanes are not identical with what we would expect if all hydrogen atoms of the alkane were equally reactive.

After experimentally determining the amount of each chlorination product obtained from various hydrocarbons, chemists were able to calculate that at room temperature it is 5·0 times easier for a chlorine radical to abstract hydrogen atom from a tertiary carbon than from a primary carbon, and it is 3·8 times easier to abstract a hydrogen atom from secondary carbon than from a primary carbon. The precise ratio differs at different temperatures.

Thus relative rates of formation of alkyl radical by a chlorine radical is

Tertiary	>	Secondary	>	Primary
5·0		3·8		1·0

To determine the relative amount of products obtained from radical chlorination of alkane, for example *n*-butane, both the **probability** factor (the number of hydrogens that can be abstracted that will lead to the formation of the particular product) and the reactivity factor (the relative rate at which a particular hydrogen is abstracted) must be taken into account.

(i) The relative amount of 1-chlorobutane = Number of hydrogens present on 1°-carbon × reactivity $= 6 \times 1{\cdot}0 = 6{\cdot}0$

(ii) The relative amount of 2-chlorobutane = Number of hydrogens present on 2° carbon × reactivity $= 4 \times 3{\cdot}8 = 15{\cdot}2$

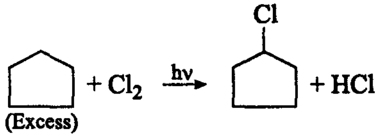
Sum of the relative amount of all products $= 6 + 15 = 21$

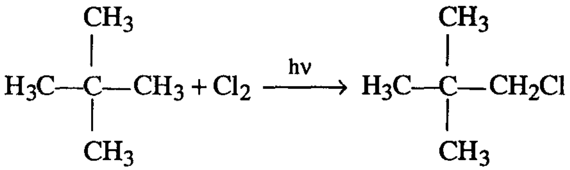
$$\text{Per cent yield} = \frac{\text{relative amount} \times 100}{\text{sum of relative amounts}}$$

$$\text{Thus per cent yield of 1-chlorobutane} = \frac{6 \times 100}{21} = 29\%$$

$$\text{Per cent yield of 2-chlorobutane} = \frac{15 \times 100}{21} = 71\%$$

Since chlorination is non-selective, it is a useful reaction only when there is one kind of hydrogen in the molecule.





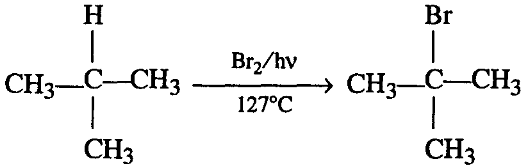
$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 + Cl_2 \xrightarrow{hv} H_3C-\underset{CH_3}{\overset{CH_3}{C}}-CH_2Cl$$

$$\underset{\text{(excess)}}{C_6H_5-CH_3} \xrightarrow{Cl_2/hv} C_6H_5-CH_2Cl$$

$$\underset{\text{(small)}}{C_6H_5-CH_3} \xrightarrow{Cl_2/hv} C_6H_5-CCl_3$$

Selectivity of Bromine : Bromine is less reactive toward alkanes than chlorine hence bromine is more selective in the site of attack when it does react.

The reaction of isobutane and bromine, for example, gives almost exclusive replacement of tertiary hydrogen atom.



$$CH_3-\underset{CH_3}{\overset{H}{C}}-CH_3 \xrightarrow[127°C]{Br_2/hv} CH_3-\underset{CH_3}{\overset{Br}{C}}-CH_3$$

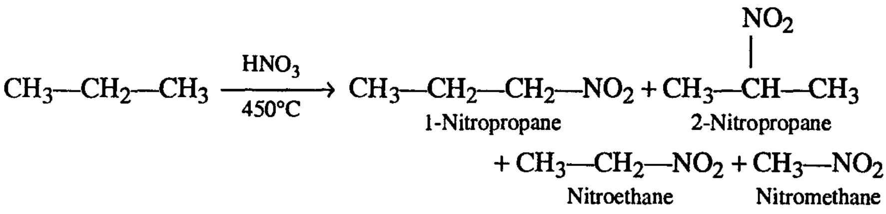
99% yield

4.8.2 Nitration

This involves the substitution of a hydrogen atom of alkane with a nitro group ($-NO_2$). Alkanes can be nitrated with nitric acid in gas phase generally at a temperature 150°–500°. The process is known a **vapour phase nitration**

$$R-H + HO-NO_2 \longrightarrow \underset{\text{Nitroalkane}}{R-NO_2} + H_2O$$

The reaction is more complicated than represented above. Since the reaction is carried out at higher temperature the C—C bonds of alkanes break during the reaction and mixtures of nitroalkanes are formed. Thus in the nitration of propane the following products are obtained.



$$CH_3-CH_2-CH_3 \xrightarrow[450°C]{HNO_3} \underset{\text{1-Nitropropane}}{CH_3-CH_2-CH_2-NO_2} + \underset{\text{2-Nitropropane}}{CH_3-\overset{NO_2}{CH}-CH_3}$$
$$+ \underset{\text{Nitroethane}}{CH_3-CH_2-NO_2} + \underset{\text{Nitromethane}}{CH_3-NO_2}$$

Nitration also proceeds through a free radical mechanism similar to halogenation.

Chain initiation $HO-NO_2 \xrightarrow[\text{Slow}]{\Delta} \dot{O}H + \dot{N}O_2$

Chain propogation $R-H + \dot{O}H \longrightarrow \dot{R} + HOH$

$\dot{R} + HO-NO_2 \longrightarrow RNO_2 + \dot{O}H$

Termination $\dot{R} + HO-NO_2 \longrightarrow R-OH + \dot{N}O_2$

4.8.3 Sulphonation

This involves the substitution of a hydrogen atom of alkane with sulphonic acid group (—SO_3H). Alkanes can be sulphonated by fuming sulphuric acid or oleum. Hexanes and higher hydrocarbons produce alkanesulphonic acids at higher temperature but lower hydrocarbons do not respond to sulphonation reaction. Sulphonation is also a free radical reaction.

$$R\text{—}H + HO\text{—}SO_3H \longrightarrow \underset{\text{Alkanesulphonic acid}}{R\text{—}SO_3H} + H_2O$$

$$C_6H_{14} + HO\text{—}SO_3H \longrightarrow \underset{\text{Hexanesulphonic acid}}{C_6H_{13}SO_3H} + H_2O$$

The ease of sulphonation is

tertiary > secondary > primary

4.8.4 Oxidation

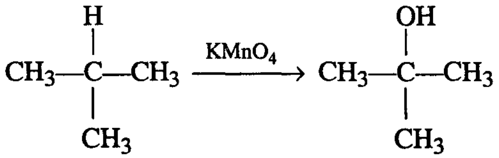
All alkanes readily burn in excess of air or oxygen to form CO_2, water and heat. The generation of heat in this process has been exploited by using them as a fuel in the internal combustion engines.

Controlled oxidation, on the other hand, under various conditions leads to different products.

Alkanes, when burnt in the presence of catalyst at higher temperature and pressure, yield alcohol, aldehydes, ketones and acids.

$$CH_4 + O \xrightarrow[\text{400°/200 Atmosphere}]{\text{Cu}} CH_3OH \xrightarrow{[O]} HCHO \xrightarrow{[O]} HCOOH$$

Alkanes with tertiary hydrogen are easily oxidised to tertiary alcohol with certain oxidising agents such as $KMnO_4$.



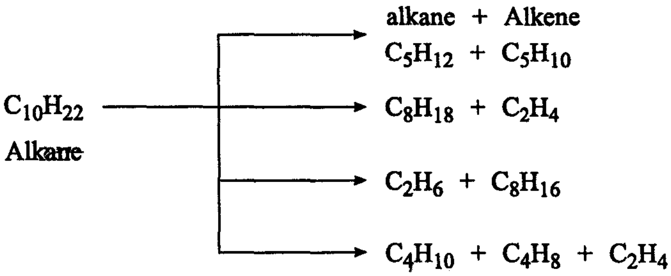
$$CH_3\text{—}\overset{H}{\underset{CH_3}{C}}\text{—}CH_3 \xrightarrow{KMnO_4} CH_3\text{—}\overset{OH}{\underset{CH_3}{C}}\text{—}CH_3$$

4.8.5 Cracking or Pyrolysis or Thermal Decomposition

Cracking is of two types :

(a) Thermal cracking : Heating of substance at very high temperature (> 400°C) in the absence of air or oxygen is known as thermal cracking. This reaction is free radical reaction in which breaking of C—C and C—H bonds takes place.

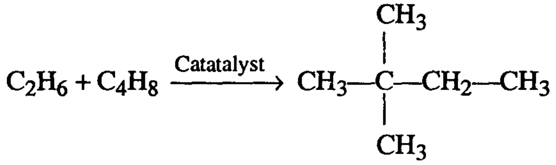
(b) Catalytic cracking : When mixture of alkanes are heated at very high temperature in the presence of catalyst (alumina, silica and aluminium silicate clay) and in the absence of air or oxygen, the process is known as catalytic cracking.



Higher boiling point alkanes can be cracked by thermal or catalytic cracking, to give products with shorter carbon chains and therefore lower boiling points. The carbon chain can break at many points.

To balance the number of hydrogens, any particular alkane must give at least one alkane and one alkene as products. Thus cracking converts larger alkanes into mixture of smaller alkanes and alkenes. Thus this method can be used for the manufacture of gasoline from kerosene. During cracking, the large amounts of the lower gaseous hydrocarbons : ethylene, propene, butenes and butanes are formed.

When cracking is carried out in the presence of catalyst (catalytic cracking) alkene combines with alkane (known as alkylation) to give highly branched lower alkanes containing five to ten carbons. This catalytic cracking is used to make high octane gasoline.



$$C_2H_6 + C_4H_8 \xrightarrow{\text{Catatalyst}} CH_3\text{—}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\text{—}CH_2\text{—}CH_3$$

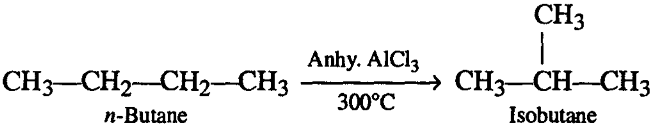
$$C_4H_{10} + C_4H_8 \xrightarrow{\text{Catalyst}} \underset{\text{Isooctane}}{C_8H_{18}}$$

Note : Thermal decomposition of any organic compound is known as pyrolysis. When pyrolysis occurs in alkane, it is called cracking.

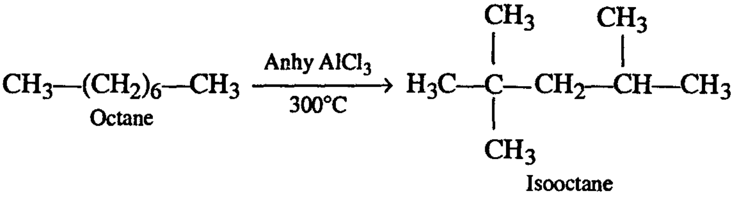
4.8.6 Reforming

Reforming alters the molecular structures of the components of low-octane gasolines to form a higher octane fuel. The two main reforming processes are isomerisation and aromatisation.

(A) Isomerisation : Straight chain alkanes are converted into their branched chain isomers when heated at 300°C in the presence of anhydrous aluminium chloride.

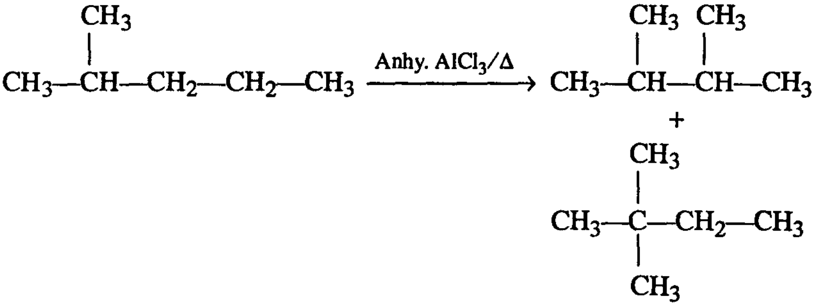


$$\underset{n\text{-Butane}}{CH_3\text{—}CH_2\text{—}CH_2\text{—}CH_3} \xrightarrow[300°C]{\text{Anhy. AlCl}_3} \underset{\text{Isobutane}}{CH_3\text{—}\overset{\overset{\displaystyle CH_3}{|}}{CH}\text{—}CH_3}$$



$$\underset{\text{Octane}}{CH_3\text{—}(CH_2)_6\text{—}CH_3} \xrightarrow[300°C]{\text{Anhy AlCl}_3} \underset{\text{Isooctane}}{H_3C\text{—}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\text{—}CH_2\text{—}\overset{\overset{\displaystyle CH_3}{|}}{CH}\text{—}CH_3}$$

In a similar manner less branched chain alkanes isomerise to give more branched isomers.



$$CH_3\text{—}\overset{\overset{\displaystyle CH_3}{|}}{CH}\text{—}CH_2\text{—}CH_2\text{—}CH_3 \xrightarrow{\text{Anhy. AlCl}_3/\Delta} CH_3\text{—}\overset{\overset{\displaystyle CH_3}{|}}{CH}\text{—}\overset{\overset{\displaystyle CH_3}{|}}{CH}\text{—}CH_3 + CH_3\text{—}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\text{—}CH_2\text{—}CH_3$$

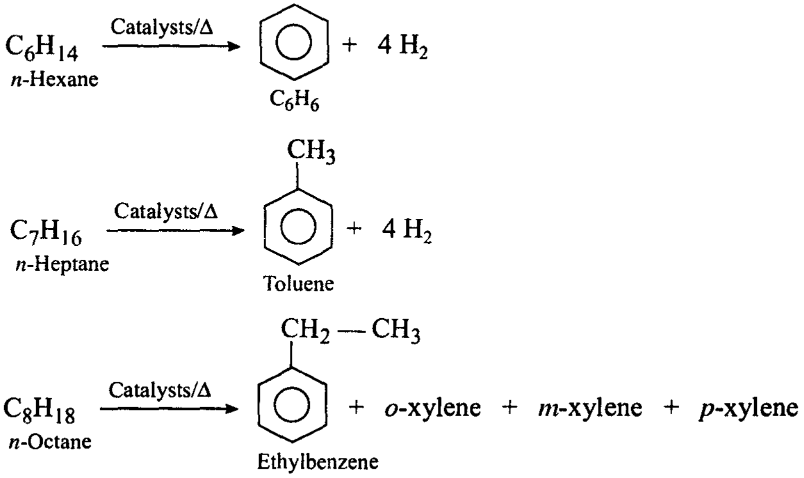
Note :

(a) For this reaction alkane should have four or more than four carbons.

(b) bp of product is always less than the bp of reactant.

(c) Reactant and products are always chain isomers.

(B) Aromatisation : The conversion of aliphatic compounds into aromatic compounds is known as aromatisation. Alkanes having six or more carbon give this reaction which takes place in the presence of catalyst (CrO_3/Al_2O_3 or CrO_3/Pt) at 600°C.



Note :

(a) The reaction is dehydrogenation.
(b) The reaction is oxidation.
(c) The reaction is cyclisation.
(d) Lower alkanes ($C \leq 5$) also undergo dehydrogenation to give alkene.

$$CH_3—(CH_2)_2—CH_3 \xrightarrow{CrO_3/Al_2O_3/600°C} \begin{array}{c} CH_3—CH_2—CH{=}CH_2 \\ + \\ CH_3—CH{=}CH—CH_3 + H_2 \end{array}$$

4.8.7. Insertion of Carbene : Insertion of carbene takes place between carbon and hydrogen.

$$H_3C—CH_2\underset{\uparrow}{—}H + CH_2N_2 \xrightarrow{h\nu} CH_3—CH_2—CH_2—H + N_2$$

4.9 CYCLOALKANES : ALICYCLIC COMPOUNDS

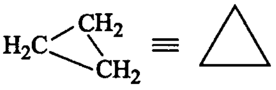
The hydrocarbons, discussed so far, have been in the form of open chain compounds. In many hydrocarbons, however, the carbon atoms are arranged to form a ring; these are called cyclic compounds. These compounds are also known collectively as carbocyclic or homocyclic compounds.

These compound have cyclic structures but resemble aliphatic (open chain) compounds in many properties, hence are called alicyclic compounds (aliphatic cyclic compounds). The saturated alicyclic hydrocarbons have the general formula C_nH_{2n}. When the molecular formula of saturated hydrocarbon corresponds to the general formula C_nH_{2n-1}, the compound contains two rings, if to C_nH_{2n-4}, three rings, etc.

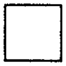
Alicyclic compounds can be classified into four groups namely (i) small rings, *i.e.*, 3 and 4 membered rings (ii) normal or common rings, *i.e.*, 5 to 7 membered rings (iii) medium rings, *i.e.*, 8 to 11 membered and (iv) large rings, *i.e.*, 12 membered and above.

4.9.1 Nomenclature of Cycloalkanes

Cycloalkanes are also called as polymethylenes because these have methylene units (CH_2) linked together in the form of a ring. Thus, cycloalkanes are named by putting a prefix such as tri, tetra, etc. before the word methylene. For example :



Trimethylene



Tetramethylene

Pentamethylene

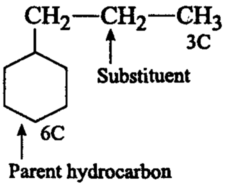
Hexamethylene

According to the IUPAC System : **1.** The saturated monocyclic hydrocarbons take the names of the corresponding open-chain hydrocarbons preceded by the prefix cyclo and they are known as cycloalkanes. For example :

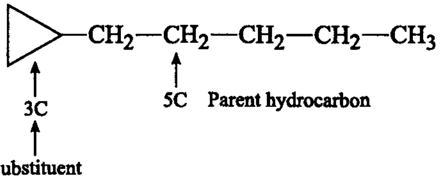
Cyclopropane

Cyclohexane

2. In the case of alkyl substituted cycloalkanes, the ring is the parent hydrocarbon unless the substituent has more carbon than the ring. In that case, the substituent is the parent hydrocarbon and the ring is named as a substituent.

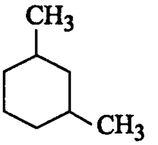


Propylcyclohexane

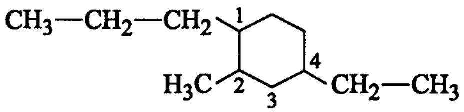


1-Cyclopropylpentane

3. If there is more than one substituent on the ring, the substituents are represented in alphabetical order. One of the substituents is given the number 1 position and the ring is numbered from that position in a direction (either clockwise or anticlockwise) that gives a second substituents the lowest possible number.



1, 3-Dimethylcyclohexane

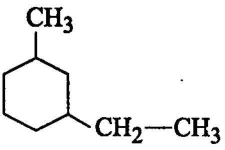


4-Ethyl-2-methyl-1-propylcyclohexane
not
1-Ethyl-3-methyl-4-propylcyclohexane

because $4+2+1=7$

$1+3+4=8$

4. If the ring has only two substituents and they are different, the substituents are cited in alphabetical order and the number 1 position is given to the first cited substituent.

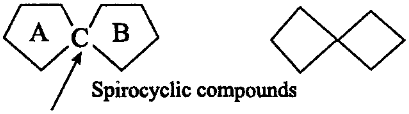


1-Ethyl-3-methylcyclohexane
not
3-Ethyl-1-methylcyclohexane

4.9.2 Bicyclic Compounds

Bicyclic compounds are compounds that contain two rings.

(i) If the two rings share one carbon, the compound is a spirocyclic compound or simply spiro compound. For example :



Spirocyclic compounds

This carbon is part of ring A as well as ring B.

(ii) If the two rings share two adjacent carbons, the compound is a fused bicyclic compound.

Fused bicyclic compounds

(iii) If the two rings share more than two carbons, the compound is a bridged bicyclic compound.

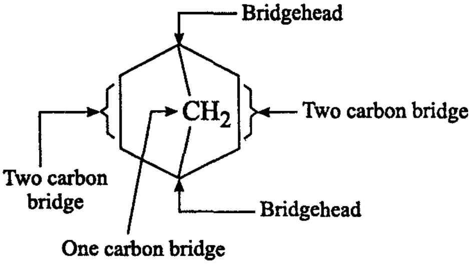
Bicyclic compound

4.9.3 Nomenclature of Bicyclic Compounds

(i) Bicyclic compounds are named by using the alkane name to designate the total number of carbons and the prefix bicyclo or spiro to indicate the number of shared carbons.

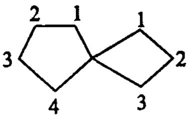
(ii) Prefix spiro indicates one shared carbon and bicyclo indicates two or more shared carbons.

The following compound, for example, contains seven carbon atoms and is therefore, a bicycloheptane.

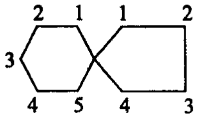


The carbon atoms common to both rings (Number of such carbons is either one in spiro or two in bicyclic) are called bridgeheads and each carbon chain of atoms, connecting the bridgehead atoms is called a bridge.

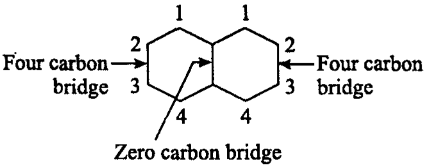
(iii) After the prefix spiro or bicyclic come brackets that contain numbers indicating the number of carbons in each bridge. These are listed in order of decreasing bridge length. For example :



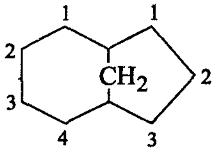
Spiro[4, 3]octane



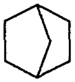
Spiro[5, 4]decane



Bicyclo[4, 4, 0]decane

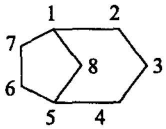


Bicyclo[4, 3, 1]decane

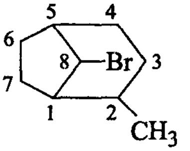


Bicyclo[2, 2, 1]heptane

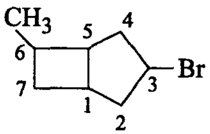
(iv) Numbering in bicyclic compounds starts at any one bridgehead carbon and moves along the longest carbon bridge to the next bridgehead carbon. Continues along the next longest carbon bridge to return to the first bridgehead carbon so that the shortest bridge is numbered last.



Bicyclo[3, 2, 1]octane



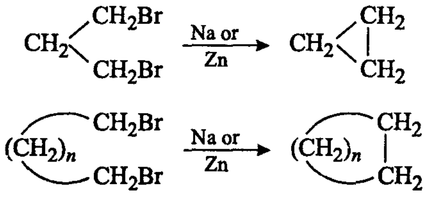
8-Bromo-2-methylbicyclo[3, 2, 1]octane



3-Bromo-6-methylbicyclo[3, 2, 0]heptane

4.9.4 Synthesis of Cycloalkanes (Saturated Alicyclic Hydrocarbons)

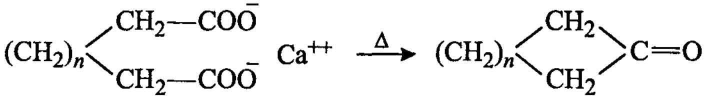
(i) From α, ω-dihalo derivatives of alkanes : When 1,3- to 1,6—dihaloalkanes are treated with metallic sodium or zinc, the corresponding cycloalkanes are formed. 1,7 and higher dihaloalkanes undergo the Wurtz reaction (intramolecular).



$n = 1$ to 4

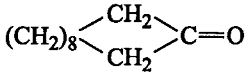
This method is mainly used for the preparation of cyclopropane and the reaction is known as **Freund method.**

(ii) From dicarboxylic acid (Ruzicka method) : Calcium salts of dicarboxylic acids give cyclic ketones on heating (Ruzicka and co-workers; 1926, onwards).

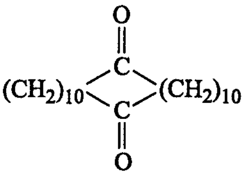


$n = 2$ to 4

Large ring compounds containing up to 34 carbon atoms have been prepared by the pyrolysis of thorium, cerium or yttrium salts of dicarboxylic acids, *e.g.*, the yttrium salt of a dibasic acid $HOOC(CH_2)_{10}COOH$ gave a cyclic hydrocarbon, the cyclic monoketone (I), and the cyclic diketone (II).

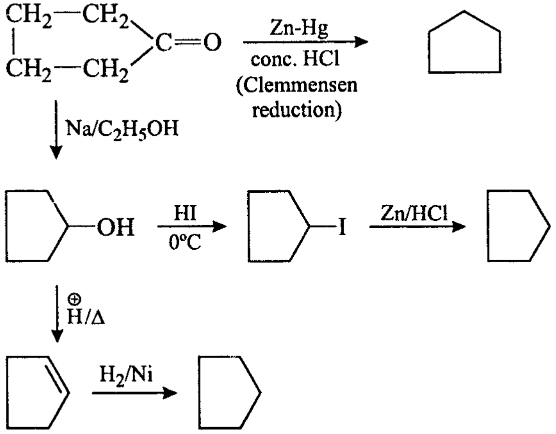


(I)

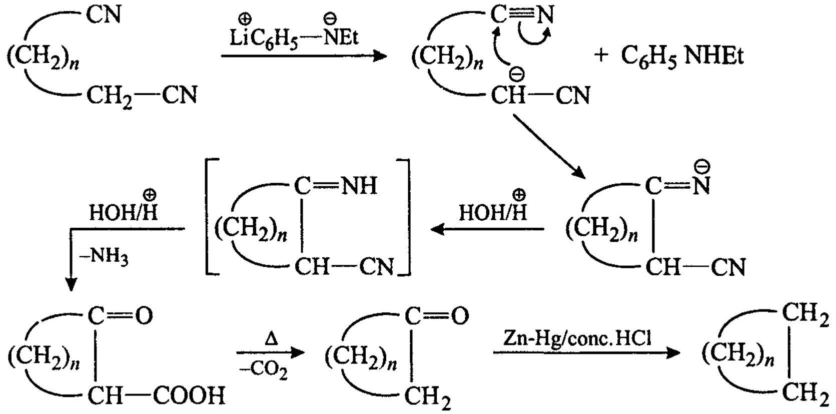


(II)

The above cyclic ketones may be converted into the corresponding cycloalkanes by means of the following methods :

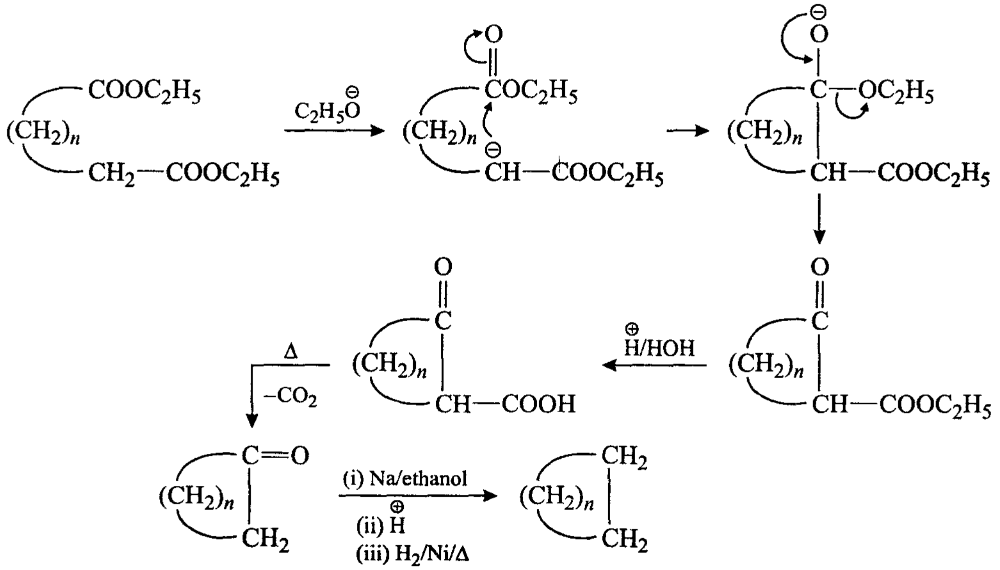


(iii) From α, ω-dinitriles (Thorpe-Ziegler reaction) : When α, ω-dinitriles are subjected to intramolecular condensation, formation of cyclic enaminonitrile takes place. This reaction gives high yield of 14 onwards membered rings if it is carried out at very high dilution condition so that intramolecular reaction is favoured over intermolecular reaction. The reaction is catalysed by sodium or lithium salt of *N*-methylaniline or *N*-ethylaniline as a base. This reaction is known as **Thorpe-Ziegler** reaction. Although this reaction works well for **small, normal and large ring compounds containing more than thirteen carbon atoms**, nine to thirteen membered rings are obtained only in poor yields.

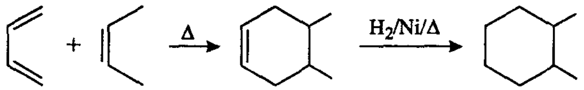


As mentioned above this method uses the high dilution technique for synthesing large ring compounds. High dilution technique (or principle) was given by Ruggli (1912) according to which in sufficiently dilute solutions the distance between groups undergoing intramolecular cyclisation becomes lesser than the intermolecular distances, thus there is better chance of intramolecular cyclisation than the intermolecular condensations.

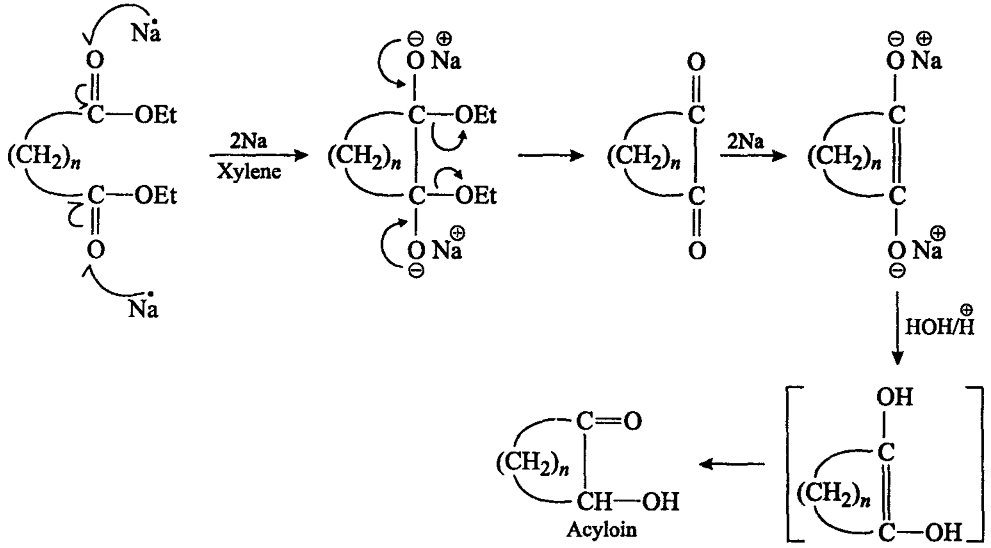
(iv) From α, ω-diesters (Dieckmann reaction) : Intramolecular Claisen condensation of α, ω-diesters in the presence of sodium ethoxide is known as Dieckmann reaction. This method is most useful for the formation of five, six and seven membered rings. The method is also useful for the synthesis of large ring compounds if high dilution technique is employed.



(v) By Diels-Alder Reaction : This is the best method for preparing six membered alicyclic compounds.

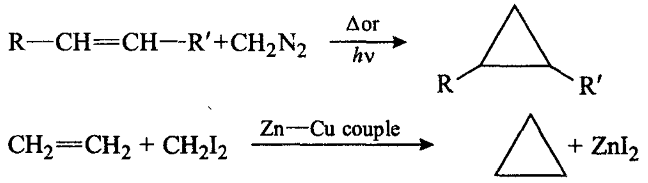


(vi) Acyloin Condensation : This is the most useful method for preparing larger ring compounds. This method does not require the high-dilution technique. α, ω-dicarboxylic esters undergo intramolecular condensation in the presence of sodium metal in xylene (ether, benzene or toluene may also be used) to give acyloin (*i.e.*, α-hydroxyketone).

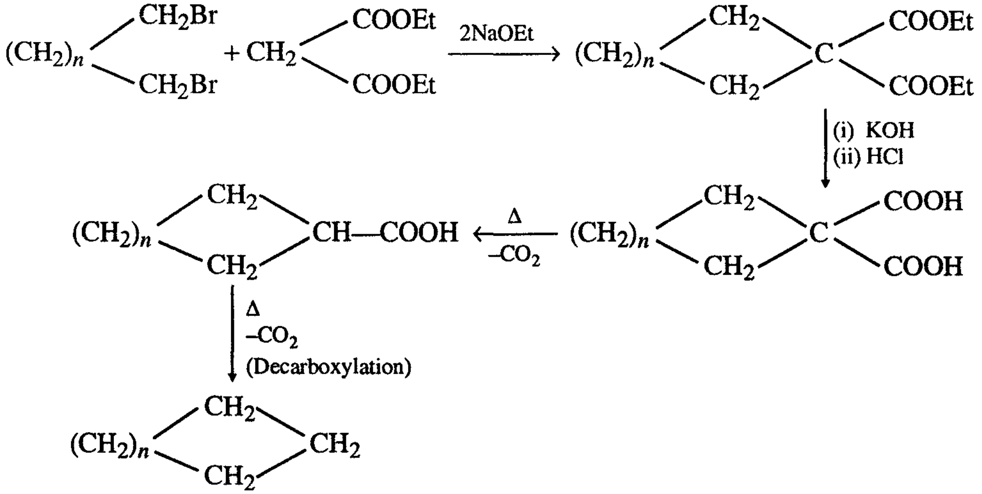


The corresponding cycloalkane is obtained by reduction of the acyloin. Acyloins may be reduded by Clemmensen method to the corresponding cycloalkanes.

(vii) From Alkenes :



(viii) From sodiomalonic ester or sodioacetoacetic easter, *e.g.* :



4.9.5 Physical Properties of Cycloalkanes

Most cycloalkanes resemble the acyclic, open-chain alkanes in their physical properties. They are nonpolar, relatively inert compounds with boiling points and melting points that depend on their molecular weights. The cycloalkanes are held in a more compact cyclic shape, so their physical properties are similar to those of the compact, branched alkanes. Due to the compact structure, melting points and boiling points of cycloalkanes are more than the correspoinding open chain alkanes (Table 4.7).

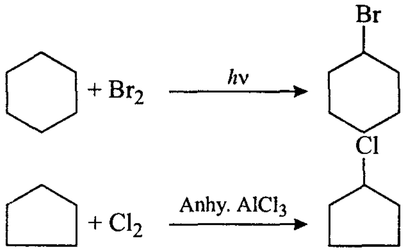
Table 4.7 ***Melting and boiling points of some alkanes and cycloalkanes***

Alkane/cycloalkane	Boiling point (°C)	Melting points (°C)
Propane	–42	–188
Cyclopropane	–33	–128
Butane	0	–138
Cyclobutane	–12	–50
Pentane	36	–130
Cyclopentane	49	–94
Hexane	69	–95
Cyclohexane	81	7
Heptane	98	–91
Cycloheptane	118	–12

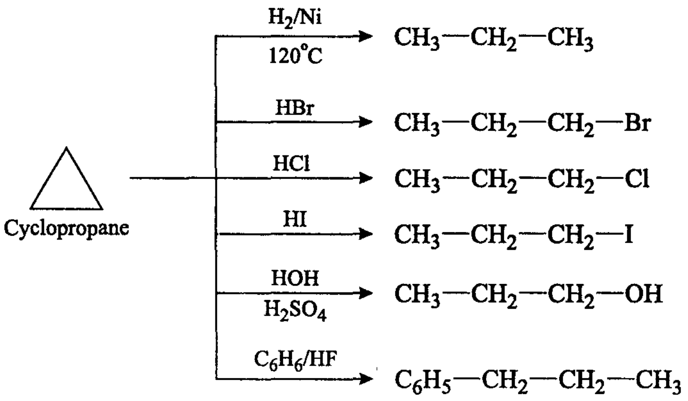
4.9.6 Reactions of Cycloalkanes

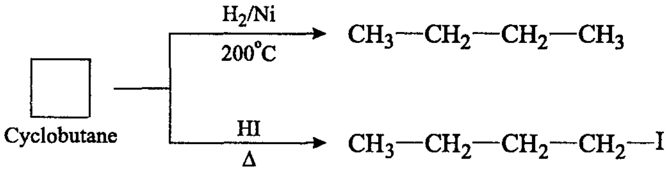
Since cyclopropane and cyclobutane bear high angle strain, they are highly reactive and they behave like alkenes in some cases. Other cycloalkanes behave like alkanes. Some of the important chemical properties are as follows :

Substitution Reactions : When cycloalkanes are treated with chlorine or bromine in the presence of a catalyst or UV light halogenocycloalkanes are obtained. Cyclopropane is the only cycloalkane which gives addition instead of substitution reaction.



Addition Reactions : Lower cycloalkanes, *e.g.*, cyclopropane and cyclobutane behave as alkenes and undergo addition reactions.





4.10 CYCLOPROPANE—BENT OR BANANA BONDS

Cyclopropane possesses a planar triangular structure. The carbons that constitute the ring have no other alternative than to lie on a plane. All the carbon-carbon bonds being equal in length, the three carbons constitute an equilateral triangle in which the C—C—C bond angles are 60°. All the carbons being in sp^3 hybrid state, the angle should have been 109°28′ (~ 109·5°), hence there is really high internal angle strain. This makes the molecule unstable and highly reactive.

The fact that cyclopropane is unstable and ring opens up very easily, would suggest that the carbon-carbon bonds of cyclopropane are not true *sigma* bonds having perfect cylindrical symmetry. Cyclopropane ring being planar, the carbon-carbon bonds are formed by the oblique overlap of sp^3

atomic orbitals to form **bent or banana bond**. The overlap being neither co-axial (as in *sigma* bond) nor parallel to axes (as in *pi* bond), the banana bond has a strength intermediate between the *sigma* and *pi* bonds. Thus overlap is off the axis, giving less effective bent (banana) bonds as shown in Fig. 4.3.

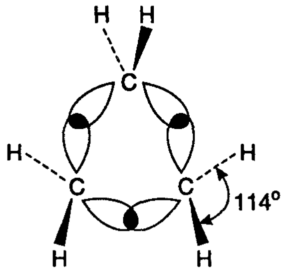
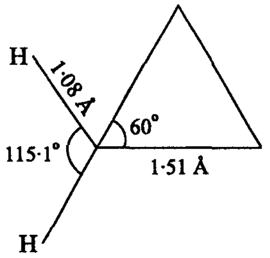


Fig. 4.3. Orbital structure of cyclopropane

According to the *X*-ray diffraction studies, the geometrical structure of cyclopropane is as follows :



The H—C—H bond angle in cyclopropane can be explained as follows :

In order to minimise angle strain (60° instead of 109·5°). The carbons develop more *p*-character in the orbitals forming the ring (*i.e.*, inner orbitals). In turn, the *p*-character of the orbitals involved in C to H bond (outer orbitals) must decrease means *s*-character should increase because the total number of atomic orbitals undergoing the mathematical manipulation must remain one *s* and three *p*. Since bond angles generated from overlapping of *p*-orbitals are 90°, additional *p*-character in the internal bonds decreases the ring strain. To get more *s*-character the hybrid orbitals for the external bonds are somewhere between sp^3 and sp^2, leading to enlargement of the angle. The carbon in outer C—H bonds is more electronegative because it acquires more *s*-character. This more *s*-character in the carbon for outer bonds decreases carbon-hydrogen bond length in comparison to the *n*-propane. Similarly this increased *s*-character of the carbon in the C—H bond increases acidity of the cyclopropane incomparison to propane.

4.11 CYCLOALKANES—RING STRAIN

Ring strain is an energy effect that can be seen clearly in the heat of formation of cycloalkanes.

In alkanes each —CH_2— group contributes about – 5 kcal/mole to ΔH° of a molecule. This means the heat of formation of compounds differing by only one CH_2 differ by a regular increment of about 5 kcal/mole, *e.g.*, ΔH°, kcal/mole.

$$4C + 5H_2 \longrightarrow nC_4H_{10} \qquad -30{\cdot}4$$

$$5C + 6H_2 \longrightarrow nC_5H_{12} \qquad -35{\cdot}1$$

$$6C + 7H_2 \longrightarrow nC_6H_{14} \qquad -39{\cdot}9$$

Since cycloalkanes have the emperical formula $(CH_2)_n$, one can obtain the ΔH° for each CH_2 group by simply dividing ΔH° for the molecule by *n*. The heats of formation of a number of cycloalkanes are given in Table 4.8.

Examination of the Table 4.8 shows that most of these cycloalkanes have less negative values of ΔH°/*n* than the alkane value of about –5 kcal/mole. That is, many cycloalkanes have a higher energy content per CH_2 group than a typical open chain alkane. This excess energy is called ring strain. The total excess energy of a cycloalkane is simply the excess energy per CH_2 multiplied by the number of CH_2 groups in the particular cycloalkane.

Table 4.8 ***Heats of formation (ΔH°) of various cycloalkanes*** $(CH_2)_n$

n	Cycloalkane	ΔH° kcal/mole	ΔH°/*n* kcal/mole per CH_2 group	Total strain energy kcal/mole
3	Cyclopropane	+12.7	+4.2	27
4	Cyclobutane	+6.8	+1.7	26
5	Cyclopentane	–18.4	–3.7	6
6	Cyclohexane	–29.5	–4.9	0
7	Cyclohepane	–28.2	–4.0	6
8	Cyclooctane	–29.7	–3.7	10
9	Cyclononane	–31.7	–3.5	13
10	Cyclodecane	–36.9	–3.7	12

Cyclohexane shows essentially no ring strain. Its CH_2 groups have essentially the same ΔH° as those of normal alkanes. For the purpose of computing the ring strain of a particular cycloalkane, cyclohexane is considered to be strain free. It is the standard for comparison.

For cyclohexane

$$\Delta H^\circ = -29{\cdot}5 \text{ kcal/mole}$$

$$\Delta H^\circ/n = -29{\cdot}5/6 = -4{\cdot}92 \text{ kcal/mole}$$

This value is taken as ΔH° for a strainless CH_2 group (because alkanes which have no strain have also the same value).

For example, ΔH° for a hypothetical strainless cyclopentane would be $-4{\cdot}92 \times 5 = -24{\cdot}6$ kcal/mole.

Hence the strain energy of cyclopentane $= -18{\cdot}4 - (-24{\cdot}6) = +6{\cdot}2$ kcal/mole.

Thus cyclopentane is 6 kcal/mole less stable than it would be if each CH_2 group were in some hypothetical strain-free state.

From the Table 4.8 it is clear that the heat of formation per methylene group reaches a maximum at cyclohexane and then begins to fall again reaching a maximum at cyclononane.

The factors which influence the heat of formation or heat of combustion per CH_2 group in this series of cycloalkanes are collectively termed strain. The extra energy given to a molecule by this strain is its strain energy. Strain energies of some cycloalkanes are given in Table 4.8. The above table shows that cyclopropane and cyclobutane have a large amount of strain and the strain decreases up to cyclohexane. This relative stability of cycloalkanes was explained by Baeyer in the form a theory known as Baeyer-strain theory. It must be kept in mind that Baeyer proposed this theory on the erroneous assumption that cycloalkanes having more than six carbons neither exist nor can be prepared and hence the theory is limited up to cyclohexane only.

4.12 BAEYER-STRAIN THEORY

Baeyer strain theory was based upon the assumption that when an open chain organic compound having the normal bond angle of 109·5° is converted into a cyclic compound, a definite distortion of this normal angle takes place leading to the development of a strain in the molecule. Thus cyclic compounds having deviation from the normal angle value (109·5°) will be having a definite amount of strain depending upon the value of deviation; greater the deviation from the normal angle, greater will be the strain in the molecule resulting in greater instability of the molecule. Baeyer also assumed that cyclic rings are planar. Assuming that the rings are planar, the amount of strain in the various cycloalkanes can be expressed in term of deviation (*d*) from the normal angle by each orbital, which can be calculated from the following equation :

$$d=\frac{1}{2}\left[109\cdot5-\frac{2(n-2)}{n}\times 90\right]$$

or

$$d=\frac{1}{2}[109\cdot5-\alpha]$$

where α is inner bond angle in the cycloalkane, and *n* is the number of carbon atoms constituting the ring.

It is important to note that the distortion of the bond angle (*d*) has been assumed to be equally shared between the two inner orbitals Fig. 4.4.

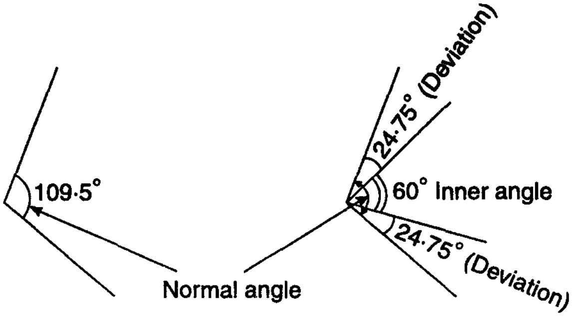
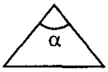
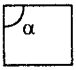
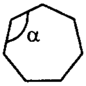
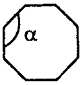


Fig. 4.4.

Now let us take the case of cyclopropane, cyclobutane cyclopentane, cyclohexane, cycloheptane and cyclooctane on the assumption that these rings are planar.

		 α	 α	 α	 α	 α	 α
Inner angle	=	60°	90°	108°	120°	128·5°	135°
d	=	+24·75°	+9·75°	+0·75°	−5·2°	−9·5°	−12·75°

The positive and negative values of valence angle deviation indicate whether the bond angle α is less or more than the normal tetrahedral angle, *i.e.*, whether the strain is inward or outward.

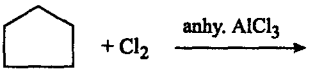
From the above data it is clear that the valence angle deviation is minimum in cyclopentane and not too large in cyclohexane. This led Baeyer to conclude that these rings are having minimum strain and hence are more stable than the cyclopropane and cyclobutane which have greater amount of bond angle deviation and hence greater ring strain.

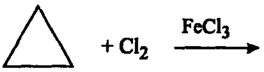
Baeyer-strain theory explains satisfactorily the relative stability of the various cyclic compounds up to five membered ring compounds but it failed beyond this. According to the valence deviation, the six-membered and larger rings must also be unstable because valency deviation in these cases is also considerably high but from the heat of formation data it is seen that these compounds are quite stable. Cyclohexane is more stable than cyclopentane and cycloalkanes, containing more than six carbon atoms in ring are almost as stable as cyclopentane. The Baeyer-strain theory failed to explain the stability of six-membered and larger rings because it was based on wrong assumption that all cyclic compounds were planar.

To explain the stability of large ring compounds, Sachse and Mohr proposed the theory of *strainless rings*. According to the Sachse-Mohr theory of strainless rings, cyclohexane and larger rings are not planar but assume strain-free puckered structure in which each carbon atom retains its valency angle of 109·5°.

VERY SHORT ANSWER QUESTIONS

1. Outline Covey-House synthesis of propane.
2. Give structure and IUPAC name of the lowest molecular weight alkane containing a quaternary carbon.
3. Arrange the following alkanes in order of increasing boiling points :
   n-heptane, 3,3-dimethylpentane, 2-methylhexane
4. Which of the isomeric pentanes will produce the largest number of isomers of monochloro derivatives.
5. How many products are formed in free radical chlorination of methane? Which of the following reaction conditions would be most suitable for the preparation of only monochloromethane :
   (a) equimolar mixture of methane and chlorine (b) excess of chlorine
   (c) excess of methane.
6. Write the sturcture and IUPAC name of the alkane with molecular formula C_8H_{18} which gives only one monochloro derivative.
7. Which of the isomeric pentanes has the lowest boiling point but the highest melting point.
8. Give the structure and name of the product obtained when $C(CH_2Br)_4$ is heated with Zn or Na.
9. Give the structure and IUPAC name of the product obtained by treating 1,2-dimethylcyclopropane with bromine in the presence of $FeBr_3$.
10. Arrange the following cycloalkanes in increasing order of stability :
    (a) cyclobutane (b) cyclopentane (c) cyclopropane (d) cyclohexane
    (e) cycloheptane
11. Arrange the following compounds in increasing order of boiling points :
    (a) pentane (b) 2-methylpentane (c) cyclopentane
12. Arrange the following cycloalkanes in order of decreasing Baeyer's angle strain :
    (a) cyclobutane (b) cyclopentane (c) cyclopropane
13. Which of the following cycloalkanes are not expected to have ring strain :
    (a) cyclobutane (b) cyclohexane (c) cyclopropane (d) cycloheptane
    (e) cyclooctane
14. Complete the following reactions :

(a) 

(b) 

15. How will you convert cyclopropane into butanoic acid?

PROBLEMS WITH SOLUTIONS

1. Provide the IUPAC name for each of the following :
   (a) $(CH_3)_2CHCH_2C(CH_3)_3$ (b) $C(CH_3)_4$
   (c) $(CH_3CH_2)_2CHCH(CH_3)CH_2CH_3$ (d) $CH_3C(Cl)_2CH(CH_3)_2$
2. Write the structural formula for each of the following compounds :
   (a) 3-chloro-2-methylhexane (b) 4-isopropylheptane
   (c) 1,4-dibromo-2-methylbutane (d) 2,2,3-trimethylbutane
3. Write the structural formulae of all the isomeric hexanes and give their IUPAC names.
4. Give the structures and IUPAC names of all dibromo derivatives of propane.
5. Which of the following will convert an alkyl halide into an alkane with the same skeleton ?
   (a) $Zn, \overset{\oplus}{H}$ (b) $LiAlH_4$
   (c) Mg/anhy. ether followed by H_2O (d) All the above
6. Prepare 2-methylpentane starting from 1- and 2-bromopropane.
7. Which of the following will convert acetophenone into ethylbenzene ?
   (a) $LiAlH_4$ (b) $NaBH_4$ (c) Bu_3SnH (d) $H_2N—NH_2/\overset{\ominus}{O}H$
8. Which of the following methods gives pure alkane from alkyl halide ?
   (a) Frankland reaction (b) Wurtz reaction (c) Corey-House synthesis (d) All the above
9. Predict which in each of the following pairs has the higher boiling point and give your reason :
   (a) 2-methylhexane and 2,2-dimethylbutane (b) *n*-hexane and 2,2-dimethylbutane
   (c) *n*-pentane and *n*-hexane
10. Arrange the following in the order of increasing boiling point :
    (a) hexane (b) pentane (c) 2,2-dimethylbutane
11. Write the structure and give the IUPAC name of an alkane or cycloalkane having the formula :
    (a) C_6H_{12} (only secondary hydrogens)
    (b) C_5H_{12} (only primary hydrogens)
    (c) C_5H_{10} (only secondary hydrogens)
    (d) C_5H_{12} (only one tertiary hydrogen)
    (e) C_6H_{14} (only primary and tertiary hydrogens)

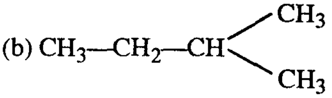
PROBLEMS FOR SELF ASSESSMENT

1. Compare the orbital overlap in cyclopropane with that in alkanes.
2. In terms of hybridisation, what assumptions are made to rationalise the observed H—C—H bond angle (~ 115°) and C—H bond length (1·08 Å) in cyclopropane. Compare the acidity of cyclopropane and propane.
3. Use ring strain to predict relative chemical reactivities of cyclopropane, cyclobutane and cyclopentane.

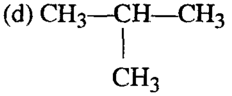
4. In each of the following pairs of compounds, predict which compound has the higher boiling point and give your reason ?
(a) octane and 2,2,3-trimethylpentane (b) heptane and 2-methylnonane.

5. Indicate a combination of a lithium dialkylcuprate and an alkyl halide which would react to form the following alkanes. More than one answer is possible for some of these :

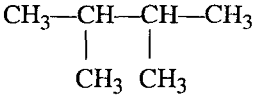
(a) $CH_3—CH_3$

(b)


(c) $CH_3—CH_2—CH_3$

(d)


$CH_3—\underset{CH_3}{\underset{|}{C}}H—CH_3$

(e)


$CH_3—\underset{CH_3}{\underset{|}{C}}H—\underset{CH_3}{\underset{|}{C}}H—CH_3$

6. Although the iodine molecule is the easiest halogen to cleave homolytically, it is the only halogen which does not react with methane. How can you account for this ?

7. Calculate the percentage of 1-chlorobutane and 2-chlorobutane expected in the free radical chlorination of butane. Since the reaction is carried out at room temperature, relative reactivities of 1°, 2° and 3° H's are 1 : 4 : 5, respectively.

8. Give suitable explanation for the following :
(a) The boiling points of isomeric alkanes decreases with the increase in the branching of the chain.
(b) Alkanes having even number of carbon atoms melt at higher temperature than those (just higher or lower homologue) having odd number of carbon atoms.

9. Select from each of the following sets of the hydrocarbons having the lowest and the highest boiling point :
(a) 3,3-dimethylpentae, 2-methylhexane, *n*-heptane
(b) *n*-butane, *n*-hexane, *n*-pentane.

10. How many organic products are obtained on photolytic chlorination of methane ? If you wish to prepare only monochloromethane, then which of the following conditions would be most suitable ?
(a) equimolar mixture of methane and chlorine (b) excess of methane
(c) excess of chlorine.

11. Discuss the synthesis of large ring compounds using the following methods :
(a) Acyloin condensation (b) Thorpe-Ziegler reaction
(c) Dieckmann condensation.

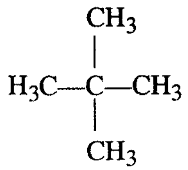
12. Give an account of Baeyer-strain theory. Why did this theory fail to explain the stabilities of larger rings ? Which theory did explain the stabilities of larger rings and how ?

13. Treatment of $C(CH_2Br)_4$ with Zn yields a compound *A* with molecular formula C_5H_8. Suggest a structure for *A*.

14. How will you bring about the following transformations ? (give equations only)
(a) $HOOC—(CH_2)_4—COOH$ into cyclopentane
(b) $EtOOC—(CH_2)_4—COOEt$ into cyclohexane
(c) $N \equiv C—(CH_2)_9—C \equiv N$ into cyclooctane.

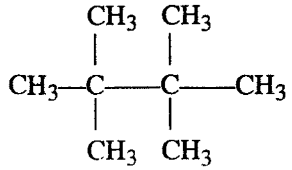
ANSWER TO VERY SHORT ANSWER QUESTIONS

1. $$CH_3I \xrightarrow[-\,LiI]{Li/ether} (CH_3)_2Li \xrightarrow[-\,LiI]{CuI} \underset{\text{lithium dimethylcuprate}}{(CH_3)_2CuLi} \xrightarrow{CH_3CH_2I} \underset{\text{Propane}}{CH_3CH_2CH_3} + \underset{\text{Methylcopper}}{CH_3Cu} + LiI$$

2. 

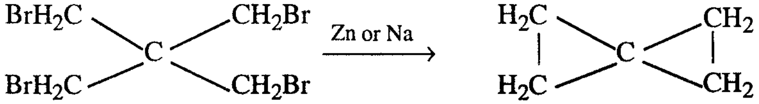
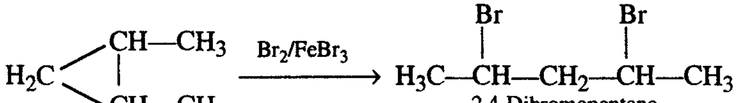
$$H_3C-\overset{\displaystyle CH_3 \atop |}{\underset{\displaystyle | \atop CH_3}{C}}-CH_3$$

2, 2-Dimethylpropane

3. As the branching increases, boiling points decreases, thus the increasing order of boiling points is : 3,3-dimenthylpentane < 2-methylhexane < *n*-heptane
4. 2-Methylbutane (isopentane), it gives four monochloro derivatives.
5. Four products, (c).
6. 

$$CH_3-\overset{\displaystyle CH_3 \atop |}{\underset{\displaystyle | \atop CH_3}{C}}-\overset{\displaystyle CH_3 \atop |}{\underset{\displaystyle | \atop CH_3}{C}}-CH_3$$

2, 2, 3, 3-Tetramethylbutane

7. Neopentane
8. 
9. 

2,4-Dibromopentane

10. Stability of rings increases as the size of the ring increases up to six-membered rings, thereafter the stability almot remains constant, thus

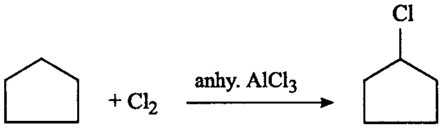
$$(c) < (a) < (b) < (d) \simeq (e)$$

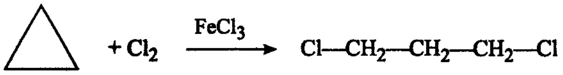
11. With the same molucular formula, the surface area of the cyclic isomer is more than the straight or branched chain acyclic isomers, hence cyclic isomer has the highest boiling point. Thus

$$(b) < (a) < (c)$$

12. Baeyer's angle strain decreases as the size of the ring increases up to five-membered rings, thereafter it keeps on increasing. Thus :

$$(c) > (a) > (b)$$

13. (b), (d) and (e).
14. (a) 

(b) 

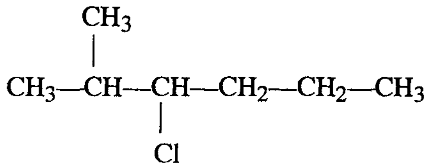
15. (a)

Butanoic acid

SOLUTIONS OF PROBLEMS

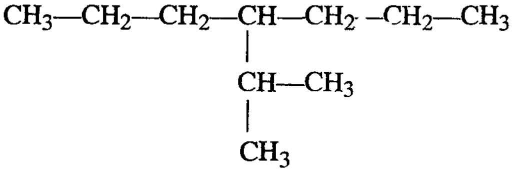
1. (a) 2,2,4-trimethylpentane (b) 2,2-dimethylpropane
(c) 3-ethyl-4-methylhexane (d) 2,2-dichloro-3-methylbutane

2. (a)



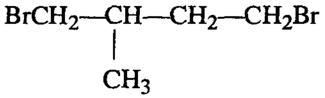
$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-\underset{\underset{\displaystyle Cl}{|}}{C}H-CH_2-CH_2-CH_3$

(b)



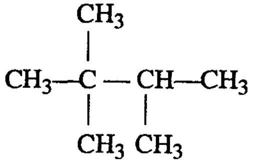
$CH_3-CH_2-CH_2-\underset{\underset{\underset{\underset{\displaystyle CH_3}{|}}{CH-CH_3}}{|}}{C}H-CH_2-CH_2-CH_3$

(c)



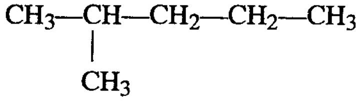
$BrCH_2-\underset{\underset{\displaystyle CH_3}{|}}{C}H-CH_2-CH_2Br$

(d)



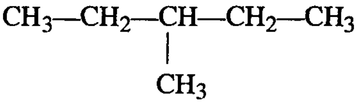
$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\underset{\underset{\displaystyle CH_3}{|}}{C}H-CH_3$

3. $CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$,
Hexane



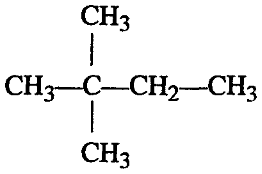
$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}H-CH_2-CH_2-CH_3$

2-methylpentane



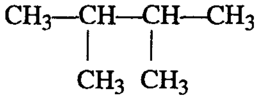
$CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{C}H-CH_2-CH_3$

3-methylpentane



$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-CH_3$

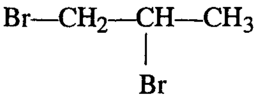
2, 2-dimethylbutane



$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}H-\underset{\underset{\displaystyle CH_3}{|}}{C}H-CH_3$

2, 3-dimethylbutane

4.

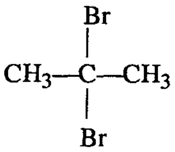


$Br-CH_2-\underset{\underset{\displaystyle Br}{|}}{C}H-CH_3$

1, 2-dibromopropane

$Br-CH_2-CH_2-CH_2-Br$
1, 3-dibromopropane

$Br_2CH-CH_2-CH_3$
1, 1-dibromopropane



$CH_3-\underset{\underset{\displaystyle Br}{|}}{\overset{\overset{\displaystyle Br}{|}}{C}}-CH_3$

2, 2-dibromopropane

5. (d)

6. Using *Corey-House synthesis* :

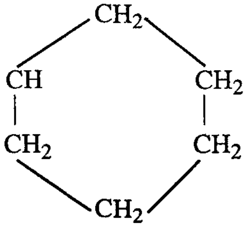
$$(CH_3)_2CHBr \xrightarrow[\text{(ii) CuI}]{\text{(i) Li}} \underset{\text{Lithium diisopropylcuprate}}{[(CH_3)_2CH]_2LiCu} \xrightarrow{CH_3CH_2CH_2Br} (CH_3)_2CHCH_2CH_2CH_3$$

7. (d) **8.** (c)

9. (a) 2-methylhexane. It has a longer less branched chain. Less branching leads to greater touchable surface area, and thus greater van der Waals attractive forces.
   (b) *n*-hexane. For the same reason as given for (a).
   (c) *n*-hexane. It has a higher molecular weight than *n*-pentane.

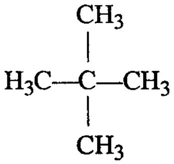
10. (b) < (c) < (a)

11. (a)



Cyclohexane

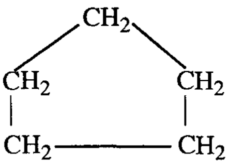
(b)



$$\begin{array}{c} CH_3 \\ | \\ H_3C-C-CH_3 \\ | \\ CH_3 \end{array}$$

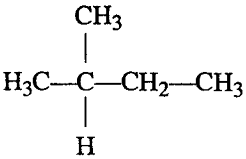
2, 2-dimethylpropane

(c)



Cyclopentane

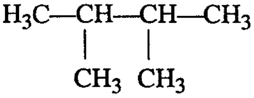
(d)



$$\begin{array}{ccccccc} & & CH_3 & & & & \\ & & | & & & & \\ H_3C & - & C & - & CH_2 & - & CH_3 \\ & & | & & & & \\ & & H & & & & \end{array}$$

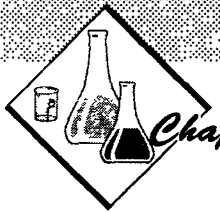
2-methylbutane

(e)



$$\begin{array}{ccccccc} H_3C & - & CH & - & CH & - & CH_3 \\ & & | & & | & & \\ & & CH_3 & & CH_3 & & \end{array}$$

2, 3-dimethylbutane



Chapter 5

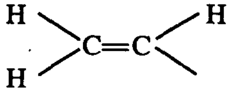
ALKENES, CYCLOALKENES, DIENES AND ALKYNES

5.0 ALKENES

Alkenes are also called *olefins* or *alkylenes*. These are open-chain hydrocarbons having a carbon-carbon double bond. The general formula of alkenes is C_nH_{2n}. The double bond is stronger than a single bond, yet paradoxically the C=C double bond is much more reactive than a carbon-carbon single bond. Unlike alkanes, which generally show rather nonspecific reactions, the double bond is the site of many specific reactions and is a functional group.

5.1 THE ALKENYL GROUP

Univalent groups that are formed by the removal of one hydrogen atom from an alkene are known as alkenyl groups. For example, the common or trivial name of alkenyl group obtained from ethylene is *vinyl group* and that from propylene is *allyl group*, and their derivatives are called *vinyl* and *allyl compounds* :



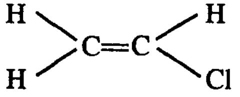
Vinyl group

IUPAC : ethenyl

$CH_2{=}CH{-}CH_2{-}$

Allyl group

IUPAC : 3-propenyl



Vinyl chloride

IUPAC : chloropropene

$CH_2{=}CH{-}CH_2{-}OH$

Allyl alcohol

IUPAC : 2-propen-1-ol

The IUPAC names of alkenyl groups are derived by replacing the "*e*" of the parent alkene by "*yl*" (*e.g.*, ethene $- e + yl =$ ethenyl). The carbon atoms constituting the alkenyl group are numbered so that the carbon with free valence is always number 1. For example :

$$\overset{3}{CH_2} = \overset{2}{CH}{-}\overset{1}{CH_2}{-}$$

2-Propenyl

5.2 NOMENCLATURE OF ALKENES

5.2.1 Common or Trivial Nomenclature

Simpler alkenes are known by their *common* or *trivial names*, *e.g.*, ethylene (C_2H_4), propylene

(C_3H_6) and butylene (C_4H_8). The three isomeric butylenes (C_4H_8) are named as α-, β- and *iso*-butylenes. This naming system is not suitable for naming higher and branched chain alkenes.

5.2.2 IUPAC Nomenclature of Alkenes

The following rules are used for naming alkenes :

(1) Determine the parent name by selecting the longest chain that contains the double bond. General parent names are :

Alkene	:	One double bond
Alkadiene	:	Two double bonds
Alkatriene	:	Three double bonds
Alkatetraene	:	Four double bonds

(2) The longest continuous chain containing the functional group **double bond** is numbered in a direction that gives the functional group the lowest possible number.

Designate the position of double bond by using the number of the first carbon atom of the double bond. For example, 1-butene signifies that double bond is between first and second carbon; 3-hexene signifies that double bond is present between carbon-3 and carbon-4.

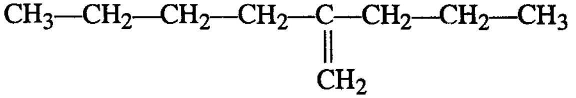
$$\overset{4}{C}H_3—\overset{3}{C}H_2—\overset{2}{C}H=\overset{1}{C}H_2$$

1-Butene

$$\overset{1}{C}H_3—\overset{2}{C}H_2—\overset{3}{C}H=\overset{4}{C}H—CH_2—CH_3$$

3-hexene

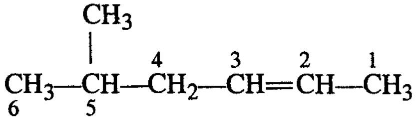
(3) The parent chain must contain the functional group (multiple bond) regardless of the fact whether it also denotes the longest continuous chain of carbon or not. For example :



$$CH_3—CH_2—CH_2—CH_2—\underset{\underset{CH_2}{\|}}{C}—CH_2—CH_2—CH_3$$

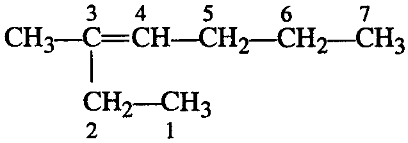
The longest continuous chain has eight carbons but the longest continuous chain containing double bond has six carbons, so the parent name of the compound is hexene.

(4) If the chain has the substituents, it is still numbered in the direction that gives the functional group the lowest possible number. For example :



$$\underset{6}{C}H_3—\underset{5}{\overset{\overset{CH_3}{|}}{C}}H—\overset{4}{C}H_2—\overset{3}{C}H=\overset{2}{C}H—\overset{1}{C}H_3$$

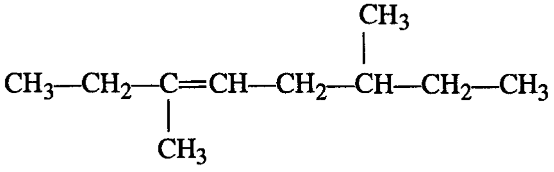
5-Methyl-2-hexene



$$CH_3—\underset{\underset{\underset{2\quad 1}{CH_2—CH_3}}{|}}{\overset{3}{C}}=\overset{4}{C}H—\overset{5}{C}H_2—\overset{6}{C}H_2—\overset{7}{C}H_3$$

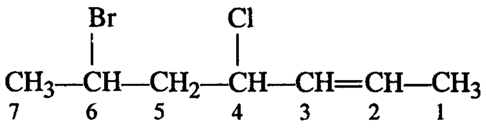
3-Methyl-3-heptene

(5) If a chain has more than one substituent, the substituents are cited in alphabetical order as in case of alkanes.



$$CH_3—CH_2—\underset{\underset{CH_3}{|}}{C}=CH—CH_2—\overset{\overset{CH_3}{|}}{C}H—CH_2—CH_3$$

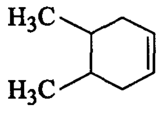
3, 6-Dimethyl-3-octene



$$\underset{7}{C}H_3—\underset{6}{\overset{\overset{Br}{|}}{C}}H—\underset{5}{C}H_2—\underset{4}{\overset{\overset{Cl}{|}}{C}}H—\underset{3}{C}H=\underset{2}{C}H—\underset{1}{C}H_3$$

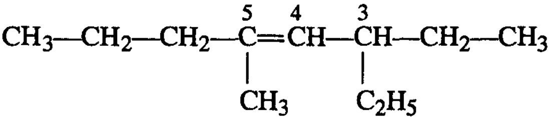
6-Bromo-4-chloro-2-heptene

(6) In cycloalkenes, a number is not needed to denote the position of the functional group since the ring is always numbered so that the double bond is between carbon-1 and carbon-2.



4, 5-Dimethylcyclohexene

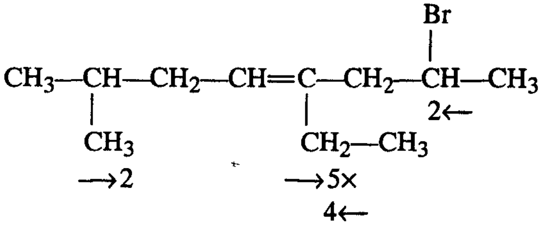
(7) If the same number for the double bond is obtained in both directions, the correct name is the one that contains the lowest substituent number (not sum of the lowest substituents).



$$\mathrm{CH_3{-}CH_2{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{5}{C}}}{=}\overset{4}{C}H{-}\underset{\displaystyle C_2H_5}{\underset{|}{\overset{3}{C}H}}{-}CH_2{-}CH_3}$$

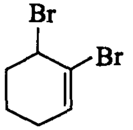
3-Ethyl-5-methyl-4-octene
not
6-Ethyl-4-methyl-4-octene

(8) If both directions lead to the same number for the functional group (double bond) and the same low numbers for one or more substituents, then these substituents are ignored and the direction is chosen that gives the lowest number to one of the remaining substituents.

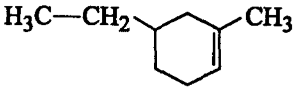


$$\mathrm{CH_3{-}\underset{\substack{\displaystyle CH_3\\ \longrightarrow 2}}{\underset{|}{C}H}{-}CH_2{-}CH{=}\underset{\substack{\displaystyle CH_2{-}CH_3\\ \longrightarrow 5\times\\ 4\longleftarrow}}{\underset{|}{C}}{-}CH_2{-}\underset{2\longleftarrow}{\overset{\displaystyle Br}{\overset{|}{C}H}}{-}CH_3}$$

2-Bromo-4-ethyl-7-methyl-4-octene
not
7-Bromo-5-ethyl-2-methyl-4-octene
because 4 < 5



1, 6-Dibromocyclohexene



5-Ethyl-1-methylcyclohexene

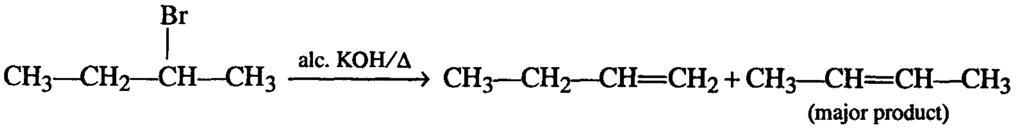
5.3 METHODS OF PREPARATION OF ALKENES

Alkenes are prepared by the following reactions :

5.3.1 Elimination Reactions

(a) Dehydrohalogenation : Alkyl halides undergo β-elimination reaction to give alkenes (for detail see Section 5.4).

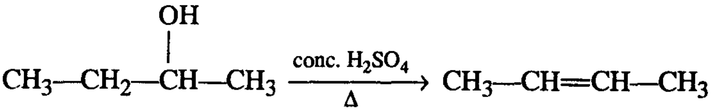
$$\mathrm{R{-}CH_2{-}CH_2{-}X \xrightarrow{alc.\ KOH/\Delta} R{-}CH{=}CH_2}$$



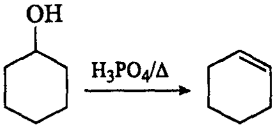
$$\mathrm{CH_3{-}CH_2{-}\overset{\displaystyle Br}{\overset{|}{C}H}{-}CH_3 \xrightarrow{alc.\ KOH/\Delta} CH_3{-}CH_2{-}CH{=}CH_2 + \underset{(major\ product)}{CH_3{-}CH{=}CH{-}CH_3}}$$

(b) Dehydration of alcohols (for details see Section 5.4) : Alcohols undergo dehydration to give alkenes.

$$R\mathrm{{-}CH_2{-}CH_2{-}OH \xrightarrow[\Delta]{conc.\ H_2SO_4}} R\mathrm{{-}CH{=}CH_2}$$

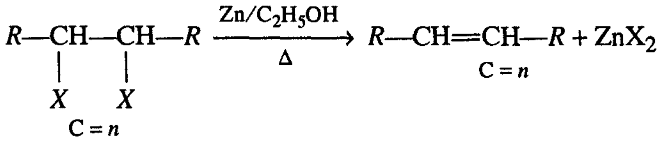


$$\mathrm{CH_3{-}CH_2{-}\overset{\displaystyle OH}{\overset{|}{C}H}{-}CH_3 \xrightarrow[\Delta]{conc.\ H_2SO_4} CH_3{-}CH{=}CH{-}CH_3}$$



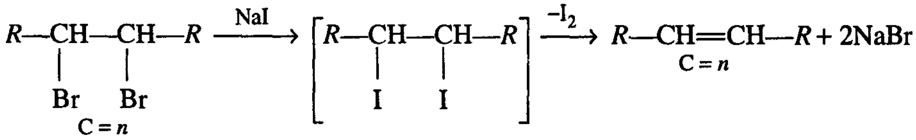
(c) Dehalogenation :

(i) *Vic* dihalides undergo dehalogenation in the presence of Zn, Ag or Mg.



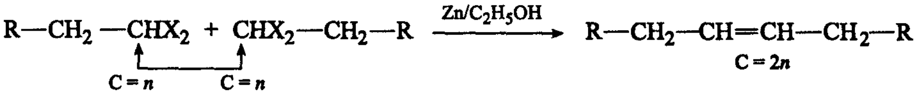
$$\underset{\substack{X \qquad X \\ C=n}}{R-CH-CH-R} \xrightarrow[\Delta]{Zn/C_2H_5OH} \underset{C=n}{R-CH=CH-R} + ZnX_2$$

Vic dihalides also undergo dehalogenation with NaI



$$\underset{\substack{Br \quad Br \\ C=n}}{R-CH-CH-R} \xrightarrow{NaI} \left[\underset{I \qquad I}{R-CH-CH-R}\right] \xrightarrow{-I_2} \underset{C=n}{R-CH=CH-R} + 2NaBr$$

(ii) *Gem* dihalides undergo coupling reaction *via* dehalogenation to give alkenes.

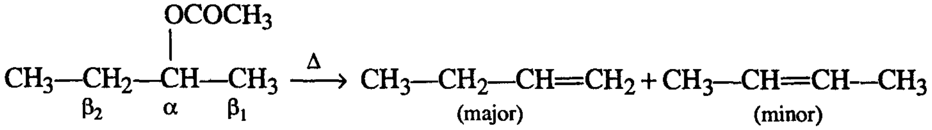


$$\underset{C=n}{R-CH_2-CHX_2} + \underset{C=n}{CHX_2-CH_2-R} \xrightarrow{Zn/C_2H_5OH} \underset{C=2n}{R-CH_2-CH=CH-CH_2-R}$$

5.3.2 Thermal Elimination Reactions

In thermal elimination reactions product formation takes place by Hofmann rule. Following compounds give thermal elimination reactions. These are *cis* eliminations and proceed through a cyclic TS (for details see Section 5.4).

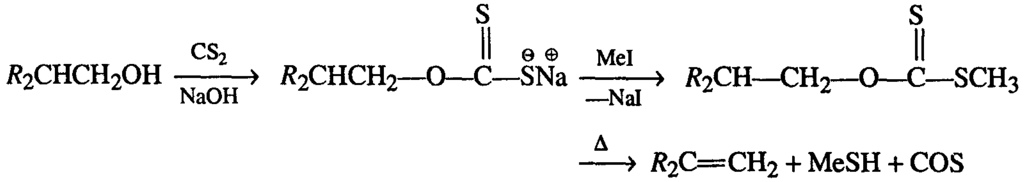
(i) Acetates :



$$CH_3-\underset{\beta_2}{CH_2}-\underset{\alpha}{\overset{\overset{\displaystyle OCOCH_3}{|}}{CH}}-\underset{\beta_1}{CH_3} \xrightarrow{\Delta} \underset{\text{(major)}}{CH_3-CH_2-CH=CH_2} + \underset{\text{(minor)}}{CH_3-CH=CH-CH_3}$$

$$CH_3-CH_2-CH_2-OH \xrightarrow{TsCl/Py} CH_3-CH_2-CH_2-OTs \xrightarrow{\Delta} CH_3-CH=CH_2$$

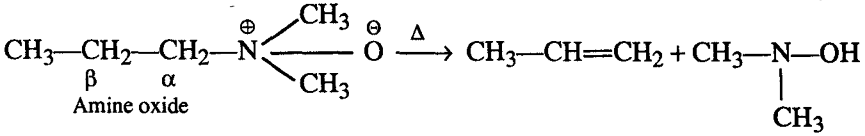
(ii) Xanthates :



$$R_2CHCH_2OH \xrightarrow[NaOH]{CS_2} R_2CHCH_2-O-\overset{\overset{\displaystyle S}{\|}}{C}-\overset{\ominus\ \oplus}{SNa} \xrightarrow[-NaI]{MeI} R_2CH-CH_2-O-\overset{\overset{\displaystyle S}{\|}}{C}-SCH_3$$

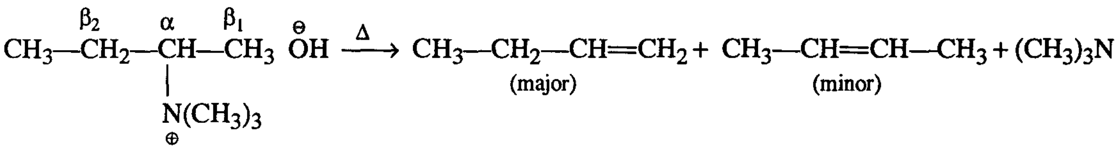
$$\xrightarrow{\Delta} R_2C=CH_2 + MeSH + COS$$

(iii) Amine oxides : Thermal elimination of amine oxides is known as Cope elimination.



$$\underset{\text{Amine oxide}}{CH_3-\underset{\beta}{CH_2}-\underset{\alpha}{CH_2}-\overset{\oplus}{N}(CH_3)_2-\overset{\ominus}{O}} \xrightarrow{\Delta} CH_3-CH=CH_2 + CH_3-\underset{\underset{\displaystyle CH_3}{|}}{N}-OH$$

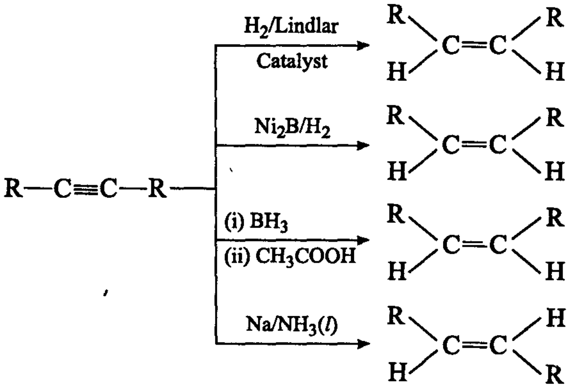
(iv) Quaternary ammonium hydroxide : Thermal elimination of this compound is known as Hofmann elimination.



$$CH_3-\overset{\beta_2}{CH_2}-\underset{\underset{\oplus}{N(CH_3)_3}}{\overset{\alpha}{CH}}-\overset{\beta_1}{CH_3}\ \overset{\ominus}{O}H \xrightarrow{\Delta} \underset{\text{(major)}}{CH_3-CH_2-CH=CH_2} + \underset{\text{(minor)}}{CH_3-CH=CH-CH_3} + (CH_3)_3N$$

5.3.3 Addition Reaction

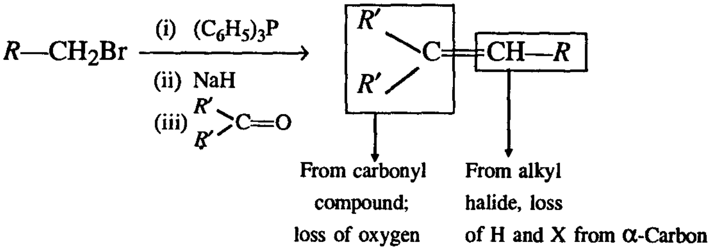
Alkynes undergo partial reduction to give alkenes in the presence of catalyst.

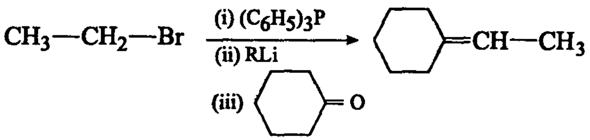


Note : Terminal alkynes cannot be reduced by Na/NH_3(*l*)

5.3.4 Wittig Reaction

Carbonyl compounds react with primary and secondary alkyl halides in the presence of triphenylphosphine and strong base (RLi, NaH, etc.) to give alkenes. This reaction is known as Wittig reaction.

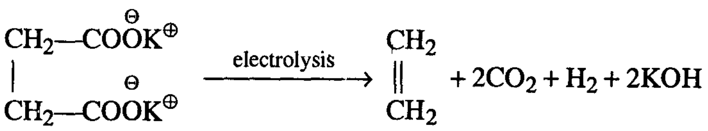




Note : For writig product; remove H and X from the α-carbon of alkyl halide and oxygen from carbonyl carbon and join these two carbons (*i.e.*, α-carbon and carbonyl carbon) by double bond.

5.3.5 Kolbe Hydrocarbon Synthesis

Electrolysis of potassium salt of succinic acid gives alkene at the anode.



$$\begin{array}{l} CH_2-CO\overset{\ominus}{O}K^{\oplus}\\ |\qquad\quad \ominus \\ CH_2-COOK^{\oplus}\end{array} \xrightarrow{\text{electrolysis}} \begin{array}{c}CH_2\\ \|\\ CH_2\end{array} + 2CO_2 + H_2 + 2KOH$$

Note : For writing product remove COOH from both α-carbons and convert single bond into double bond between two α-carbons.

5.4 ELIMINATION REACTIONS

Removal of two atoms or two groups or one atom and one group from a molecule is known as **elimination reaction.**

In elimination reactions the leaving group is removed as a nucleophile and is called a nucleofuge. The following are examples of leaving groups :

$$X\text{ (halogens)}, OH, OR, \overset{\oplus}{N_2}, N_3, H_2\overset{\oplus}{O}, R_3\overset{\oplus}{N}, R_2\overset{\oplus}{S}$$

Elimination reactions are generally endothermic and take place on heating.

5.4.1 Types of Elimination Reactions

Elimination reactions can be classified into two categories :

(1) α-elimination reactions or 1, 1-elimination reactions

(2) β-elimination reactions or 1, 2-elimination reactions

(1) α-Elimination Reactions

A reaction in which both the groups or atoms are removed from the same carbon of the molecule is called α-elimination reaction. This reaction is mainly given by *gem* dihalides and *gem* trihalides having at least one α-hydrogen.

$$CHX_3 \xrightarrow{\text{Alc. KOH}/\Delta} \ddot{C}X_2 + \overset{\ominus}{X} + \overset{\oplus}{H}$$

$$CH_2X_2 \xrightarrow{\text{Alc. KOH}/\Delta} \ddot{C}HX + \overset{\ominus}{X} + \overset{\oplus}{H}$$

$$CH_3CHI_2 + Zn \xrightarrow{\Delta} CH_3\ddot{C}H + ZnI_2$$

Product of the reaction are halocarbenes or dihalocarbenes. Carbenes are key intermediates in a wide variety of chemical and photochemical reactions.

(2) β-Elimination Reactions

Consider the following reaction :

$$CH_3-\underset{\beta}{CH_2}-\underset{\alpha}{CH_2}-L \longrightarrow CH_3-CH=CH_2 + \overset{\oplus}{H} + \overset{\ominus}{L}$$

(1) Removal of functional group (*i.e.*, leaving group) from α-carbon and other group (generally hydrogen atom) from the β-carbon is called β-elimination reaction.

(2) In this reaction there is loss of two σ bonds and gain of one π bond.

(3) Product of the reaction is generally less stable than the reactant.

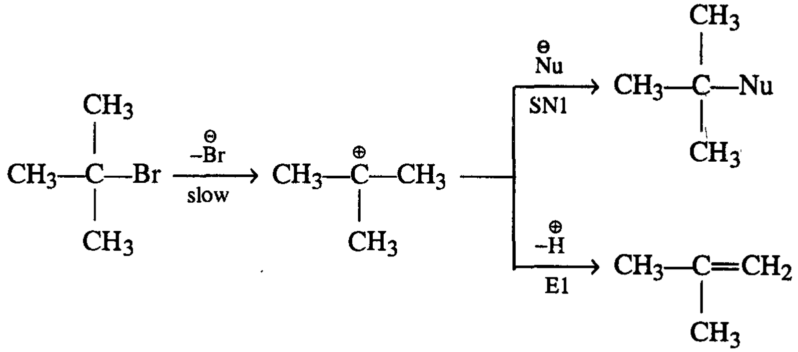
(4) Reaction is generally endothermic reaction which takes place on heating.

5.4.2 Types of β-Elimination Reactions

In analogy with substitution reactions, β-elimination reactions are divided into E_1 (elimination unimolecular), E_2 (elimination bimolecular) and E_{1cb} (elimination unimolecular conjugate base) reactions.

5.4.3 E1 Reactions

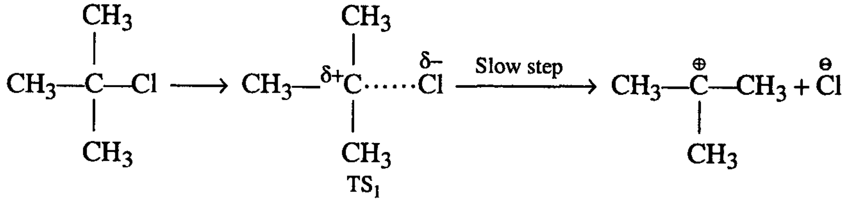
In case of SNl reaction (for details of SNl and SN2 reactions see Section 7.6) formation of product takes place *via* the formation of intermediate carbocation. This carbocation is a high energy, unstable intermediate that quickly undergoes further reaction. One way a carbocation can reach a stable product is by combining with nucleophile. This is known as SNl reaction. However, there is alternative; the carbocation can lose a proton to a base leading to overall elimination reaction resulting in the formation of an alkene. In this case, the reaction is known as E1 elimination.



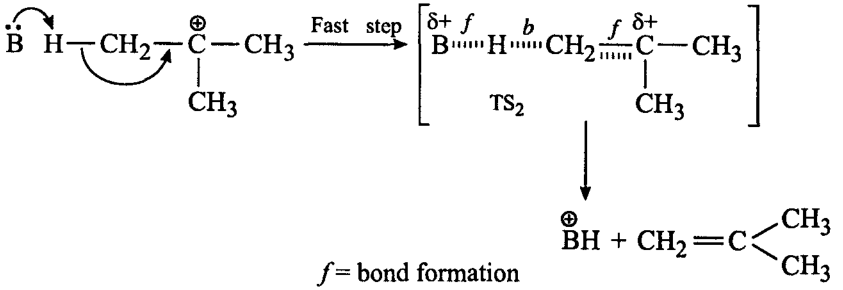
E1 mechanism

The mechanism of E1 reaction involves the following two steps :

Step I. Formation of carbocation intermediate :



Step II. Removal of proton by a base :



f = bond formation
b = bond breaking

Energy profile diagram of E1 reaction is given in Fig. 5.1.

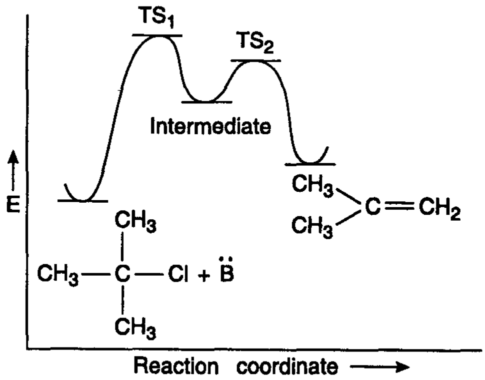


Fig. 5.1.

5.4.4 Characteristics of E1 Reactions

(i) The rate of the E1 reactions depends only on the concentration of substrate. The rate is independent of the concentration of the base.

Rate ∝ [Substrate]

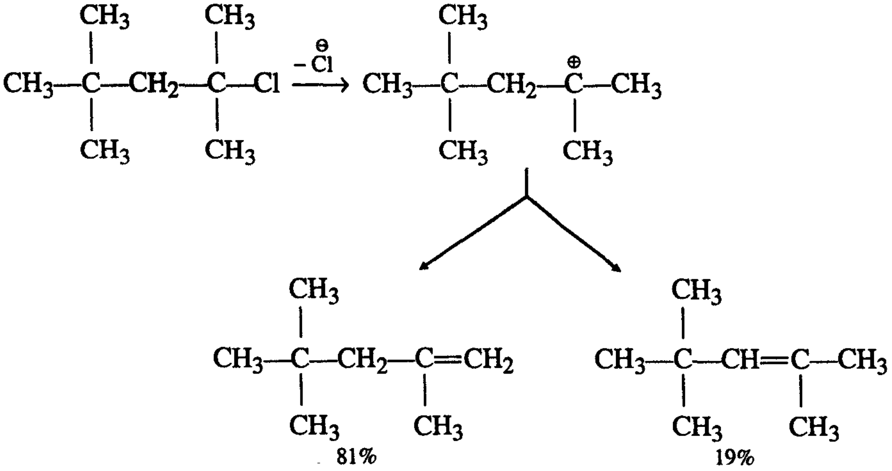
(ii) The rate of the reaction depends on the nature of the leaving group. In general, iodides react faster than bromides which react faster than chlorides.

R—I > *R*—Br > *R*—Cl > *R*—F

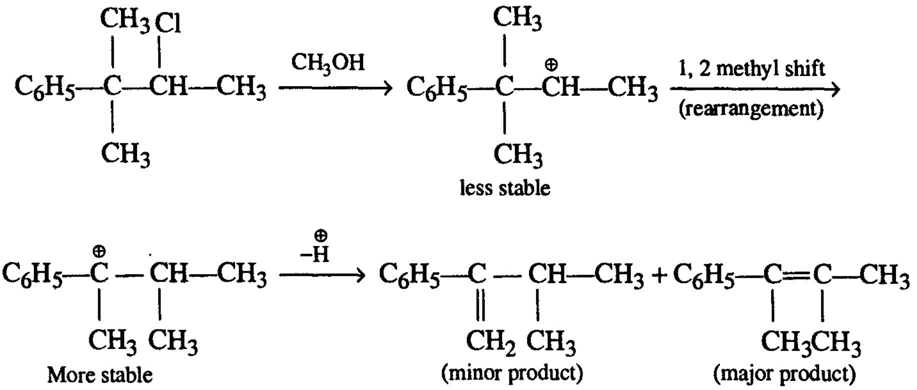
(iii) The reaction does not show primary kinetic isotope effect that is C—D bond and C—H bond are broken with the same ease.

(iv) Product formation takes place by Saytzeff rule but there are some exceptions, *i.e.*, in some cases product formation takes place by Hofmann rule. For example :

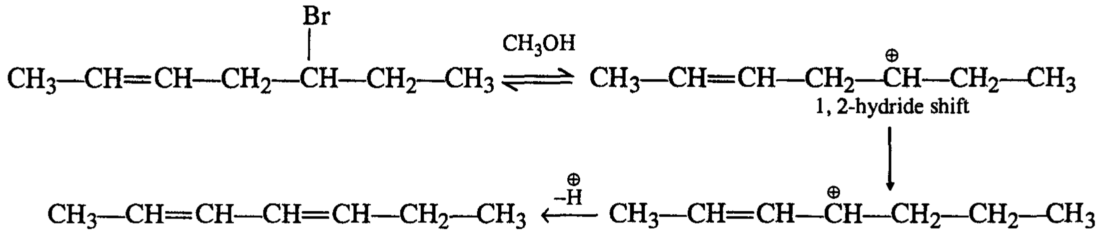
The E1 reaction of 2-chloro-2, 4, 4-trimethylpentane is interesting because it produces an excess of less substituted alkene. This is due to steric effect which leads to Hofmann elimination in an E1 reaction.



(v) Rearrangement : Because the E1 reaction involves the formation of a carbocation intermediate, rearrangement of the carbon skeleton can occur before the proton is lost. For example, the secondary carbocation that is formed from 3-chloro-2-methyl-2-phenylbutane undergoes a 1, 2 methyl shift to form a more stable tertiary benzyl carbocation.



In the following example, the secondary alkyl carbocation undergoes a 1, 2-hydride shift to form a more stable secondary allylic carbocation.



$$CH_3-CH=CH-CH_2-\overset{\overset{Br}{|}}{C}H-CH_2-CH_3 \xrightleftharpoons{CH_3OH} CH_3-CH=CH-CH_2-\overset{\oplus}{C}H-CH_2-CH_3$$

1, 2-hydride shift

$$CH_3-CH=CH-CH=CH-CH_2-CH_3 \xleftarrow{-\overset{\oplus}{H}} CH_3-CH=CH-\overset{\oplus}{C}H-CH_2-CH_2-CH_3$$

5.4.5 Factors Influencing E1 Reaction Rate

(1) Substrate structure and the reactivity : Carbocation being an intermediate in the E1 reaction, the rate and the reactivity of the reaction depends on the stability of the carbocation. Since + I effect, hyperconjugative effect and conjugative effect stabilise carbocation, any structure which forms stable carbocation will be reactive. Taking all these the order of the reactivity of the compounds is expected to be :

3° benzyl ≈ 3° allylic > 2° benzyl ≈ 2° allylic ≈ 3° alkyl > 1° benzyl ≈ 1° allylic
≈ 2° alkyl > 1° alkyl > vinyl

Thus alkyl or aryl substituents on α and β-positions with respect to the leaving group increases reactivity and the rate of the E1 reactions.

(2) Basicity and concentration of the base : Since E1 reactions do not usually require any added base (the solvent molecules surve the purpose), the strength and the concentration of the base have nothing to do with the rate of the E1 reactions. Usually the SN1 product dominates over E1 product because of the weak base character of the solvent.

(3) Nature of the leaving group : Reactivity of the substrate depends largely on the nature of the leaving group. Thus reactivity order is as follows :

$$\overset{\ominus}{I} > \overset{\ominus}{Br} > \overset{\ominus}{Cl} > \overset{\ominus}{F}$$

(4) Nature of the solvents : Since E1 reactions involve an ionic intermediate, the carbocation, the rate of the E1 reaction increases with increasing polarity of the solvent. Polar solvents of poor nucleophilicity favour E1 reactions. If the temperature of the reaction is increased, E1 reactions are favoured. Thus increase in temperature increases E1/SN1 ratio.

5.4.6 E2 Reactions

The given reaction is an example of E2 reaction.

$$CH_3-CH_2-CH_2-Br \xrightarrow[\Delta]{Base} CH_3-CH=CH_2 + \overset{\oplus}{H} + \overset{\ominus}{X}$$

Energy profile diagram of this reaction is given in Fig. 5.2.

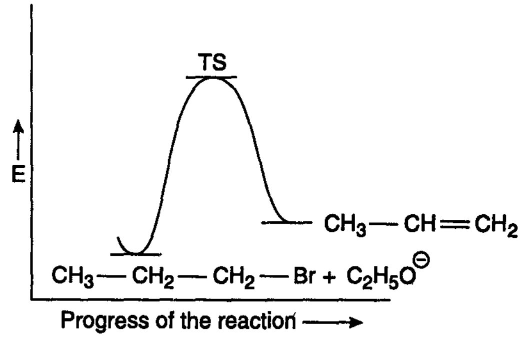


Fig. 5.2.

Characteristics of E2 reactions

(i) Rate $\propto$ [R—X] [Base]

(ii) Rate depends on the nature of leaving group, *i.e.*,
Rate $\propto$ leaving power of the group, *e.g.*, bromides react faster than chlorides.

(iii) Reaction has high primary kinetic isotope effect :

$CH_3—CH_2—Br$ K_H (velocity constant of the reaction)

$CD_3—CD_2—Br$ K_D (velocity constant of the reaction)

$$\frac{K_H}{K_D} = 7$$

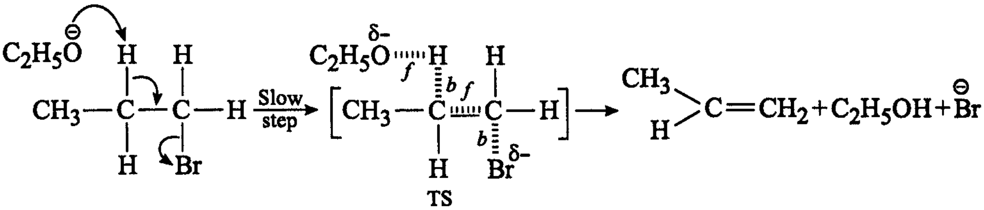
Results (ii) and (iii) show that C—X bond breaking and C—H bond breaking take place in the rate determining step.

(iv) Since the reaction is a bimolecular reaction, the product formation will take place by formation of transition state.

Reaction :

$$CH_3—CH_2—CH_2—Br + C_2H_5\overset{\ominus}{O} \longrightarrow CH_3—CH{=}CH_2 + C_2H_5OH + Br^{\ominus}$$

Mechanism :



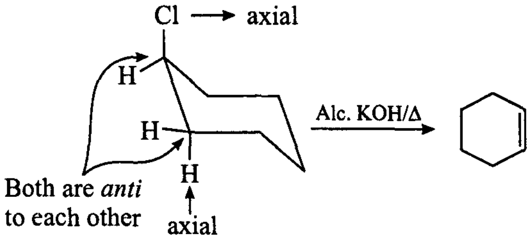
f = bond formation
b = bond breaking
RI = reaction intermediate

(v) In E2 reaction product formation takes place by formation of TS which is neutral species and has less energy content (whereas in E1, RI is carbocation and in E1*cb*, RI is carbanion, both species are charged species having high energy content). Thus E2 elimination is lowest energy path [<<<<E_a] in comparison to E1 and E_{1cb} reactions. Due to this E2 reaction is the most common reaction.

(vi) In E2 reaction, both the leaving groups should be *anti*-periplanar, *i.e.*, both leaving groups should be in the same plane but should have anti conformation (*i.e.*, angle is 180°) *i.e.*, E2 mechanism is stereospecific.

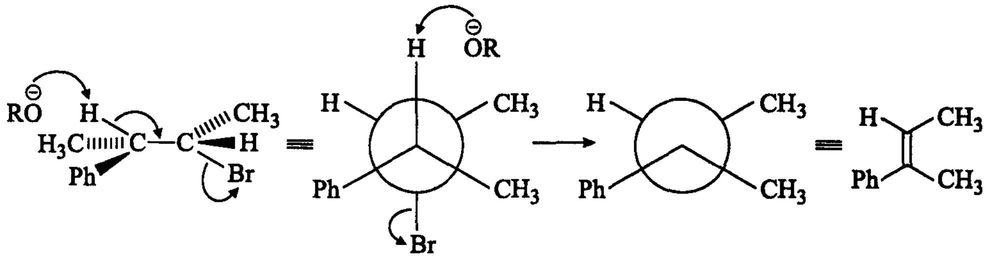
(vii) In acyclic compounds, E2 elimination is given by the most stable conformation in which both leaving groups are *anti*-periplanar.

(viii) The elimination in six membered cyclic compounds (*i.e.*, cyclohexane derivatives) proceeds best when leaving groups are diaxial (*trans* or *anti*). In this case *anti*-periplanarity is available. 1, 2-Diaxial groups are always periplanar and *anti* to each other.



5.4.7 Stereochemistry of E2 reactions

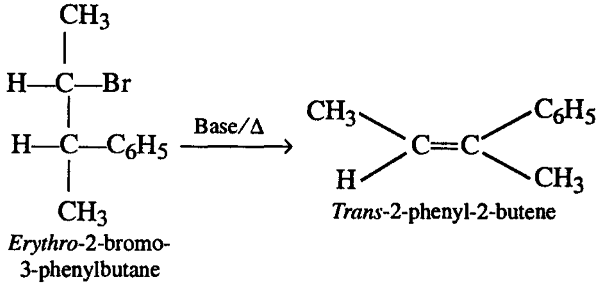
It has been observed that in the transition state of E2 elimination, the attacking base and the leaving group are generally *anti* or as far apart as possible. For this reason, the E2 elimination is often referred as *anti*-elimination. In majority of cases, *anti*-elimination is favoured over *syn* elimination because TS for the former has staggered conformation with lower energy than that for the eclipsed or gauche conformation in the *syn* elimination.



Anti elimination

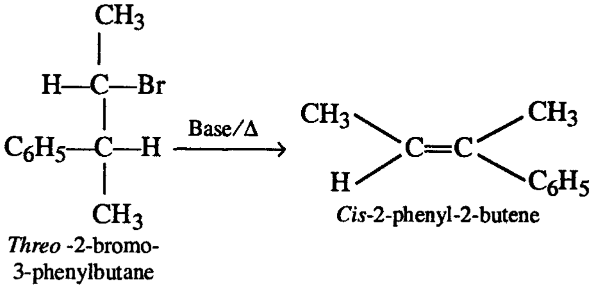
The interesting feature about *anti*-elimination is that *anti*-positioning of the eliminating groups (H and Br) determines the stereochemistry of the product alkene.

For example, *erythro* form of halide gives *E* or *trans* alkene whereas *threo* form gives *Z* or *cis* alkene.



Erythro-2-bromo-3-phenylbutane

Trans-2-phenyl-2-butene



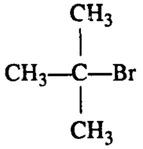
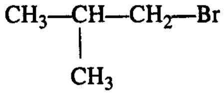
Threo -2-bromo-3-phenylbutane

Cis-2-phenyl-2-butene

In open chain compounds the molecules can easily adopt the *anti*-periplanar conformation owing to free-rotation about C—C single bond. Hence, *anti* (*trans*) E2 reaction is a general rule in the case of open chain compounds. Some cyclic compounds also show the *trans* E2 reaction. However, some cyclic compounds which have *cis* coplanar groups, are incapable of adopting *anti*-periplanar conformation do not follow *trans* E2 elimination and undergo *syn* E2 elimination.

5.4.8 Factors Influencing E2 Reaction Rate

(1) Structure of Substrate : It has been found that the increasing branching at α and β-carbon increases the rate of the E2 reaction. This is because as the number of alkyl or aryl groups increases on the carbon atoms of the developing double bond, the stability of the TS increases.

Substrate	% yield	Rate
$CH_3—CH_2—Br$	0.9	1.0×10^5
$CH_3—CH_2—CH_2—Br$	8.9	$5{\cdot}3 . 10^5$
 $CH_3—C(CH_3)_2—Br$	97	4.7×10^5
 $CH_3—CH(CH_3)—CH_2—Br$	59.5	8.5×10^5

The above table shows that the order of the rate and reactivity is 3° > 2° > 1°.

Since the TS of SN2 reaction involves high steric strain, the α and β-branches slow down the SN2 reaction rate while speed up to E2 reaction rate. Thus with increasing branching at α and β-carbons, the E2/SN2 ratio increases.

It has also been found that electron withdrawing groups (*– I* or *–R* group) on the β-carbon increases the rate of the E2 reaction. This is because *-I* group or *–R* group increases acidity of the β-hydrogen and stabilises the carbocation character of the T.S.

(2) Nature of the Leaving Group : In general, the better the leaving group, the higher is the rate of the E2 reaction.

Substrate	$PhCH_2—CH_2—Cl$	$PhCH_2CH_2Br$	$PhCH_2CH_2I$
Rate	0.007×10^3	4.2×10^3	27×10^3

It has also been found that with the increasing leaving power of the halogen atom E2/SN2 ratio increases but to a minimum extent.

(3) Strength and Concentration of the Base : With the increasing basicity and the concentration of the added base, the rates of the E2 reactions have been found to increase. In the presence of strong base the E2/SN2 ratio increases.

(4) The Naure of the Solvent : The yield of the E2 product decreases with the decrease in the polarity of the solvent.

(5) The Effect of Temperature : As the temperature of the E2 reaction increases, the rate of the reaction also increases. Thus the E2/SN2 ratio also increases.

5.4.9 Competition Between E2 and E1 Reactions

Primary alkyl halides undergo only E2 elimination reactions. They cannot undergo El reactions because of the difficulty encountered in forming primary carbocations. Secondary and tertiary alkyl halides undergo both El and E2 reactions. For those alkyl halides that can undergo both E2 and El reactions, the E2 reaction is favoured by a high concentration of a strong base and an aprotic solvent (*e.g.*, DMSO, DMS, acetone). An El reaction is favoured by a weak base and a protic solvent (*e.g.*, HOH, ROH).

Substrate	Elimination Reaction
Primary alkyl halide	E2 only
Secondary alkyl halide	El and E2
Tertiary alkyl halide	El and E2

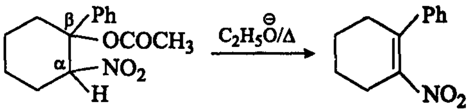
5.4.10 E1*cb* Reactions :

There is third mechanism of β-elimination reactions. This begins with the rapid loss of a proton to a base. Loss of this proton leads to a formation of a carbanion. The carbanion is then converted to an alkene. Conversion of carbanion to alkene is slow step and hence the rate determining step. Since this reaction proceeds through the conjugate base of the starting material, this elimination is abbreviated as E1*cb* (elimination unimolecular conjugate base).

The following are some examples of E1*cb* reactions :

$$CF_3{-}CHCl_2 \xrightarrow{C_2H_5\overset{\ominus}{O}} CF_2{=}CCl_2$$

$$C_6H_5{-}CH_2{-}CH_2{-}F \xrightarrow{C_2H_5\overset{\ominus}{O}} C_6H_5{-}CH{=}CH_2$$



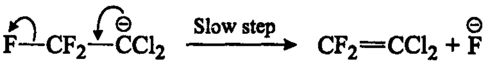
Mechanism of E1cb reaction :

First step :

$$CF_3{-}CHCl_2 \underset{\text{Fast step}}{\overset{C_2H_5\overset{\ominus}{O}}{\rightleftharpoons}} CF_3{-}\overset{\ominus}{C}Cl_2$$

conjugate base of substrate which is stabilised by CF_3 and Cl.

Second step :



$$F{-}CF_2{-}\overset{\ominus}{C}Cl_2 \xrightarrow{\text{Slow step}} CF_2{=}CCl_2 + \overset{\ominus}{F}$$

The E1*cb* reaction is first order in base and first order in substrate just like the E2 reaction. However, it is unimolecular, because only one species is involved in the rate—determining step. That species is the carbanion.

The following are important points regarding E1*cb* reaction :

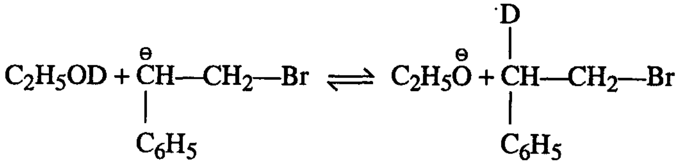
(1) E1*cb* mechanism is limited to substrates with substituents which can stabilise the carbanion as reaction intermediate.

Thus β-carbon should contain strong –*I* group, *e.g.*, carbonyl group, nitro group, cyano group, sulphonyl group or other carbanion stabilising group.

(2) This reaction is given by those compounds which have poor leaving group, otherwise carbanion will not be formed.

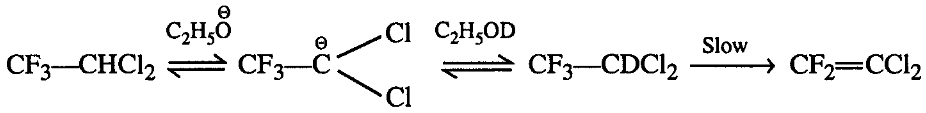
(3) β-hydrogen should be highly acidic so that it can easily be removed as proton to give carbanion.

The E1*cb* reaction completes with the E2 reaction. The use of deuterium labelling can help to distinguish the E1*cb* from the E2 pathway. The first step of the E1*cb* mechanism is reversible, when the reaction is carried out in C_2H_5OD instead of C_2H_5OH, the intermediate carbanion should pick up deuterium, and one would recover deuterated substrate after partial transformation.



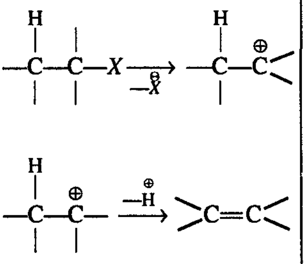
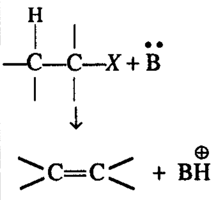
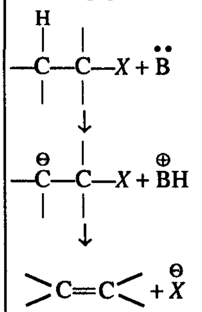
$$C_2H_5OD + \underset{\substack{|\\C_6H_5}}{\overset{\ominus}{C}H}{-}CH_2{-}Br \rightleftharpoons C_2H_5\overset{\ominus}{O} + \underset{\substack{|\\C_6H_5}}{\overset{\substack{D\\|}}{C}H}{-}CH_2{-}Br$$

On the other hand, there should be no deuterium uptake if E2 mechanism is operating. E1*cb* mechanism operates only in some special cases where the intermediate carbanion is stabilised either by inductive or mesomeric effect. For instance, 1, 1, 1 trifluoro-2, 2-dichloroethane undergoes β-elimination *via* E1*cb* pathway.



5.4.11 Comparison between E1, E2 and E1*cb* pathways

Comparison between these reaction pathways are given in the table below :

	E1	E2	Elcb
1. Steps	Two step process 	One step process 	Two step process 
2. RI or TS	Carbocation as *RI*	*TS*	Carbanion as *RI*
3. Kinetics	First order, unimolecular; Rate = K_1[RX]; rate of ionisation	Second order, bimolecular Rate = K_2 [*R*—*X*][*B*]	Second order, Rate = K_2 [*R*—*X*][*B*]
4. Driving force	Ionisation of *R*—*X*	Attack by base on β-hydrogen	Attack by base on β-hydrogen
5. Stereochemistry	Nonstereospecific and non-stereoselective	Stereoselective and stereo specific	Nonstereospecific and nonstereoselective
6. Regioselectivity	Saytzeff	Saytzeff as well as Hofmann	Hofmann
7. Rearrangement	Common	No rearrangement except for , allylic (SN2′)	no rearrangement
8. Completing reaction	SN1	SN2	No
9. Reactivity order	3° > 2° > 1°	3° > 2° > 1°	3° > 2° > 1°

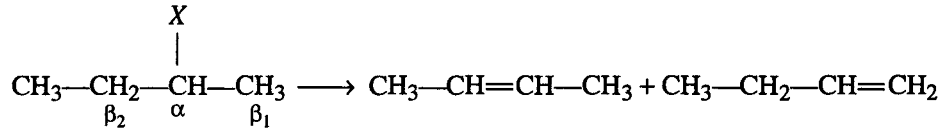
5.4.12 Number of Products in β-Elimination Reactions

Number of products depends on the number of different types of β-carbons having hydrogen(s).

Number of products in a β-elimination reaction = Number of different types of β carbons having hydrogen(s).

$$CH_3—\underset{\beta}{CH_2}—\underset{\alpha}{CH_2}—X \longrightarrow CH_3—CH=CH_2$$

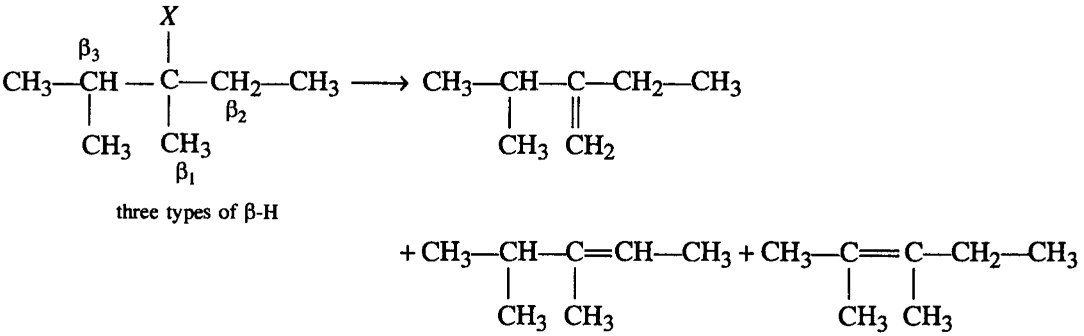
only one type of β—H only one product



$$\underset{\beta_2}{CH_3-CH_2}-\underset{\alpha}{\overset{X}{CH}}-\underset{\beta_1}{CH_3} \longrightarrow CH_3-CH=CH-CH_3 + CH_3-CH_2-CH=CH_2$$

two types of β-H

two products



$$CH_3-\overset{\beta_3}{\underset{CH_3}{CH}}-\overset{X}{\underset{\underset{\beta_1}{CH_3}}{C}}-\underset{\beta_2}{CH_2}-CH_3 \longrightarrow CH_3-\underset{CH_3}{CH}-\underset{CH_2}{\overset{}{C}}-CH_2-CH_3$$

three types of β-H

$$+\,CH_3-\underset{CH_3}{CH}-\underset{CH_3}{C}=CH-CH_3 + CH_3-\underset{CH_3}{C}=\underset{CH_3}{C}-CH_2-CH_3$$

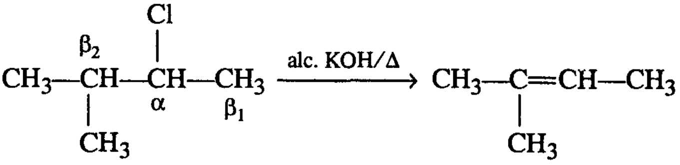
three products

5.5 ORIENTATION IN ELIMINATION REACTIONS

If a substrate has different types of β-hydrogens then it will give more than one product. Major product of the reaction can be known by two empirical rules.

5.5.1 Saytzeff Rule

According to this rule, major product is the most substituted alkene, *i.e.*, the most stable alkene. Thus, the major product is obtained by elimination of $\overset{\oplus}{H}$ from that β-carbon which has the least number of hydrogen. Product of the reaction in this case is known as Saytzeff product.

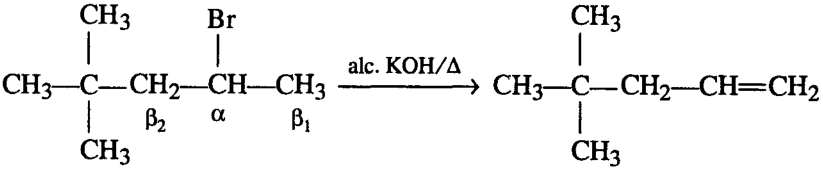


$$CH_3-\overset{\beta_2}{\underset{CH_3}{CH}}-\underset{\alpha}{\overset{Cl}{CH}}-\underset{\beta_1}{CH_3} \xrightarrow{\text{alc. KOH}/\Delta} CH_3-\underset{CH_3}{C}=CH-CH_3$$

Saytzeff product

5.5.2 Hofmann Rule

According to this rule major product is always least substituted alkene, *i.e.*, the least stable alkene. Thus, the major product is formed from β-carbon which has maximum number of hydrogens. Product of the reaction in this case is known as Hofmann product.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{\beta_2}{CH_2}-\underset{\alpha}{\overset{Br}{CH}}-\underset{\beta_1}{CH_3} \xrightarrow{\text{alc. KOH}/\Delta} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH=CH_2$$

Hofmann product

Note :

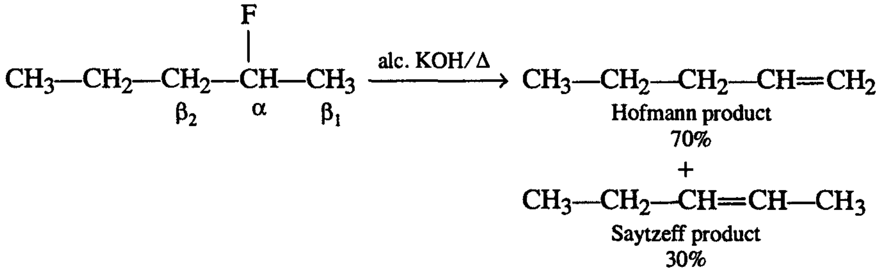
(i) In E1 reactions, product formation always takes place by Saytzeff rule.

(ii) In E1*cb* reactions, product formation always takes place by Hofmann rule.

(iii) In E2 reaction, product formation takes place by Saytzeff as well as Hofmann rule.

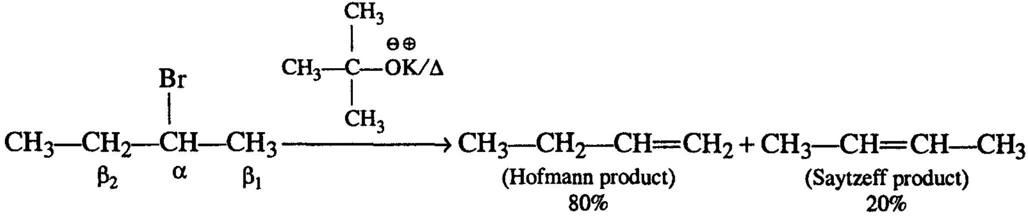
In almost all E2 reactions product formation takes place by Saytzeff rule. **Only in four cases product formation takes place by Hofmann Rule.**

(1) Dehydrohalogenation of alkyl halides when leaving group is very poor, *e.g.*, alkyl fluoride (primary or secondary)



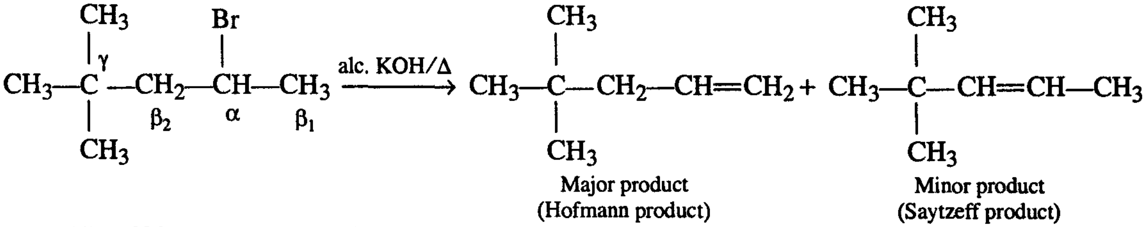
$$CH_3-CH_2-\underset{\beta_2}{CH_2}-\underset{\alpha}{\overset{\overset{F}{|}}{CH}}-\underset{\beta_1}{CH_3} \xrightarrow{\text{alc. KOH}/\Delta} \underset{\substack{\text{Hofmann product}\\70\%}}{CH_3-CH_2-CH_2-CH{=}CH_2} + \underset{\substack{\text{Saytzeff product}\\30\%}}{CH_3-CH_2-CH{=}CH-CH_3}$$

(2) Primary and *sec*-alkyl halides gives Hofmann elimination when the size of the base is bulky, *i.e.*, sodium or potassium *ter*-butoxide.



$$CH_3-\underset{\beta_2}{CH_2}-\underset{\alpha}{\overset{\overset{Br}{|}}{CH}}-\underset{\beta_1}{CH_3} \xrightarrow{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{\ominus\oplus}{OK}/\Delta} \underset{\substack{\text{(Hofmann product)}\\80\%}}{CH_3-CH_2-CH{=}CH_2} + \underset{\substack{\text{(Saytzeff product)}\\20\%}}{CH_3-CH{=}CH-CH_3}$$

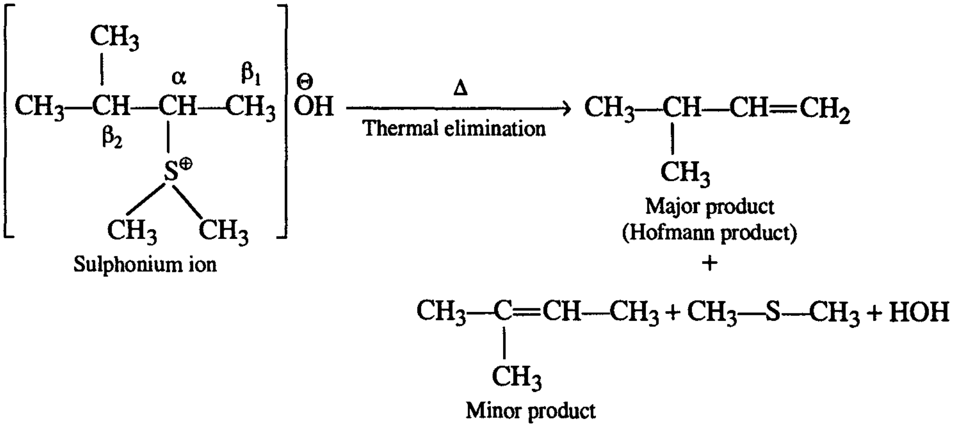
(3) Primary and *sec*-alkyl halides having quarternary γ-carbon gives Hofmann elimination



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{}^{\gamma}-\underset{\beta_2}{CH_2}-\underset{\alpha}{\overset{\overset{Br}{|}}{CH}}-\underset{\beta_1}{CH_3} \xrightarrow{\text{alc. KOH}/\Delta} \underset{\substack{\text{Major product}\\\text{(Hofmann product)}}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH{=}CH_2} + \underset{\substack{\text{Minor product}\\\text{(Saytzeff product)}}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH{=}CH-CH_3}$$

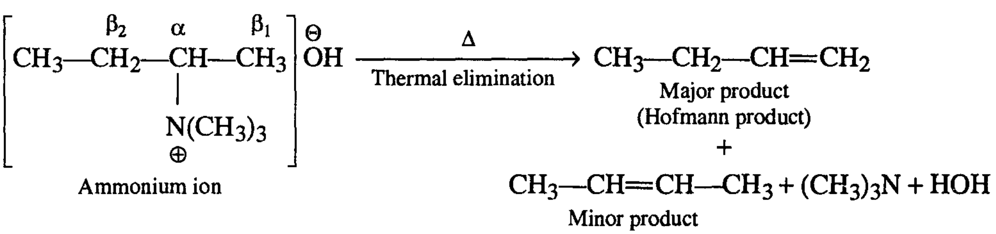
(4) If leaving group is bulky, then compound gives Hofmann elimination reaction.

The most common type of large, bulky leaving groups which lead to Hofmann products have positively charged nitrogen ($\overset{\oplus}{N}R_3$) or positively charged sulphur ($\overset{\oplus}{S}R_2$)



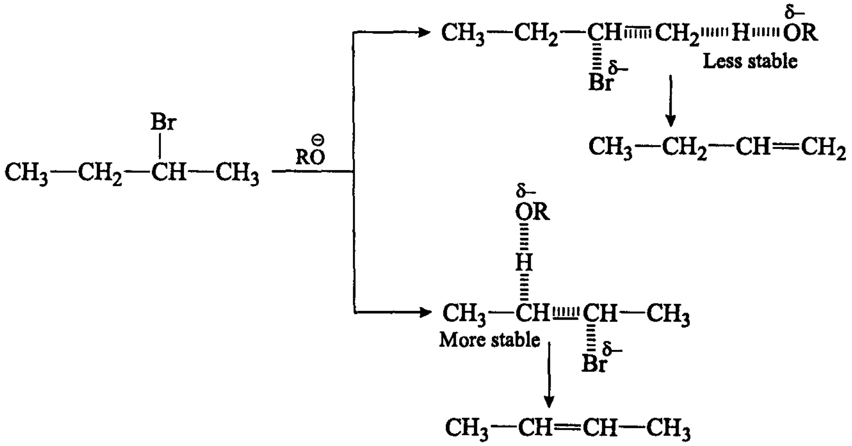
$$\left[CH_3-\underset{\beta_2}{\overset{\overset{CH_3}{|}}{CH}}-\overset{\alpha}{\underset{\underset{\overset{\oplus}{S}(CH_3)_2}{|}}{CH}}-\overset{\beta_1}{CH_3}\right]\overset{\ominus}{O}H \xrightarrow[\text{Thermal elimination}]{\Delta} \underset{\substack{\text{Major product}\\\text{(Hofmann product)}}}{CH_3-\underset{\underset{CH_3}{|}}{CH}-CH{=}CH_2} + \underset{\text{Minor product}}{CH_3-\underset{\underset{CH_3}{|}}{C}{=}CH-CH_3} + CH_3-S-CH_3 + HOH$$

Sulphonium ion



5.5.3 Theoretical Explanation for Saytzeff Rule

Explanation for the more stable alkene (Saytzeff product) being formed in preference to the less stable alkene, is available from the transition states leading to these two alkenes. In either transition state, the removal of a proton and the formation of the double bond is taking place simultaneously. The transition state has some double-bond character which is represented by the dotted line.



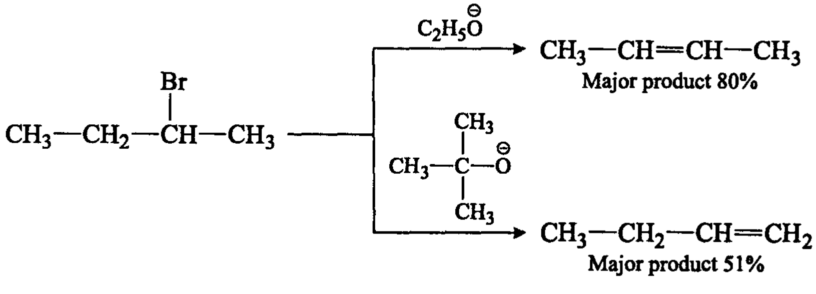
Because both transition states leading to the alkene have some double bond character, the transition state leading to the more stable alkene is itself more stabilised and is of lower energy. The reaction with the lower energy transition state proceeds at a faster rate; therefore the more stable alkene is the predominant product (Fig. 5.3).

In the case of E1 reactions the Saytzeff product (most stable alkene) is always the major product because it is formed through a lower energy TS from the carbocation intermediate. As we have noted above, the TS leading to the more stable alkene is itself more stabilised and is of lower energy.

5.5.4 Theoretical Explanation of Hofmann Rule

A common phenomenon leading to the less substituted alkene (Hofmann product) is steric hindrance in the transition state leading to the least substituted alkene. Steric hindrance can raise the energy of this transition state so much so that the reaction follows a different course and yields the less substituted alkene. The steric hindrance is caused by any one of the following four factors.

(1) Size of attacking base : In the elimination reaction of 2-bromopentane with ethoxide the most substituted alkene predominates but with the bulky *t*-butoxide ion, the 1-butane predominates.



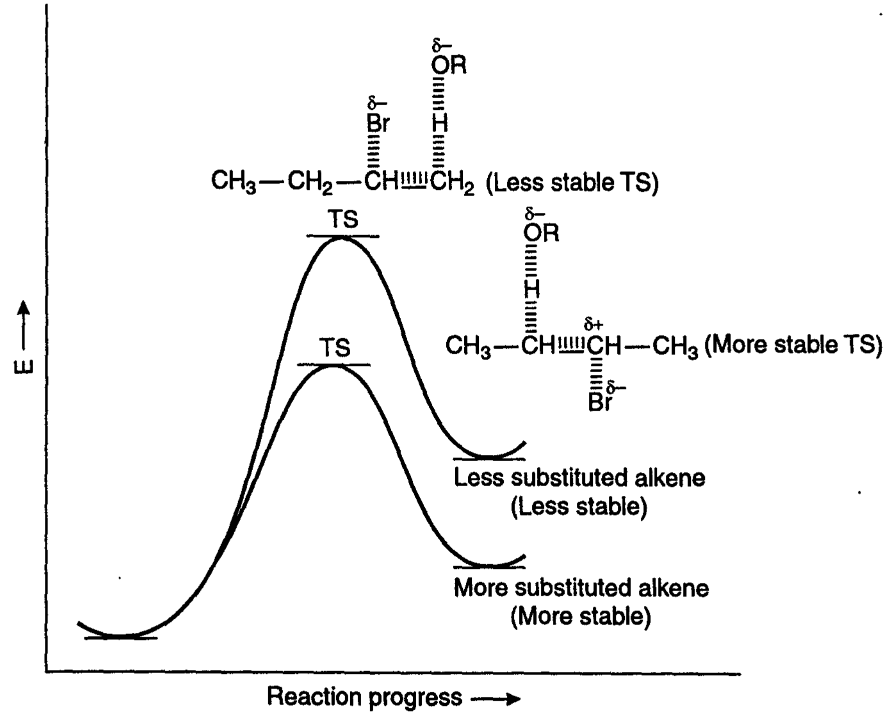
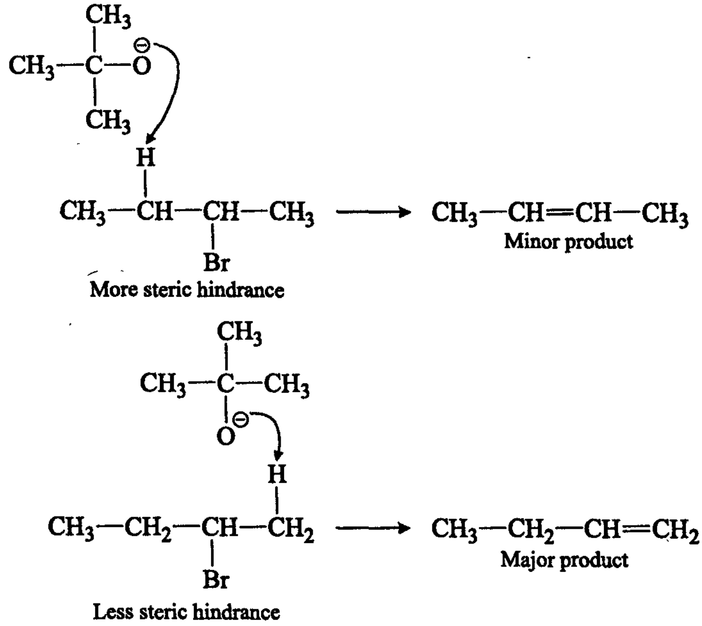
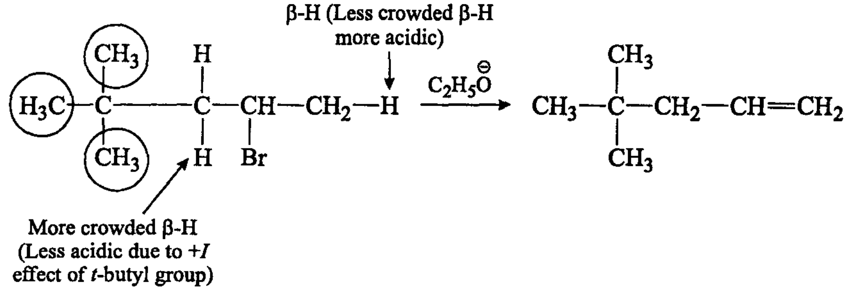


Fig. 5.3. Energy diagram for a typical E2 reaction, showing why the more substituted alkene predominates.



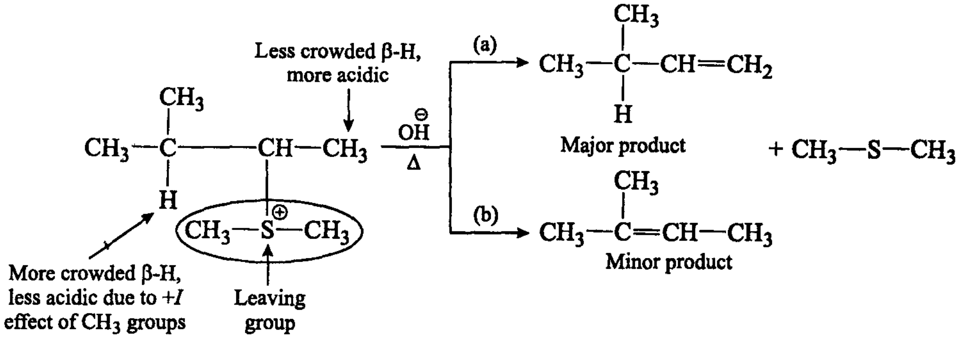
(2) Bulkiness of groups surrounding the leaving group : The hindered β-hydrogen (*i.e.*, γ carbon is quaternary) yields the less substituted alkene in E2 reaction even with a small base like the ethoxide ion.


β-H (Less crowded β-H more acidic)

More crowded β-H (Less acidic due to +*I* effect of *t*-butyl group)

Above two factors decide whether the orientation of elimination will follow Saytzeff rule or Hofmann rule.

(3) Large and bulky leaving groups : The most common type of large bulky leaving groups which lead to Hofmann products have positively charged nitrogen ($-\overset{\oplus}{N}R_3$) or positively charged sulphur ($-\overset{\oplus}{S}R_2$).


Less crowded β-H, more acidic

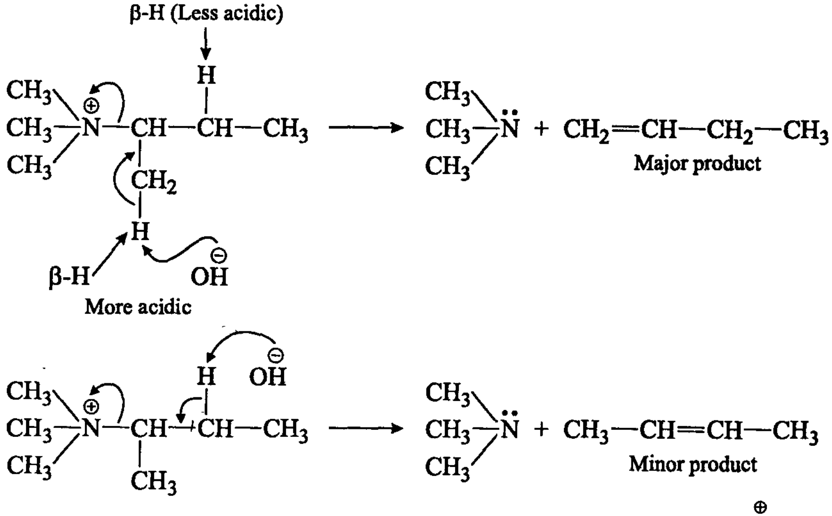
More crowded β-H, less acidic due to +*I* effect of CH_3 groups

Leaving group

Major product

Minor product

Similarly *sec*-butyl trimethyl ammonium cation has two different types of β-hydrogen. The loss of one type leads to 1-butene while the loss of the other type leads to 2-butene.

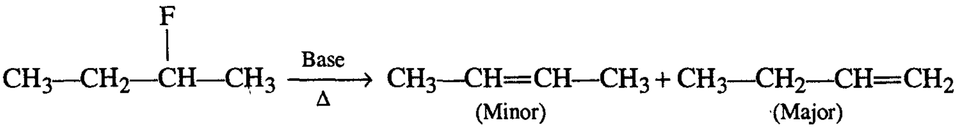

β-H (Less acidic)

β-H More acidic

Major product

Minor product

(4) Poor leaving groups : The presence of poor leaving groups, *e.g.*, F, $\overset{\oplus}{N}R_3$ and $\overset{\oplus}{S}R_2$ leads to the formation of Hofmann product.



$$CH_3-CH_2-\overset{\overset{F}{|}}{C}H-CH_3 \xrightarrow[\Delta]{\text{Base}} \underset{\text{(Minor)}}{CH_3-CH=CH-CH_3} + \underset{\text{(Major)}}{CH_3-CH_2-CH=CH_2}$$

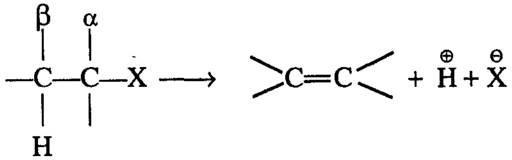
In general, in the case of alkyl halides the size of attacking base and the bulkiness of groups surrounding the leaving group govern the orientation, *i.e.*, the formation of Saytzeff or Hofmann product. On the other hand, in the case of substrates with F, $\overset{\oplus}{N}R_3$ and $\overset{\oplus}{S}R_2$ leaving groups, the acidity of the eliminating hydrogen governs the orientation. The most acidic hydrogen is preferably removed to give the major product.

5.6 TYPES OF E1 AND E2 REACTIONS

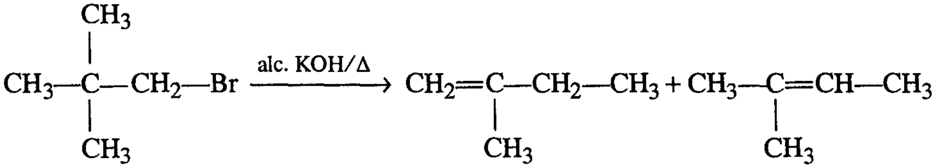
There are various classes of organic compounds that undergo E1 and E2 reactions. The following are most important of these reactions :

5.6.1 Dehydrohalogenation

(1) This reaction is given by aliphatic halides having at least two carbon atoms.

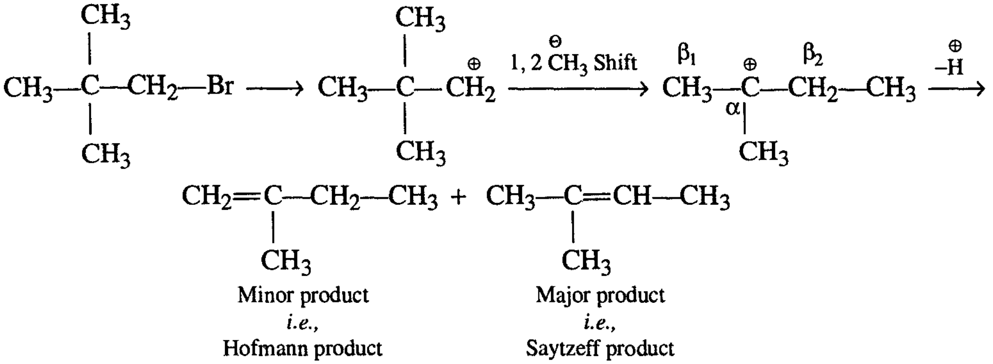


(2) Tertiary alkyl halides always give E1 reaction, secondary and primary alkyl halides whose β-carbon is either 3° or 4° also give E1 reaction.



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-Br \xrightarrow{\text{alc. KOH}/\Delta} CH_2=\underset{\underset{CH_3}{|}}{C}-CH_2-CH_3 + CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_3$$

The above reaction takes place as follows :



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-Br \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\oplus}{C}H_2 \xrightarrow{1,2\,\overset{\ominus}{C}H_3\text{ Shift}} CH_3-\overset{\beta_1}{}\underset{\underset{CH_3}{\alpha|}}{\overset{\oplus}{C}}-\overset{\beta_2}{C}H_2-CH_3 \xrightarrow{-\overset{\oplus}{H}}$$

$$\underset{\substack{\text{Minor product}\\ \textit{i.e.,}\\ \text{Hofmann product}}}{CH_2=\underset{\underset{CH_3}{|}}{C}-CH_2-CH_3} + \underset{\substack{\text{Major product}\\ \textit{i.e.,}\\ \text{Saytzeff product}}}{CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_3}$$

(3) *p*-Alkyl halides whose β-carbon is 1° or 2° give E2 reaction.

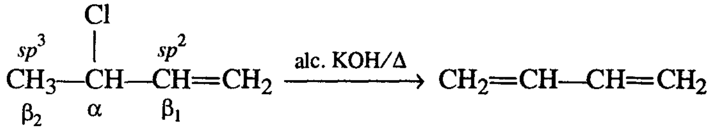
(4) E2 reaction is carried out with a high concentration of a strong base (thus, a high concentration of a strong nucleophile), *i.e.*, alc. KOH/Δ, NaH/Δ, $NaNH_2/\Delta$ and sodium or potassium alkoxide.

(5) E_1 reaction is carried out in the presence of a weak base and above the room temperature. Weak base is generally NaOH/Δ, KOH/Δ and $C_2H_5\overset{\ominus}{O}/\Delta$.

(6) Following factors favour E1 and E2 reactions

		Favours E1	Favours E2
(a)	Alkyl group	3° > 2° > 1°	3° > 2° > 1°
(b)	Base strength	Weak base	Strong base
(c)	Leaving group	Good leaving group	Good leaving group
(d)	Catalyst	$Ag^{\oplus}$, $AlCl_3$	Phase transfer catalyst

(7) If halide has sp^3 as well as sp^2 hybrid β-carbons then elimination takes place only with sp^3 hybrid β-carbon because in this case diene is conjugated.



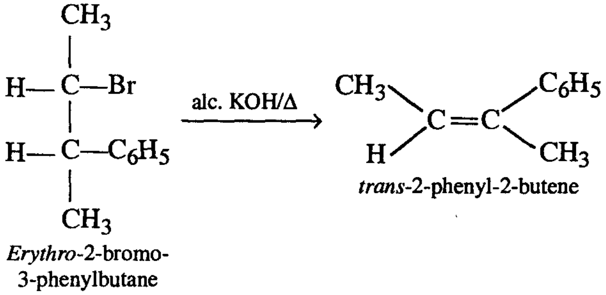
$$\underset{\beta_2}{\overset{sp^3}{CH_3}}-\underset{\alpha}{\overset{\overset{Cl}{|}}{CH}}-\underset{\beta_1}{\overset{sp^2}{CH}}=CH_2 \xrightarrow{\text{alc. KOH}/\Delta} CH_2=CH-CH=CH_2$$

Stereochemistry of E2 Elimination Reactions of Dehydrohalogenation : Optically active alkyl halides, in which α and β carbons are chiral, give stereoselective as well as stereospecific dehydrohalogenation reaction. Geometry of alkene depends on the configuration of the substrate as follows :

(i) *Erythro* form gives *E* or *trans* alkene and

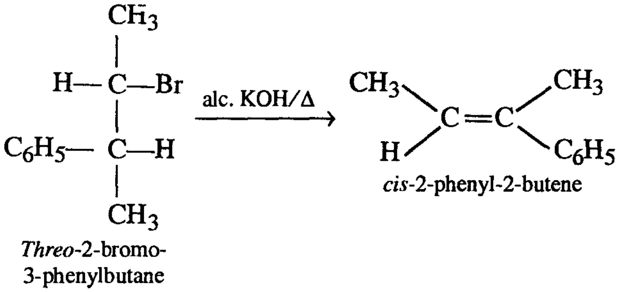
(ii) *Threo* form gives *Z* or *cis* alkene.

Examples are :



Erythro-2-bromo-3-phenylbutane

trans-2-phenyl-2-butene



Threo-2-bromo-3-phenylbutane

cis-2-phenyl-2-butene

5.6.2 Dehydration of Alcohols

(1) Secondary and tertiary alcohols always give E_1 reaction. Primary alcohols whose β-carbon is 3° or 4° also give E1 reaction.

(2) Primary alcohols whose β-carbon is 1° or 2° give E2 reaction.

(3) Dehydrating reagents for alcohols are :

conc. H_2SO_4/Δ, $KHSO_4/\Delta$, H_3PO_4/Δ, anhy. Al_2O_3/Δ
anhy. PCl_5/Δ, anhy. $ZnCl_2/\Delta$, BF_3/Δ and P_2O_5/Δ.

(4) Reactivity of alcohols for elimination reaction is as follows :

ter. alcohol > *sec.* alcohol > *prim.* alcohol

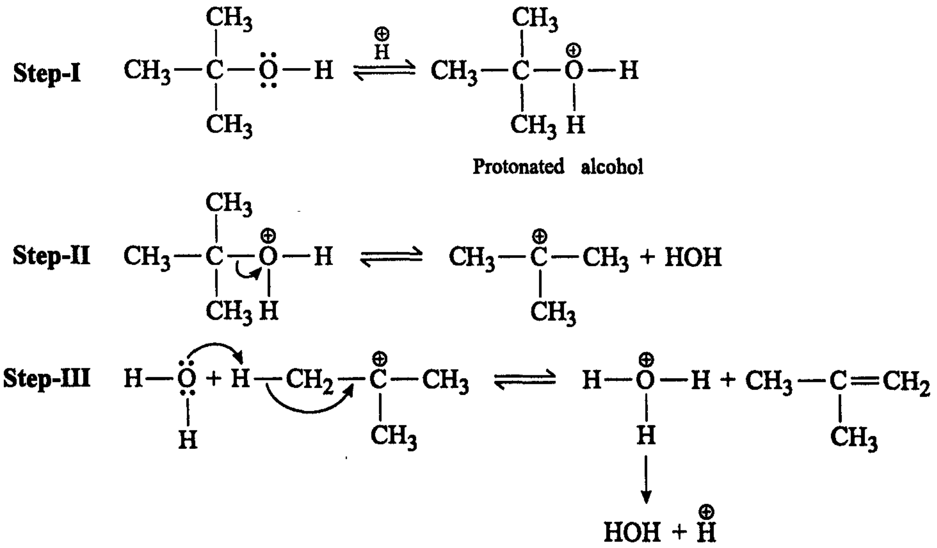
$$\xrightarrow{\hspace{6cm}}$$

Reactivity in decreasing order

(5) Rearrangement occurs in E1 as well as in E2 reactions.

Mechanism of Dehydration of Alcohols

Mechanism of E1 reaction :

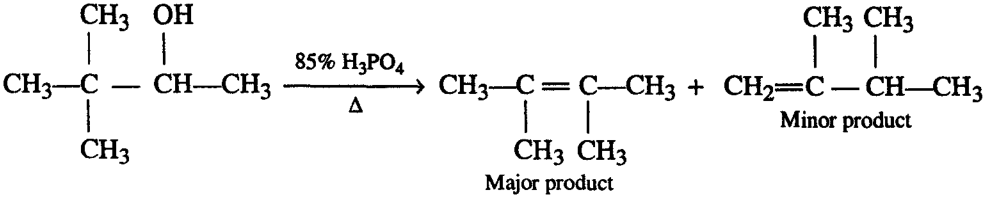


$$\text{Step-I}\quad (CH_3)_3C-\ddot{\underset{..}{O}}-H \xrightleftharpoons{\overset{\oplus}{H}} (CH_3)_3C-\overset{\oplus}{O}H_2$$

$$\text{Step-II}\quad (CH_3)_3C-\overset{\oplus}{O}H_2 \rightleftharpoons CH_3-\overset{\oplus}{C}(CH_3)-CH_3 + HOH$$

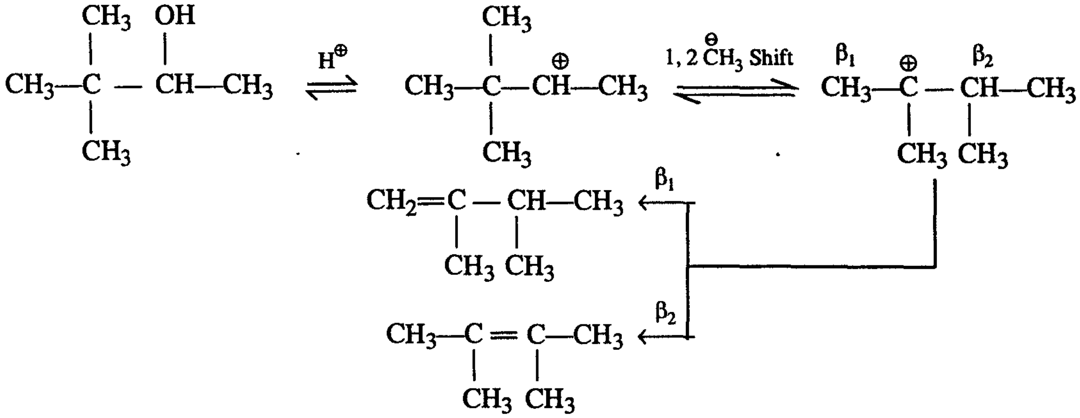
$$\text{Step-III}\quad H-\ddot{\underset{..}{O}}-H + H-CH_2-\overset{\oplus}{C}(CH_3)-CH_3 \rightleftharpoons H-\overset{\oplus}{O}H_2 + CH_3-C(CH_3)=CH_2;\quad H_3O^{\oplus} \rightarrow HOH + \overset{\oplus}{H}$$

Rearrangement in E1 reactions : Consider the following E1 reaction.



$$CH_3-C(CH_3)_2-CH(OH)-CH_3 \xrightarrow[\Delta]{85\%\ H_3PO_4} \underset{\text{Major product}}{CH_3-C(CH_3)=C(CH_3)-CH_3} + \underset{\text{Minor product}}{CH_2=C(CH_3)-CH(CH_3)-CH_3}$$

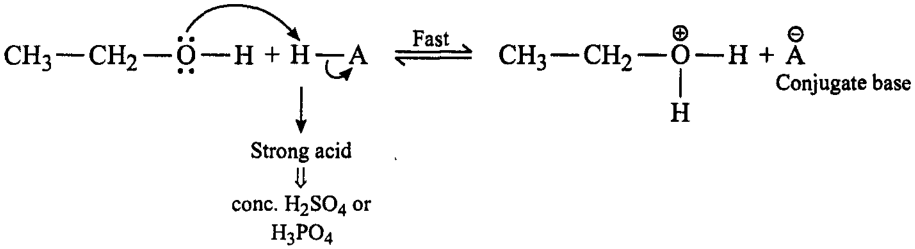
This reaction takes place as follows :



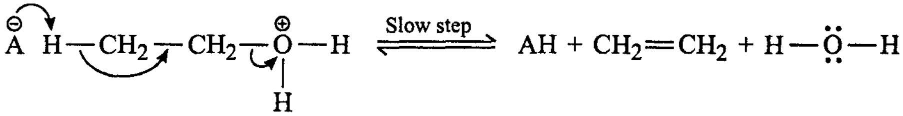
$$CH_3-C(CH_3)_2-CH(OH)-CH_3 \xrightleftharpoons{H^{\oplus}} CH_3-C(CH_3)_2-\overset{\oplus}{C}H-CH_3 \xrightleftharpoons{1,2\ \overset{\ominus}{C}H_3\ \text{Shift}} CH_3-\overset{\oplus}{C}(CH_3)-CH(CH_3)-CH_3$$

$$\xrightarrow{\beta_1} CH_2=C(CH_3)-CH(CH_3)-CH_3 \qquad \xrightarrow{\beta_2} CH_3-C(CH_3)=C(CH_3)-CH_3$$

Mechanism of E2 reaction



$$CH_3—CH_2—\ddot{\underset{\cdot\cdot}{O}}—H + H—A \underset{}{\overset{\text{Fast}}{\rightleftharpoons}} CH_3—CH_2—\underset{\underset{H}{|}}{\overset{\oplus}{O}}—H + \overset{\ominus}{A}$$



$$\overset{\ominus}{A}\ H—CH_2—CH_2—\underset{\underset{H}{|}}{\overset{\oplus}{O}}—H \overset{\text{Slow step}}{\rightleftharpoons} AH + CH_2{=}CH_2 + H—\ddot{\underset{\cdot\cdot}{O}}—H$$

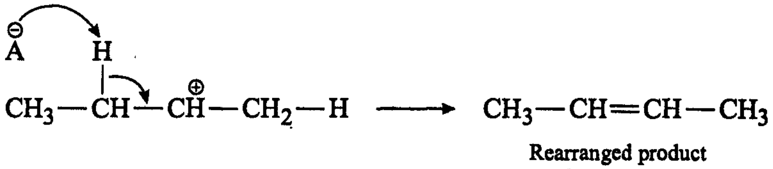
Rearrangement in E2 reactions : The given reaction is E2 reaction :

$$CH_3—CH_2—CH_2—CH_2—OH \xrightarrow[\Delta,\ E_2]{HA} CH_3—CH_2—CH{=}CH_2 + HOH + CH_3—CH{=}CH—CH_3$$

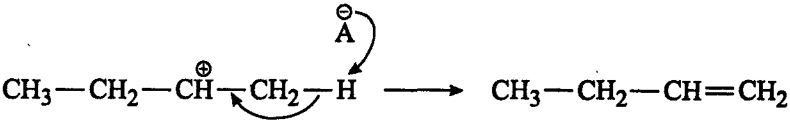
In E_2 reactions rearrangement take place after the formation of alkene because alkene reacts with $\overset{\oplus}{H}$ of acid to give carbocation. This carbocation gives rearranged product.

Step I : $CH_3—CH_2—CH{=}CH_2 + \overset{\oplus}{H} \longrightarrow CH_3—CH_2—\overset{\oplus}{C}H—CH_3$

Step II :



$$\overset{\ominus}{A}\quad CH_3—\overset{\overset{H}{|}}{C}H—\overset{\oplus}{C}H—CH_2—H \longrightarrow CH_3—CH{=}CH—CH_3$$



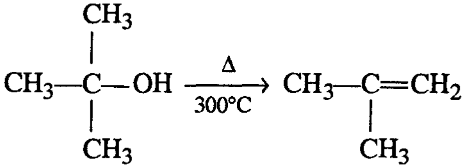
$$CH_3—CH_2—\overset{\oplus}{C}H—CH_2—H \quad \overset{\ominus}{A} \longrightarrow CH_3—CH_2—CH{=}CH_2$$

Thus the overall reaction is

$$CH_3—CH_2—CH_2—CH_2—OH \xrightarrow{\text{conc. } H_2SO_4/\Delta} \underset{\text{Minor product}}{CH_3—CH_2—CH{=}CH_2} + \underset{\text{Major product}}{CH_3—CH{=}CH—CH_3}$$

(6) On the basis of the mechanism, one can conclude that product formation takes place according to Saytzeff rule in E1 as well as in E2 reaction.

(7) Tertiary alcohols are so reactive that they undergo dehydration on strong heating even in the absence of dehydrating agent. In this process Cu works as catalyst.



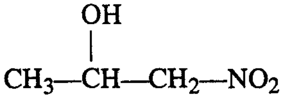
$$CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—OH \xrightarrow[300°C]{\Delta} CH_3—\underset{\underset{CH_3}{|}}{C}{=}CH_2$$

(8) (a) $-I$ group present in an alcohol increases its reactivity for dehydration, and

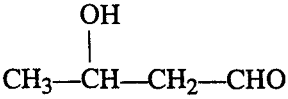
Reactivity $\propto$ $-I$ power of the group present in the alcohol.

(b) Alcohols having $-I$ group undergo dehydration in the presence of acids as well as bases.

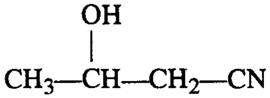
Problem. Which alcohol will be most reactive for dehydration reaction?

(a) 

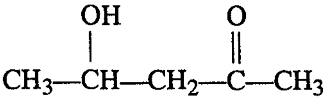
$CH_3-\overset{OH}{\overset{|}{C}}H-CH_2-NO_2$

(b) 

$CH_3-\overset{OH}{\overset{|}{C}}H-CH_2-CHO$

(c) 

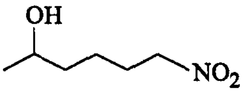
$CH_3-\overset{OH}{\overset{|}{C}}H-CH_2-CN$

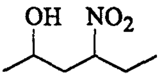
(d) 

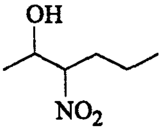
$CH_3-\overset{OH}{\overset{|}{C}}H-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

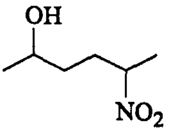
Solution : (a)

Problem. Arrange reactivity of given four alcohols in decreasing order for dehydration reaction.

(A) 

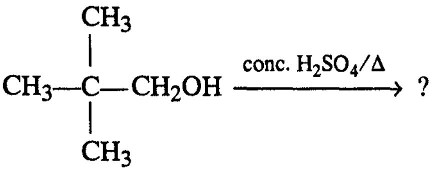
(B) 

(C) 

(D) 

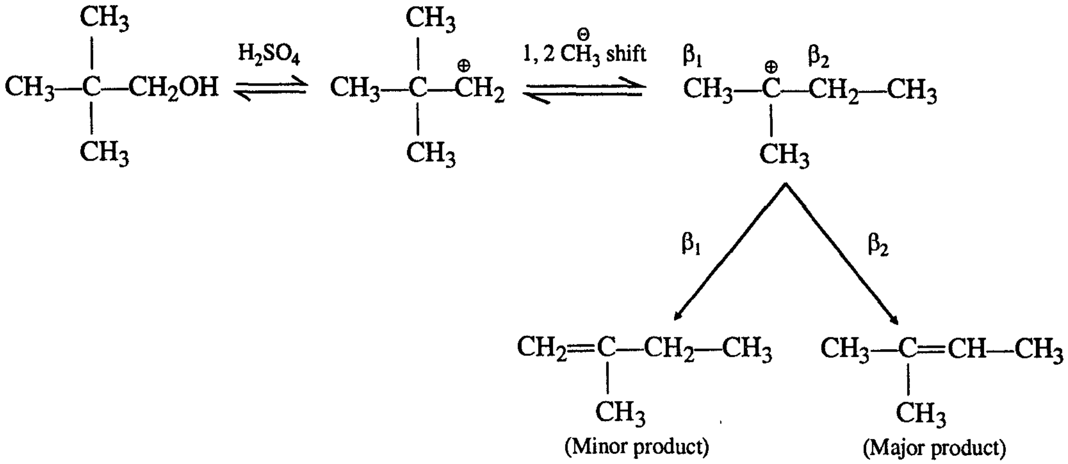
Solution : C > B > D > A.

Problem. Complete the following reaction :



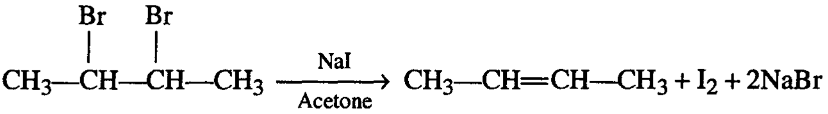
$$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2OH \xrightarrow{\text{conc. } H_2SO_4/\Delta} ?$$

Solution : Compound will give E1 reaction because alcohol is *prim*-alcohol whose β-carbon is 4°.

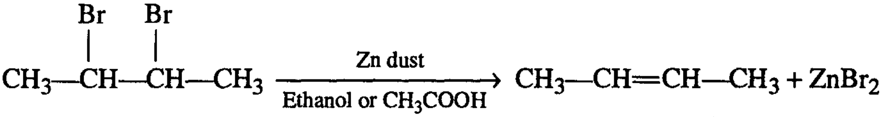


5.6.3 Dehalogenation (Dechlorination and Debromination)

Vicinal (*Vic*) dihalides undergo dehalogenation when they are treated with solution of NaI in acetone or with Zn dust/ethanol or Ag/ethanol.

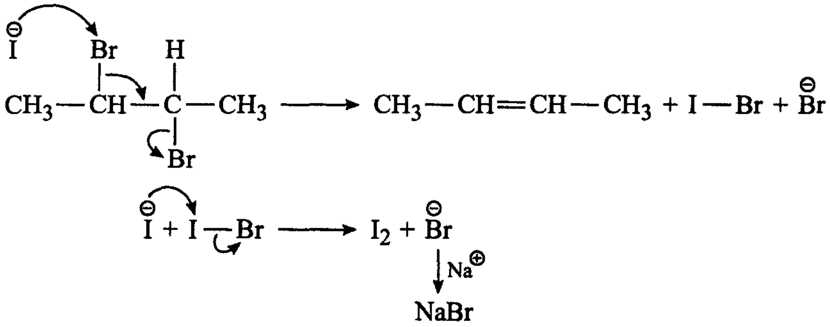


$$CH_3-\underset{}{\overset{Br}{CH}}-\overset{Br}{CH}-CH_3 \xrightarrow[\text{Acetone}]{\text{NaI}} CH_3-CH{=}CH-CH_3 + I_2 + 2NaBr$$



$$CH_3-\overset{Br}{CH}-\overset{Br}{CH}-CH_3 \xrightarrow[\text{Ethanol or } CH_3COOH]{\text{Zn dust}} CH_3-CH{=}CH-CH_3 + ZnBr_2$$

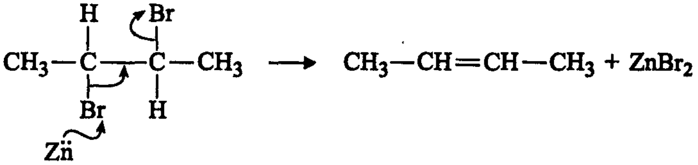
Dehalogenation by NaI takes place by an E2 mechanism



$$\overset{\ominus}{I} \quad CH_3-\overset{Br}{CH}-\underset{Br}{\overset{H}{C}}-CH_3 \longrightarrow CH_3-CH{=}CH-CH_3 + I-Br + \overset{\ominus}{Br}$$

$$\overset{\ominus}{I} + I-Br \longrightarrow I_2 + \overset{\ominus}{Br} \xrightarrow{Na^{\oplus}} NaBr$$

Dehalogenation by Zn or Ag also takes place by E2 mechanism as follows :

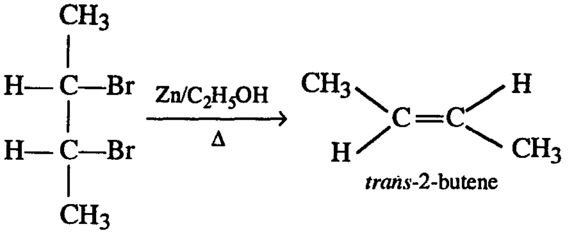


$$CH_3-\underset{Br}{\overset{H}{C}}-\underset{H}{\overset{Br}{C}}-CH_3 \longrightarrow CH_3-CH{=}CH-CH_3 + ZnBr_2$$

Stereochemistry of Dehalogenation Reactions : Dehalogenation reactions are *anti*-elimination reactions. These reactions are also stereoselective as well as stereospecific reactions. Geometry of alkenes depends on the configuration of the α, β-dihaloalkanes in which α and β-carbons are chiral.

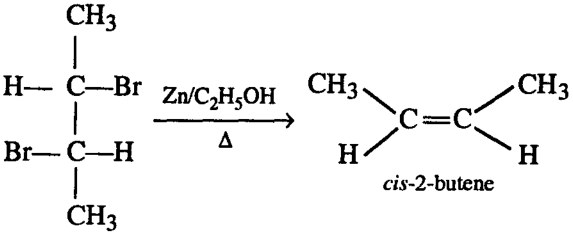
(i) *Meso* form gives *trans* alkene and (ii) *d* and *l* forms gives *cis* alkene.

Examples are :



trans-2-butene

Meso-2, 3-dibromo-butane

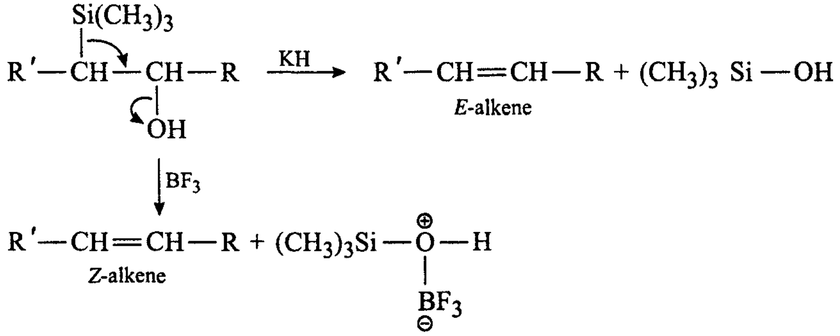


cis-2-butene

(*d*) or (*l*)

5.6.4 Peterson Reaction

β-Hydroxy silane gives elimination reaction in the presence of acid as well as base and stereochemistry depends on the nature of the reagent.



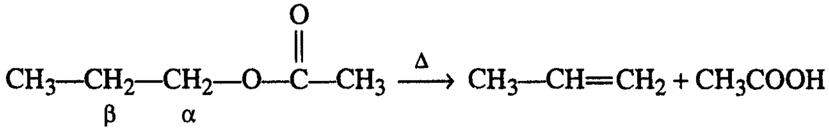
5.6.5 Thermal (Pyrolytic) Eliminations or Cyclic Eliminations

Thermal elimination is given by a small family of organic compounds like acetates, xanthates and amine oxides.

In this elimination, product formation takes place via formation of cyclic TS hence no carbon skeleton rearrangement occurs. Thus elimination is always *syn* elimination. This elimination takes place in gaseous state. This elimination does not involve acid or base as catalyst.

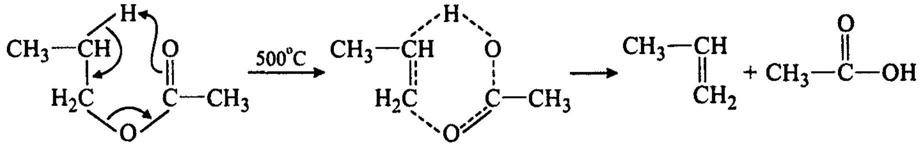
In thermal elimination, product formation always takes place by **Hofmann rule.**

(i) Thermal elimination of acetates :

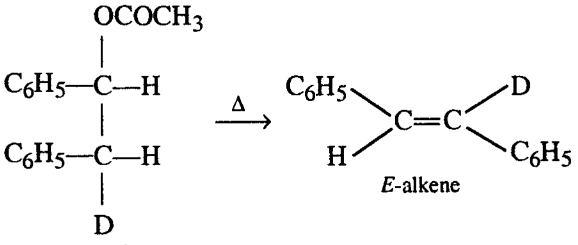


$$\underset{\beta}{CH_3}—\underset{\alpha}{CH_2}—CH_2—O—\overset{\overset{\large O}{\|}}{C}—CH_3 \xrightarrow{\Delta} CH_3—CH{=}CH_2 + CH_3COOH$$

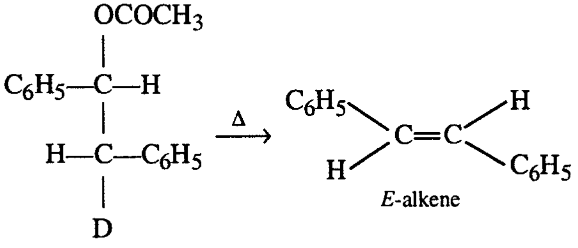
The reaction proceeds through a cyclic TS as shown below :



If substrate is optically active having two asymmetric carbons, then alkene is always *E*-alkene.

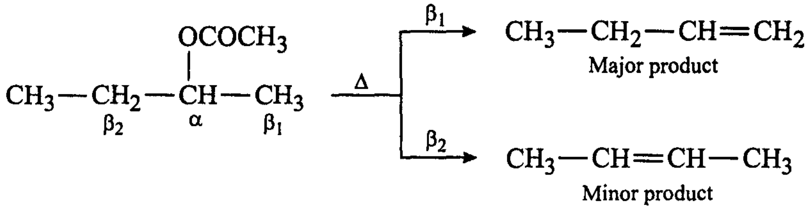


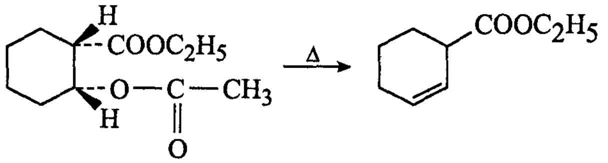
Erythro form



Threo form

Some other examples are :



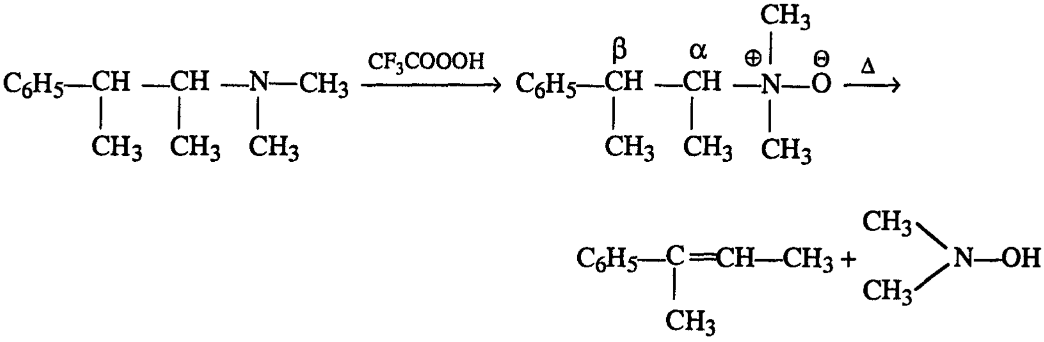


(ii) Thermal Elimination of Amine Oxides :
(COPE REACTION OR COPE ELIMINATION)

Tertiary amines are oxidised by hydrogen peroxide and per acids into amine oxides.

$$R_3\ddot{N} \xrightarrow[CF_3COOOH]{H_2O_2 \text{ or}} \underset{\text{N-oxide}}{R_3-\overset{\oplus}{N}-\overset{\ominus}{O}}$$

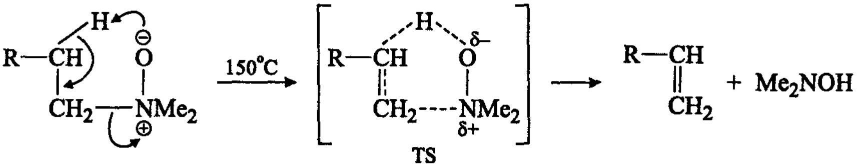
When an amine oxide of 3°-amines containing at least one β-hydrogen is heated at about 150°C, it decomposes to form an alkene and a derivative of hydroxylamine. This elimination is an example of thermal elimination known as Cope elimination or Cope reaction.



$$C_6H_5-\underset{CH_3}{CH}-\underset{CH_3}{CH}-\underset{CH_3}{N}-CH_3 \xrightarrow{CF_3COOOH} C_6H_5-\underset{CH_3}{\overset{\beta}{CH}}-\underset{CH_3}{\overset{\alpha}{CH}}-\underset{CH_3}{\overset{CH_3}{\overset{\oplus}{N}}}-\overset{\ominus}{O} \xrightarrow{\Delta}$$

$$C_6H_5-\underset{CH_3}{C}=CH-CH_3 + \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>N-OH$$

The reaction proceeds through a cyclic TS as shown below :

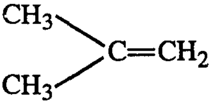


5.7 PHYSICAL PROPERTIES AND RELATIVE STABILITIES OF ALKENES

Alkenes containing 2-4 carbon atoms are gases; 5–17 are liquids; 18 onwards are solids at room temperature. In general, the physical properties of alkenes are similar to those of alkanes because alkenes are also subject only to van der Waals attractive forces. Geometrical isomers (*cis* and *trans*) behave differently because of their geometry.

On the basis of heat of hydrogenation (or heat of combustion, or heat of formation) of alkenes, it has been found that an alkene is stabilised by the presence of an alkyl group on the double bonded carbon. An alkene with a greater number of alkyl groups on the double bonded carbons is usually more stable. In general, the order of stability of alkenes is :

$$R_2C{=}CR_2 > R_2C{=}CHR > R_2CH{=}CH_2 \sim RCH{=}CHR\ (\textit{trans} > \textit{cis}) > RCH{=}CH_2 > CH_2{=}CH_2$$

This order may be explained in terms of hyperconjugation and steric effects. It should be noted that a molecule with two small alkyl groups on the double bonded carbon is more stable than its isomer with one large group on the double bonded carbon, *e.g.*,  $(CH_3)_2C{=}CH_2$ is more stable that $CH_3CH_2CH{=}CH_2$; this is because greater number (six) of hyperconjugative forms are possible in the case of the former than that in the latter (only two). Similarly a *trans* alkene is stabler than its isomeric *cis* alkene. This is because of steric repulsion between the closer alkyl groups in the *cis* isomer, which destabilises the molecule due to steric strain.

5.8 ADDITION REACTIONS OF ALKENES

The average bond energy for C=C is 146 kcal/mole. This value is 63 kcal/mole higher than the normal C—C bond strength of 83 kcal/mole. This difference may be considered roughly as the bond strength of the second bond or π-bond in alkene. Thus the π-bond is substantially weaker that the σ-bond.

The reaction of this weak π-bond with a normal single bond compound to produce a molecule containing two new single bonds is generally a thermodynamically favourable process.

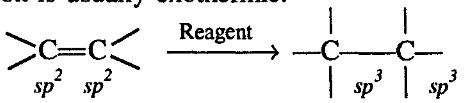
$$CH_2{=}CH_2 + H_2 \longrightarrow CH_3{-}CH_3, \quad \Delta H = -32{\cdot}7 \text{ kcal/mole}$$

$$CH_2{=}CH_2 + Cl_2 \longrightarrow CH_2Cl{-}CH_2Cl, \quad \Delta H = -43{\cdot}2 \text{ kcal/mole}$$

$$CH_2{=}CH_2 + HBr \longrightarrow CH_3{-}CH_2Br, \quad \Delta H = -19{\cdot}0 \text{ kcal/mole}$$

$$CH_2{=}CH_2 + H_2O \longrightarrow CH_3{-}CH_2OH, \quad \Delta H = -10{\cdot}9 \text{ kcal/mole}$$

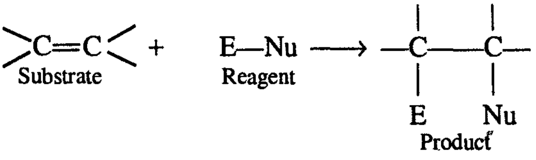
Each of these reactions is an **addition reaction.** In each case, a reagent has added to the alkene without the loss of any atom. Thus the principal characteristic of unsaturated compounds is the addition of reagents to *pi* bonds. In each case the sp^2 carbon atoms are rehybridised to sp^3. Compound containing π-bonds are of higher energy than comparable compounds containing only σ-bonds, consequently an addition reaction is usually exothermic.



The reaction in this case may be electrophilic, nucleophilic or a free radical addition.

5.9 ELECTROPHILIC ADDITION REACTIONS

To introduces the mechanism of **electrophilic addition**, let us consider the following general reaction.

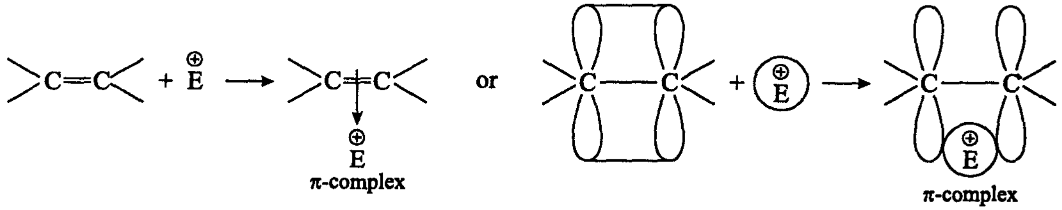


For E—Nu to react with the substrate, there must be some attractive force that could cause the two species to come together.

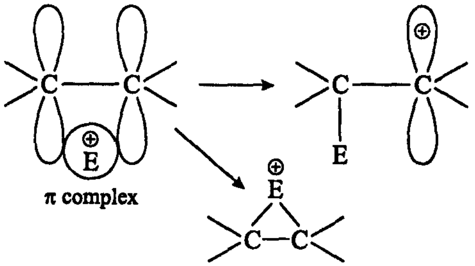
The reagent E—Nu can be thought to be divisible into an electrophile $\overset{\oplus}{E}$ and a nucleophile $\overset{\ominus}{Nu}$.

The region above and below a double bond is electron rich because of the π-bond. Consequently π-bonds have tendency to act as *Lewis bases*. The electrophile $\overset{\oplus}{E}$, is attracted to this cloud of π electrons and can be embeded in it. Now the reacting species $\overset{\oplus}{E}$ has made contact and the reaction can commence. Since electrophile initiated this contact, the reaction is termed as electrophilic addition.

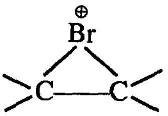
The species that results from the interaction of π-electron clouds of alkene with an electrophile is known as π complex. During the interaction vacant orbital on the electrophile overlaps a π-orbital of the alkene. In this complex electrophile is not localised on a particular atom. The formation of π-complex can be represented as follows :



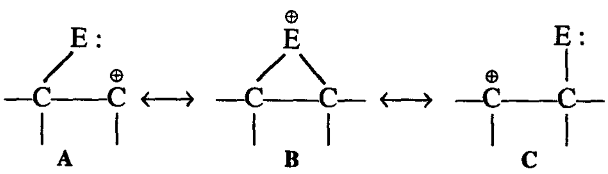
Thus the initial step of an electrophilic addition is the formation of a π-complex. Such a complex does not actually involve a formal covalent bond and may be regarded as an association in which electrophile gets embeded in the π-electron clould of alkene leading to the formation of open chain or a cyclic intermediate.



Most of the electrophiles which have a nonbonding electron pair on the electrophilic atom may form a true three-membered cyclic intermediate. For example, bromine forms a three-membered cyclic bromonium ion.



Cations such as these may be described in terms of three resonating structures.

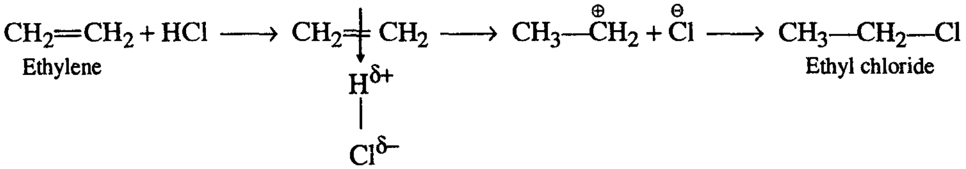


If both **A** and **C** correspond to unstable carbocations then structure **B** is a more important contributor to the actual structure of the ion. If either **A** or **C** corresponds to relatively stable carbocation, then that structure contributes more and the ion has substantial carbocation character without much cyclic ion character.

5.9.1 Addition of Hydrogen Halides

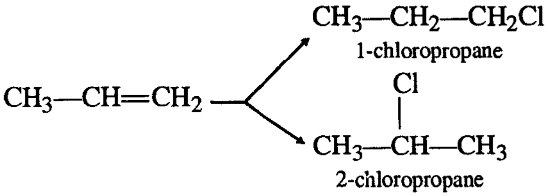
Hydrogen halides add to the *pi* bonds of alkenes to yield alkyl halide. This reaction is often used as a synthetic reaction. The relative reactivity of H*X* in this reaction is HI > HBr > HCl > HF. The strongest acid (HI) is the most reactive towards alkene, while the weakest acid (HF) is the least reactive.

A hydrogen halide contains a highly polar H—*X* bond and can easily lose $\overset{\oplus}{H}$ to the *pi* bond of an alkene. The result of the attack of $\overset{\oplus}{H}$ is an intermediate carbocation, which quickly undergoes reaction with the negative halide ion $(\overset{\ominus}{X})$ to yield an alkyl halide.

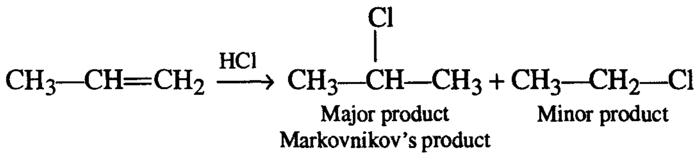


$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + HCl \longrightarrow \underset{\substack{H^{\delta+}\\ | \\ Cl^{\delta-}}}{CH_2{=}CH_2} \longrightarrow CH_3{-}\overset{\oplus}{C}H_2 + \overset{\ominus}{Cl} \longrightarrow \underset{\text{Ethyl chloride}}{CH_3{-}CH_2{-}Cl}$$

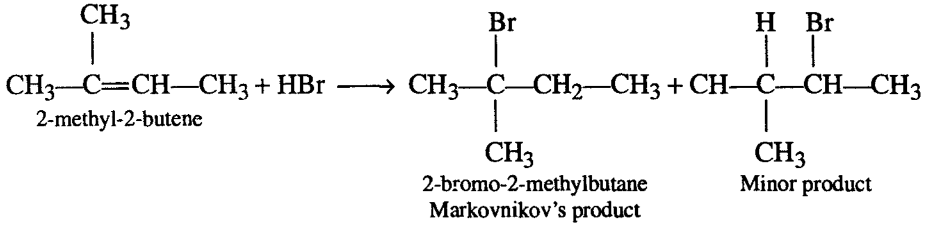
(I) Markovnikov's Rule : If an alkene is unsymmetrical there is the possibility of two different products from the addition of H*X*.



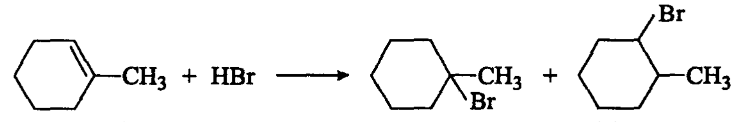
In an electrophilic addition that can lead to two products, one product usually predominates over the other. In 1869, the Russian chemist, Vladimir Markovnikov formulated the following empirical rule : ***"In additions of HX to unsymmetrical alkenes, the*** $\overset{\oplus}{H}$ ***of HX goes to that double-bonded carbon which already has the greater number of hydrogens."*** Examples of reactions that obey Markovnikov's rule follow :



$$CH_3{-}CH{=}CH_2 \xrightarrow{HCl} \underset{\substack{\text{Major product}\\ \text{Markovnikov's product}}}{CH_3{-}\overset{\overset{Cl}{|}}{C}H{-}CH_3} + \underset{\text{Minor product}}{CH_3{-}CH_2{-}Cl}$$



$$\underset{\text{2-methyl-2-butene}}{CH_3{-}\overset{\overset{CH_3}{|}}{C}{=}CH{-}CH_3} + HBr \longrightarrow \underset{\substack{\text{2-bromo-2-methylbutane}\\ \text{Markovnikov's product}}}{CH_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}}{-}CH_2{-}CH_3} + \underset{\text{Minor product}}{CH{-}\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}{-}\overset{\overset{Br}{|}}{C}H{-}CH_3}$$

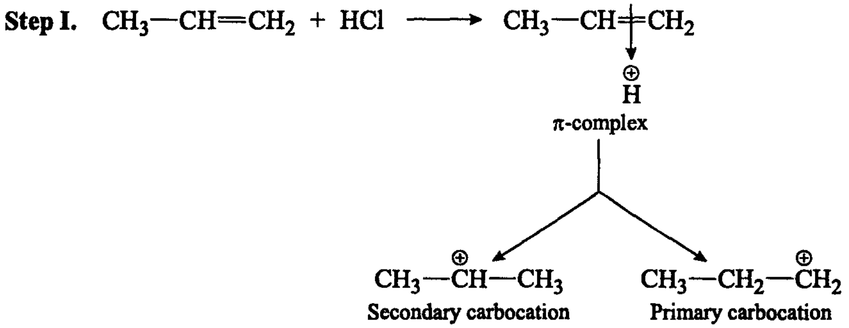


1-methylcyclohexene

1-Bromo-1-methylcyclohexane (Major product)

2-bromo-1-methylcyclohexane (Minor product)

Explanation of Markovnikov's Rule : Markovnikov formulated the rule on the basis of experimental observations. Why is this rule followed ? To answer this question consider the mechanism of this reaction.



Step I. $CH_3—CH{=}CH_2 + HCl \longrightarrow CH_3—CH\overset{}{\underset{\overset{\oplus}{H}}{\downarrow}}CH_2$

π-complex

$CH_3—\overset{\oplus}{C}H—CH_3$ Secondary carbocation

$CH_3—CH_2—\overset{\oplus}{C}H_2$ Primary carbocation

In this reaction first step involves the formation of carbocation. For propene, two possible carbocations could be formed. The order of stability of carbocations is tertiary > secondary > primary.

For propene, the two positions of $\overset{\oplus}{H}$ addition lead to (1) a high energy unstable primary carbocation or (2) a low-energy more stable secondary carbocation (Fig. 5.4). Since secondary carbocation is more stable than primary, it is formed preferentially. The chlorine ion attacks the more stable carbocation to give 2-chloropropane, the major product.

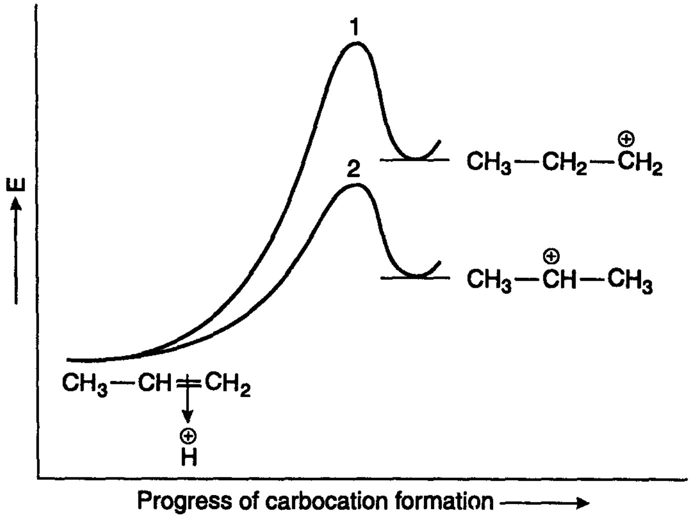
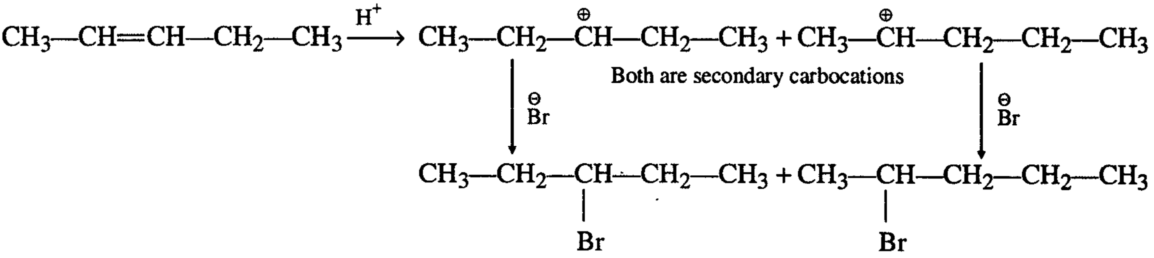


Fig. 5.4. Conversion of π-complex into carbocation. Formation of $CH_3\overset{\oplus}{C}H—CH_3$ occurs more rapidly than the formation of $CH_3—CH_2—\overset{\oplus}{C}H_2$

Addition of a reagent to an unsymmetrical alkene proceeds by formation of the more stable carbocation intermediate. This is the reason that Markovnikov's rule is followed.

The Markovnikov's rule in modern term can be stated as "when an unsymmetrical reagent adds to an unsymmetrical alkene, the electrophilic portion of the reagent adds to that double bonded carbon, which results in the formation of a more stable carbocation."

If both possible carbocations are equally stable, then they both will be formed in significant amounts. In turn, this means that both isomeric products are formed in comparable amounts. The reaction of 2-pentene with HBr illustrates this :



$$CH_3{-}CH{=}CH{-}CH_2{-}CH_3 \xrightarrow{H^+} CH_3{-}CH_2{-}\overset{\oplus}{C}H{-}CH_2{-}CH_3 + CH_3{-}\overset{\oplus}{C}H{-}CH_2{-}CH_2{-}CH_3$$

Both are secondary carbocations

$$\xrightarrow{\overset{\ominus}{Br}} CH_3{-}CH_2{-}\underset{Br}{\underset{|}{C}H}{-}CH_2{-}CH_3 + CH_3{-}\underset{Br}{\underset{|}{C}H}{-}CH_2{-}CH_2{-}CH_3$$

Both are formed in comparable amounts

Conditions For The Use of Markovnikov's Rule

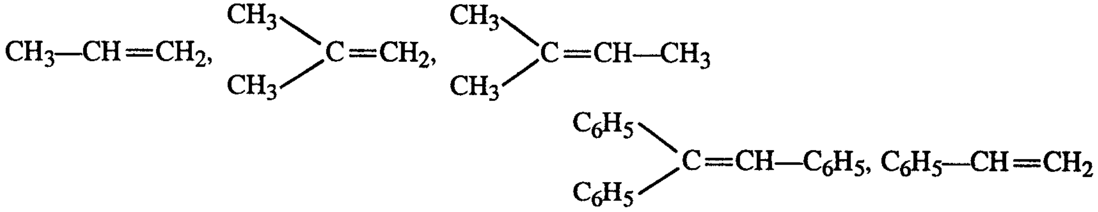
This rule can be used only in those alkenes which fulfil the following two conditions :

(a) Alkene should be unsymmetrical.

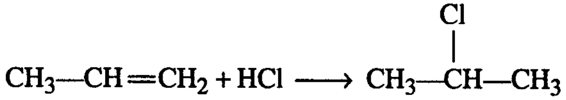
(b) Substituent/substituents present on doubly bonded carbon(s) should only be + I group.

(c) If phenyl group is present on doubly bonded carbons, then one, or both doubly bonded carbons should be substituted by phenyl groups only.

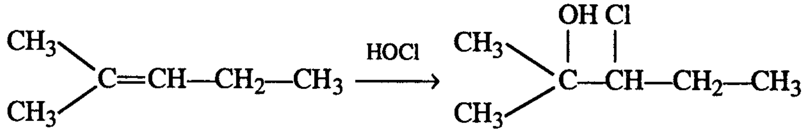
For example, the following alkenes will give addition according to the Markovnikov's rule.

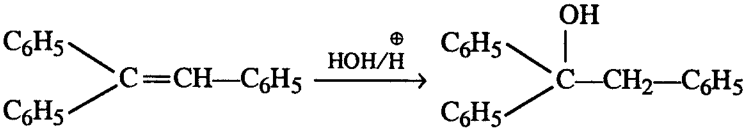


Examples of some addition reactions :

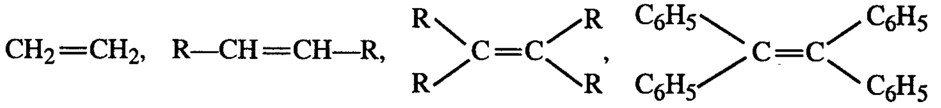


$$CH_3{-}CH{=}CH_2 + HCl \longrightarrow CH_3{-}\overset{\overset{Cl}{|}}{C}H{-}CH_3$$

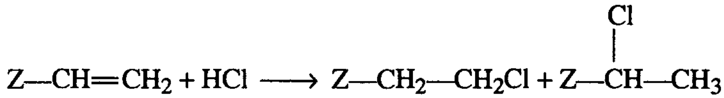




Following alkenes will not give addition reaction according to Markovnikov's rule.



(II) *Anti*-Markovnikov Addition : Rarely an acid will add to an alkene so that the incoming proton (positive part) is placed on the carbon bearing the smallest number of hydrogens. These rather unusual reactions are described as *anti*-Markovnikov additions. *Anti*-Markovnikov addition is observed if the alkene bears a powerful electron withdrawing group attached directly to the double bond.

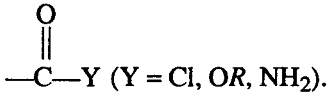


$$Z{-}CH{=}CH_2 + HCl \longrightarrow \underset{\text{Major product}}{Z{-}CH_2{-}CH_2Cl} + \underset{\text{Minor product}}{Z{-}\overset{\overset{\displaystyle Cl}{|}}{C}H{-}CH_3}$$

Major product Minor product

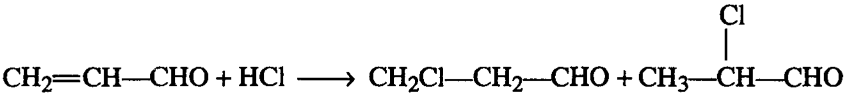
Anti-Markovnikov product

where Z = —CX_3 (X = halogen), —NO_2, —CN, —CHO, —COR, —COOH,



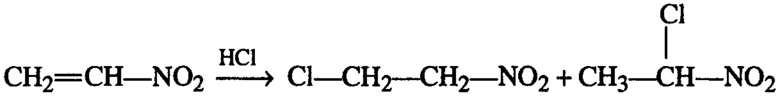
$$-\overset{\overset{\displaystyle O}{\|}}{C}-Y \quad (Y = Cl, OR, NH_2).$$

The following are some examples :



$$CH_2{=}CH{-}CHO + HCl \longrightarrow CH_2Cl{-}CH_2{-}CHO + CH_3{-}\overset{\overset{\displaystyle Cl}{|}}{C}H{-}CHO$$

Major product Minor product

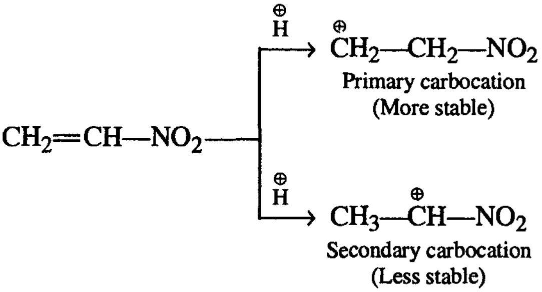


$$CH_2{=}CH{-}NO_2 \xrightarrow{HCl} Cl{-}CH_2{-}CH_2{-}NO_2 + CH_3{-}\overset{\overset{\displaystyle Cl}{|}}{C}H{-}NO_2$$

Major product Minor product

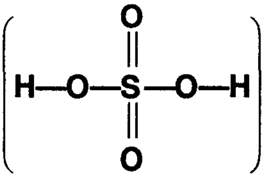
Anti-Markovnikov product

These *anti*-Markovnikov additions do proceed through the most stable carbocations.



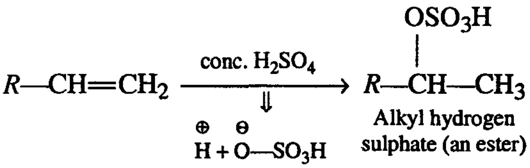
In the above case, the primary carbocation is more stable than the secondary because the secondary carbocation is destabilised by the adjacent electron-withdrawing group due to intensification of the prositive charge. This leads to the formation of *anti*-Markovnikov product as the major product.

5.9.2 Addition of conc. H_2SO_4



$$\left(H{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{-}O{-}H \right)$$

Alkenes give electrophilic addition with cold concentrated sulphuric acid and addition takes place according to Markovnikov's rule.



$$R{-}CH{=}CH_2 \xrightarrow[\Downarrow \atop \overset{\oplus}{H} + \overset{\ominus}{O}{-}SO_3H]{\text{conc. } H_2SO_4} R{-}\overset{\overset{\displaystyle OSO_3H}{|}}{C}H{-}CH_3$$

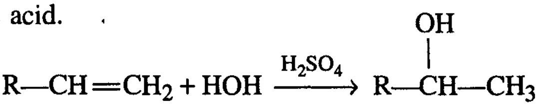
Alkyl hydrogen sulphate (an ester)

(a) Alkenes are soluble in conc. H_2SO_4 because alkenes react with conc. H_2SO_4 to form soluble alkyl hydrogen sulphate.

(b) Alkyl hydrogen sulphate is ester which on hydrolysis gives alcohol and acid (H_2SO_4).

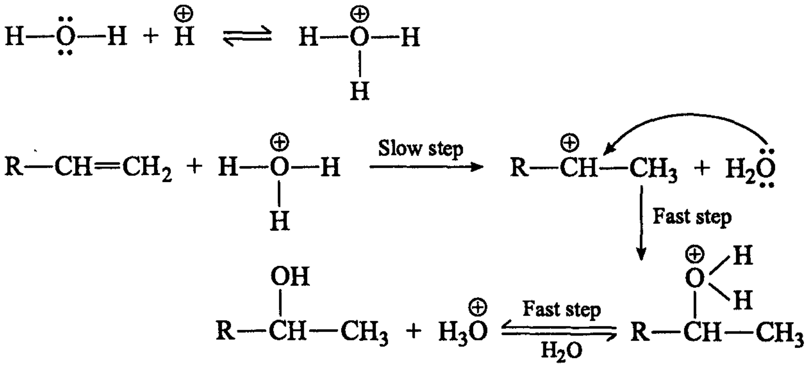
5.9.3 Hydration of Alkenes : Addition of water

Alkenes give addition reaction with water only in the presence of acid as catalyst. The catalyst of the reaction is sulphuric acid.

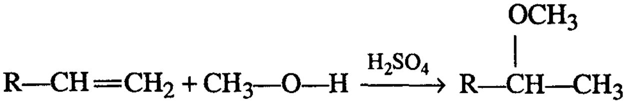


$$R{-}CH{=}CH_2 + HOH \xrightarrow{H_2SO_4} R{-}\underset{}{\overset{\displaystyle OH}{\overset{|}{C}}}H{-}CH_3$$

Mechanism :



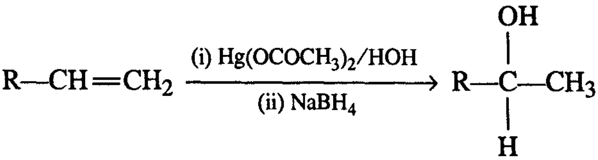
Note : Alcohols react with alkenes in the same way that water does. The product of the reaction is ether.



$$R{-}CH{=}CH_2 + CH_3{-}O{-}H \xrightarrow{H_2SO_4} R{-}\overset{\displaystyle OCH_3}{\overset{|}{C}}H{-}CH_3$$

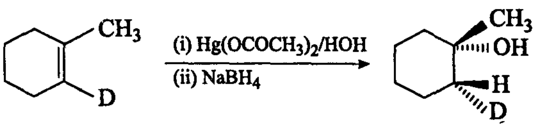
5.9.4 Oxymercuration-demercuration

Addition of alkene with mercuric acetate in the presence of water is called oxymercuration reaction. In this case product formation takes place by the formation of bridged carbocation as reaction intermediate. The adduct on reduction with sodium borohydride gives alcohol. This step is known as demercuration and the overall reaction is also called oxymercuration reduction.



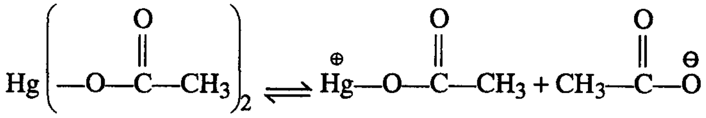
$$R{-}CH{=}CH_2 \xrightarrow[\text{(ii) NaBH}_4]{\text{(i) Hg(OCOCH}_3)_2\text{/HOH}} R{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}{-}CH_3$$

Experimentally it has been found that the product of the reaction is result of the *anti* addition reaction. For example



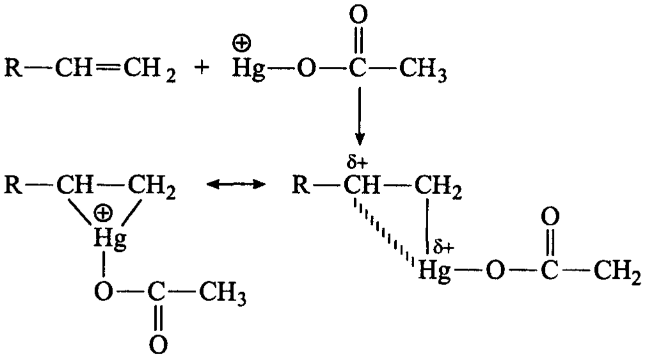
Anti addition can be only explained if product formation takes place by the formation of cyclic intermediate.

Mechanism :

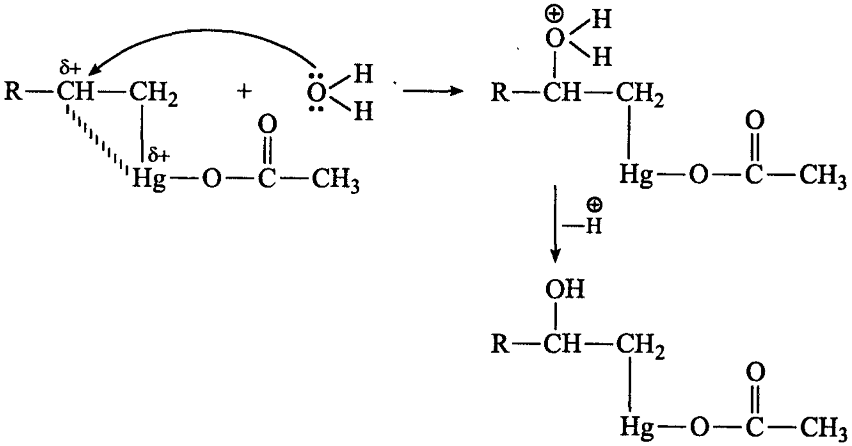


$$\mathrm{Hg}\left(-\mathrm{O}-\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{CH_3}\right)_2 \rightleftharpoons \overset{\oplus}{\mathrm{Hg}}-\mathrm{O}-\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{CH_3} + \mathrm{CH_3}-\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\overset{\ominus}{\mathrm{O}}$$

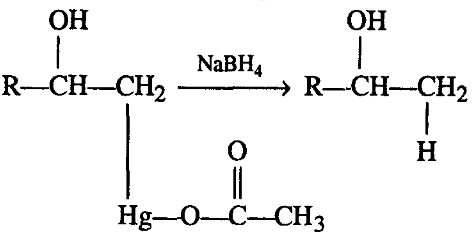
First step :



Second step : In the second step nucleophile attacks on the opposite face of the Hg. Nucleophile will attack on the carbon which has more carbocation character.



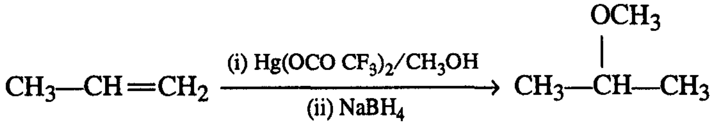
Third step : Sodium borohydride converts carbon-mercury bond into a carbon-hydrogen bond. Because the reaction results in the loss of mercury, it is called demercuration.



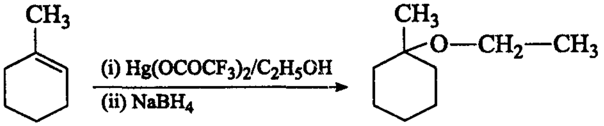
In the product both —OH and H are *anti* to each other.

Note 1. Product of the reaction is identical to hydration of alkenes.

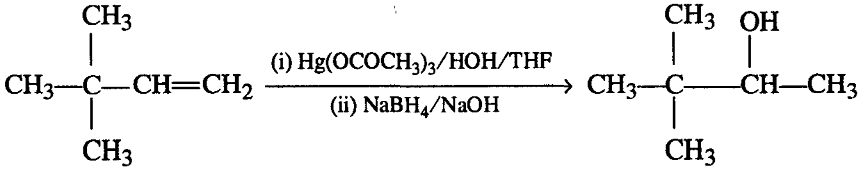
Note 2. If alcohol is used in place of water as nucleophile then this reaction is called **alkoxy mercuration-dermercuration** and product of the reaction is ether. Addition of alcohol works better in the presence of mercuric trifluoroacetate.



$$CH_3—CH=CH_2 \xrightarrow[\text{(ii) NaBH}_4]{\text{(i) Hg(OCO CF}_3)_2/\text{CH}_3\text{OH}} CH_3—\overset{\overset{OCH_3}{|}}{C}H—CH_3$$



Note 3. Oxymercuration-demercuration allows the Markovnikov addition of —H and —OH without any rearrangement. The net result of the reaction is addition of HOH.

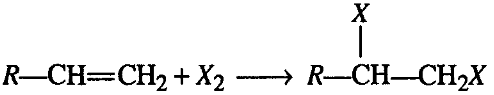


$$CH_3—\underset{CH_3}{\overset{CH_3}{C}}—CH=CH_2 \xrightarrow[\text{(ii) NaBH}_4/\text{NaOH}]{\text{(i) Hg(OCOCH}_3)_3/\text{HOH/THF}} CH_3—\underset{CH_3}{\overset{CH_3}{C}}—\overset{OH}{C}H—CH_3$$

(No rearrangement)

5.9.5 Addition of Halogens

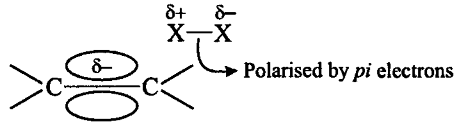
An important general reaction of double bonds is the addition of halogens.



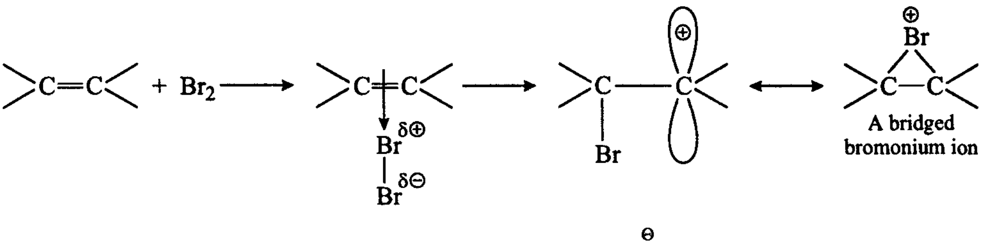
$$R—CH=CH_2 + X_2 \longrightarrow R—\overset{\overset{X}{|}}{C}H—CH_2X$$

This reaction is rapid and serves as a single diagnostic method for unsaturation.

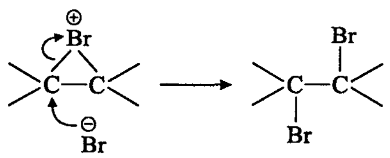
The reaction of X_2 with alkene is similar to HX. But what is the source of the electrophile in X_2 ? Although Cl_2, and Br_2 are nonpolar, as they approach the π-electron cloud of the double bond, the repulsion between π-electron cloud and the non-bonding electrons in the outer shell of the halogen molecule, momentarily polarises the halogen molecule $(\overset{\delta+}{X}—\overset{\delta-}{X})$.



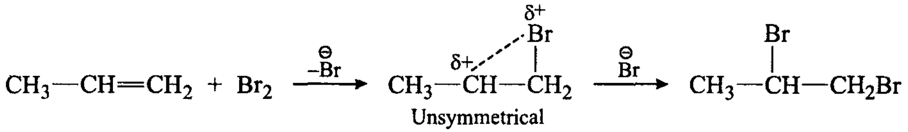
As the *X—X* bond becomes more polarised, it becomes progressively weaker until it finally breaks. The result is a halide ion and a positively charged organohalogen ion, called a **halonium ion.** The halonium ion is not a simple carbocation but is bridged. In the case of addition of X_2 to symmetrical alkene, the bridged halonium ion is symmetrical, with *X* equally bonded to each carbon.



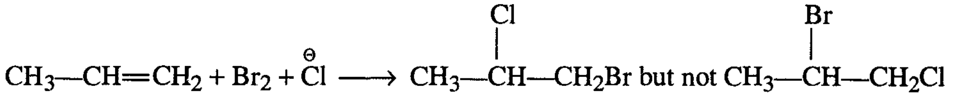
The cyclic halonium ion is attacked by the nucleophile $(\overset{\ominus}{X})$ at the carbon which is part of the three-membered ring. They are attacked because the $\overset{\oplus}{X}$ makes them slightly positive.



If the alkene is unsymmetrical, most of the positive charge is carried on the more substituted carbon. In this case carbocation stability is followed :

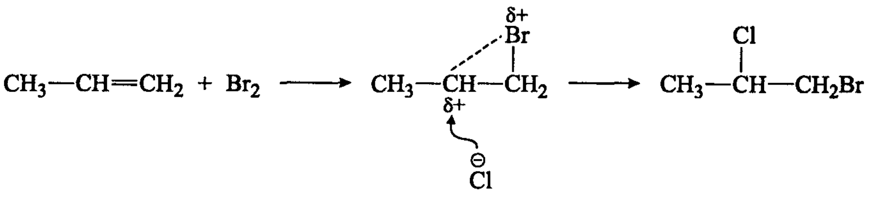


Formation of unsymmetrical bromonium ion can best be demonstrated in the following case :

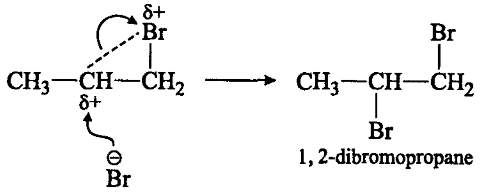


$$CH_3{-}CH{=}CH_2 + Br_2 + \overset{\ominus}{Cl} \longrightarrow CH_3{-}\overset{\overset{Cl}{|}}{C}H{-}CH_2Br \text{ but not } CH_3{-}\overset{\overset{Br}{|}}{C}H{-}CH_2Cl$$

Formation of 2-chloro-1-bromopropane can only be possible if bromonium ion is unsymmetrical. In this bromonium ion *C*-1 Br bond is stronger than the *C*-2 Br bond. In doing this the presence of positive charge should be on *C*-2 rather than on *C*-1. This is not unreasonable, since the methyl group should stabilise some positive charge at *C*-2. The net result is to produce an unsymmetrical bromonium ion.

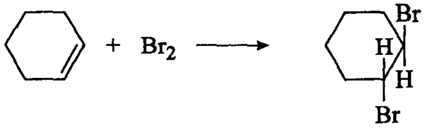


The cyclic halonium ion intermediate has an important effect on the stereochemistry of halogen addition. When halide ion reacts with a cyclic ion the reaction is a nucleophilic displacement reaction. A negative $\overset{\ominus}{\text{Br}}$ cannot attack a carbon of the bridged intermediate from the top (as shown in the structure), that path is blocked by the Br bridge. Therefore, $\overset{\ominus}{\text{Br}}$ attacks from the opposite side of the intermediate. The result is *anti* addition of Br_2 to the double bond.



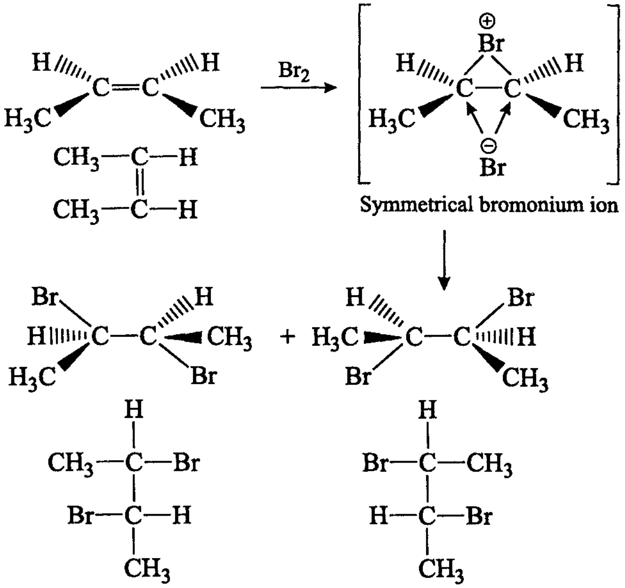
Two pieces of evidence indicate a bridged ion as the intermediate in halogen addition (X_2) and to *anti* addition as the mechanism. Both pieces of evidence are based upon the fact that only one stereoisomeric product is observed in reactions whereas two or more products would be expected from a simple carbocation intermediate.

Bromine adds *anti* to cyclohexene. This firmly establishes the stereochemistry of addition.



trans-1, 2-dibromocyclohexane

Additional evidence for *anti* addition is encountered in the reactions of geometrical isomers of open chain alkenes. When *cis* or *trans*-2-butene is treated with Br_2, two asymmetric carbons are generated. The product of this addition 2, 3-dibromobutane can exist in three stereoisomeric forms; a pair of enantiomers and a *meso* form. The addition of Br_2 to *cis*-2-butene yields only the enantiomeric pair. No *meso* form is produced in this reaction.



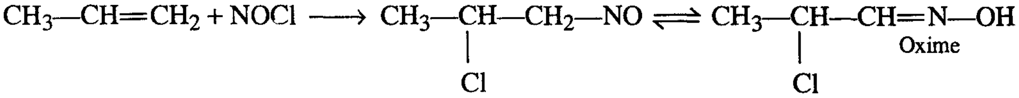
Enantiomers

Addition of X_2 is catalysed only by anhy. AlX_3 because AlX_3 reacts with X_2 to give $\overset{\oplus}{X}$.

$$AlX_3 + X_2 \longrightarrow \overset{\ominus}{AlX_4} + \overset{\oplus}{X}$$

5.9.6 Addition of Nitrosyl Chloride

Nitrosyl chloride, nitrosyl bromide and oxides of nitrogen add to alkenes, *e.g.*, nitrosyl chloride adds to propene to give methylethylene nitrosochloride, here chlorine (*X*) atom is the negative end of the dipole in NO*X*. If a hydrogen is present at the carbon bearing the NO group, the product readily tautomerises to the corresponding oxime which is more stable.



$$CH_3{-}CH{=}CH_2 + NOCl \longrightarrow CH_3{-}\underset{\displaystyle Cl}{\underset{|}{C}H}{-}CH_2{-}NO \rightleftharpoons CH_3{-}\underset{\displaystyle Cl}{\underset{|}{C}H}{-}CH{=}N{-}OH$$

Oxime

5.9.7 Addition of Borane : Hydroboration Oxidation

Alkenes undergo electrophilic addition reactions with borane serving as the electrophile. When an addition reaction is over, an aqueous solution of sodium hydroxide and hydrogen peroxide is added to the reaction mixture and the resulting product is an alcohol. The addition of borane to an alkene followed by reaction with hydroxide ion and hydrogen peroxide is called **hydroboration oxidation.**

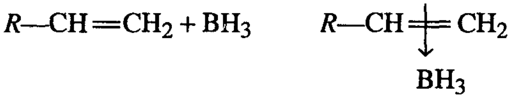
$$R\text{—}CH{=}CH_2 \xrightarrow[\text{(ii) NaOH/H}_2\text{O}_2]{\text{(i) BH}_3\text{/THF/H}_2\text{O}} R\text{—}CH_2\text{—}CH_2\text{—}OH$$

Hydroboration-oxidation reaction is regioselective. The net result of hydroboration- oxidation is an apparent ***anti*-Markovnikov's** addition of water.

Additioin of borane to an alkene is an example of a concerted reaction in which all the bond-making and bond-breaking processes occur in single step. Addition of borane to an alkene is also an example of a pericyclic reaction (pericyclic means "around the circle"). A pericyclic reaction is concerted reaction that takes place by the formation of cyclic transition state.

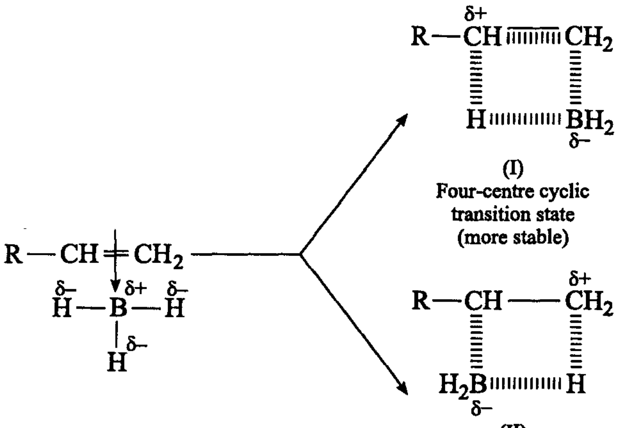
Mechanism :

Step I : Alkene is nucleophile and borane is electrophile. The first step is the formation of π-complex.



π complex

Step II : In this step π complex gives cyclic four-centre transition state.



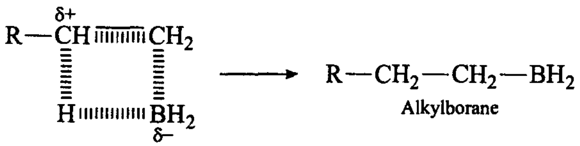
(I) Four-centre cyclic transition state (more stable)

(II) Four-centre cyclic transition state (less stable)

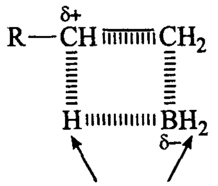
Cyclic four-cenrre transition state has some carbocation character, hence TS (I) is more stable than TS (II).

Formation of four-centre cyclic transition state suggests that addition of boron atom of BH_3 is on less hindered or less substituted olefinic carbon.

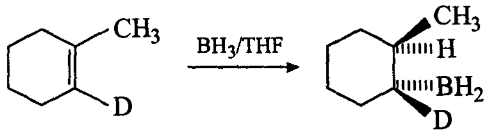
Step III : Four-centre transition state finally converts into addition product.



Formation of four-centre transition state confirms that addition of H on one sp^2-hybrid carbon and addition of BH_2 on other sp^2-hybrid carbon is *syn* addition.



H and BH_2 are *syn* to each other



Syn-addition

The alkylborane formed reacts with another molecule of alkene to form a dialkyl borane which then reacts with yet another molecule of alkene to form a trialkyl borane.

$$R\text{—}CH{=}CH_2 + RCH_2\text{—}CH_2\text{—}BH_2 \longrightarrow (R\text{—}CH_2\text{—}CH_2)_2BH \xrightarrow{R\text{—}CH{=}CH_2} \underset{\text{Trialkylborane}}{(R\text{—}CH_2\text{—}CH_2)_3B}$$

Thus one molecule of BH_3 reacts with three molecules of alkene to give one molecule of trialkylborane.

$$3R\text{—}CH{=}CH_2 + BH_3 \longrightarrow (R\text{—}CH_2\text{—}CH_2)_3B$$

Trialkyl borane is very useful reagent for the preparation of the following compounds.

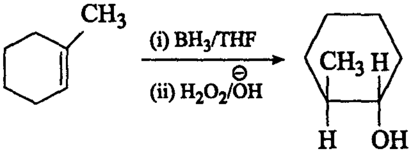
(a) Trialkyl borane on oxidation with hydrogen peroxide in basic medium gives alcohol.

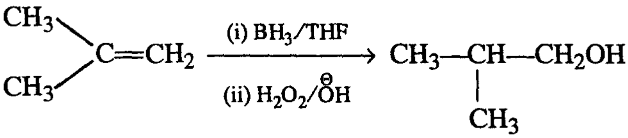
$$(R\text{—}CH_2\text{—}CH_2)_3B \xrightarrow{H_2O_2/\overset{\ominus}{O}H} R\text{—}CH_2\text{—}CH_2\text{—}OH$$

Thus addition of borane followed by oxidation is known as **Hydroboration oxidation reaction.**

$$R\text{—}CH{=}CH_2 \xrightarrow[\text{(ii) } H_2O_2/\overset{\ominus}{O}H]{\text{(i) } BH_3/THF} R\text{—}CH_2\text{—}CH_2OH$$

The net result of this reaction is addition of H and OH according to *anti*-Markovnikov rule. No rearrangement occurs in this reaction. Addition of **—H** and **—OH** is *syn* addition. All terminal alkenes give primary alcohol.

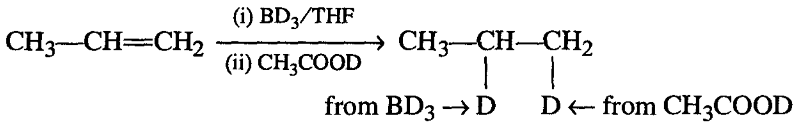




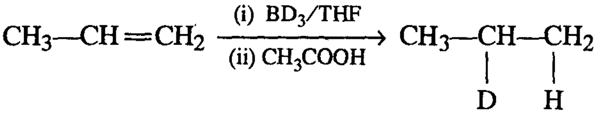
$$(CH_3)_2C{=}CH_2 \xrightarrow[\text{(ii) } H_2O_2/\overset{\ominus}{O}H]{\text{(i) } BH_3/THF} CH_3\text{—}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{—}CH_2OH$$

(b) Trialkylborane reacts with organic acid, generally acetic acid, to give alkane corresponding to alkene.

$$(R\text{—}CH_2\text{—}CH_2)_3B \xrightarrow{CH_3COOH} R\text{—}CH_2\text{—}CH_3$$



$$CH_3{-}CH{=}CH_2 \xrightarrow[\text{(ii) } CH_3COOD]{\text{(i) } BD_3/THF} \underset{\text{from } BD_3 \rightarrow D}{CH_3{-}\underset{|}{CH}}{-}\underset{D \leftarrow \text{from } CH_3COOD}{\underset{|}{CH_2}}$$



$$CH_3{-}CH{=}CH_2 \xrightarrow[\text{(ii) } CH_3COOH]{\text{(i) } BD_3/THF} CH_3{-}\underset{D}{\underset{|}{CH}}{-}\underset{H}{\underset{|}{CH_2}}$$

In this reaction both hydrogens are in the same plane because addition is *syn*.

(c) Trialkyl boranes undergo coupling reaction in the presence of $AgNO_3/NaOH$.

$$\underset{C=n}{(R{-}CH_2{-}CH_2)_3B} \xrightarrow{AgNO_3/NaOH} \underset{C=2n}{R{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}R}$$

$$CH_3{-}CH{=}CH_2 \xrightarrow[\text{(ii) } AgNO_3/NaOH]{\text{(i) } BH_3/THF} CH_3{-}(CH_2)_4{-}CH_3$$

(d) Trialkylborane reacts with NH_2Cl to give primary amine after hydrolysis.

$$(R{-}CH_2{-}CH_2)_3B \xrightarrow[\text{(ii) } HOH/\Delta]{\text{(i) } NH_2Cl} R{-}CH_2{-}CH_2{-}NH_2$$

Thus alkene can be converted to primary amine by this sequence of reactions :

$$R{-}CH{=}CH_2 \xrightarrow[\text{(iii) } HOH/\Delta]{\substack{\text{(i) } BH_3/HF \\ \text{(ii) } NH_2Cl}} R{-}CH_2{-}CH_2{-}NH_2$$

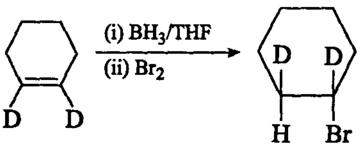
(e) Trialkylborane reacts with bromine to give alkyl bromide.

$$(R{-}CH_2{-}CH_2)_3B \xrightarrow{Br_2} R{-}CH_2{-}CH_2{-}Br$$

The overall reaction can be as follows :

$$R{-}CH{=}CH_2 \xrightarrow[\text{(ii) } Br_2]{\text{(i) } BH_3/THF} R{-}CH_2{-}CH_2{-}Br$$

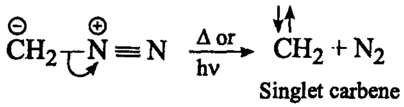
Thus the net result of this reaction is addition of —H and —Br according to anti Markovnikov rule and addition is *syn*.



5.9.8 Addition of Divalent Carbon Compounds

Carbenes ($\ddot{C}H_2$, $\ddot{C}HX$, $\ddot{C}X_2$) : First member of carbene is methylene, $\ddot{C}H_2$. Carbenes are of two types, singlet and triplet (see reaction intermediate).

Singlet carbene is generated by the thermolysis or the photolysis of diazomethane or ketene.



$$\overset{\ominus}{C}H_2{-}\overset{\oplus}{N}{\equiv}N \xrightarrow[h\nu]{\Delta \text{ or}} \overset{\downarrow\uparrow}{C}H_2 + N_2$$

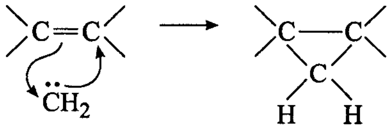
Singlet carbene

$$CH_2{=}C{=}O \xrightarrow[h\nu]{\Delta \text{ or}} \ddot{C}H_2 + CO$$

The triplet carbene cannot be prepared directly. However, if singlet methylene is dissolved in inert gas it undergoes a slow transformation to triplet methylene.

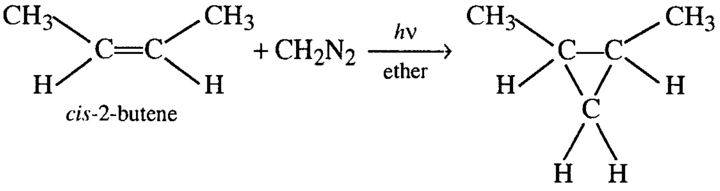
Carbene generated in the **absence of nitrogen gas** or in the presence of **inert solvent** is always **singlet carbene**. Carbene generated in the **presence of nitrogen** atmosphere is **triplet carbene.**

Carbene reacts with alkenes by adding to the double bond to form cyclopropanes.



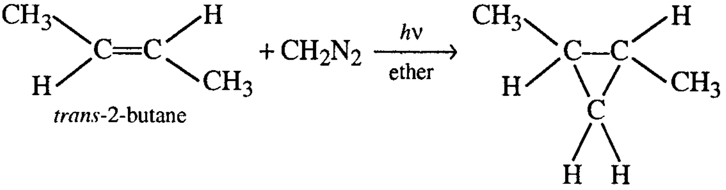
Cyclopropane

Singlet carbene gives concerted one step *syn* addition reaction. In this addition geometry of reactant is maintained in the product.



cis-2-butene

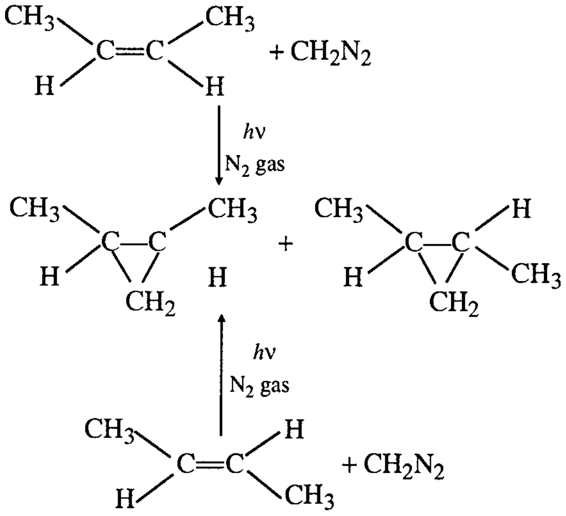
cis-1, 2-dimethyl-cyclopropane



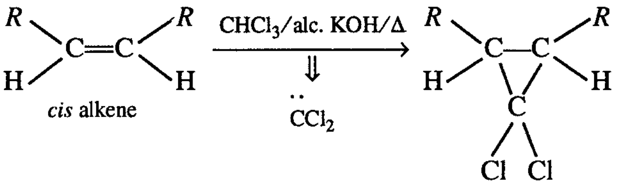
trans-2-butane

trans-1.2-dimethyl-cyclopropane

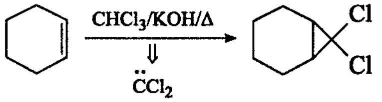
Triplet carbene, on the other hand, gives two step, non-concerted free radical addition. In this reaction product is alway mixture of *cis* and *trans* cyclopropanes. In this case geometry of reactant is not maintained.



Addition of dichlorocarbene : Dihalocarbenes : Dihalocarbenes always exist in singlet state, hence addition will be concerted *syn* addition reaction in which geometry of the reactant is maintained in the product.



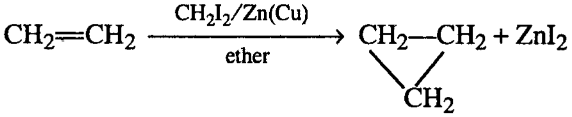
cis-1, 1-Dichloro-2, 3-dialkylcyclopropane



Conversion of alkene into cyclopropane by carbenoid species : Diiodomethane and zinc-copper couple react with each other to give an intermediate known as **carbenoid.**

$$CH_2I_2 + Zn(Cu) \longrightarrow \underset{\text{A carbenoid}}{I-CH_2-Zn-I}$$

This carbenoid behaves as singlet carbene.



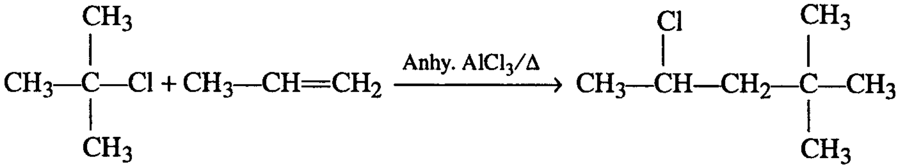
Cyclopropane

The reaction is known as **Simmon-Smith** reaction.

5.9.9 Friedel-Crafts Reaction (Addition of Alkyl Halides and Acid Chlorides)

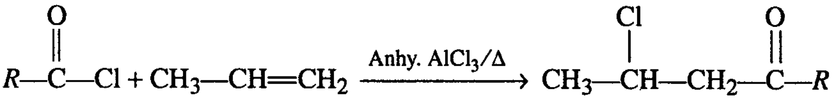
Alkenes give electrophilic addition reaction with acid chlorides and alkyl halides in the presence of anhydrous aluminium chloride. This reaction is known as Friedel-Crafts reaction.

(i) Friedel-Crafts alkylation : Only tertiary alkyl halides give Friedel-Crafts alkylation reaction. Reaction takes place according to the Markovnikov's rule.



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Cl + CH_3-CH=CH_2 \xrightarrow{\text{Anhy. AlCl}_3/\Delta} CH_3-\overset{\overset{Cl}{|}}{CH}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

(ii) Friedel-Crafts acylation reaction : This reaction also takes place according to Markovnikov's rule.

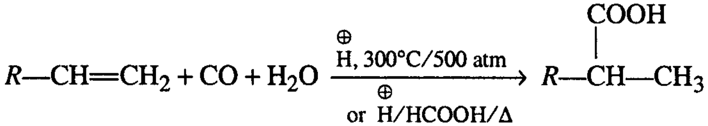


$$R-\overset{\overset{O}{\|}}{C}-Cl + CH_3-CH=CH_2 \xrightarrow{\text{Anhy. AlCl}_3/\Delta} CH_3-\overset{\overset{Cl}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-R$$

5.9.10 Hydrocarboxylation Reaction

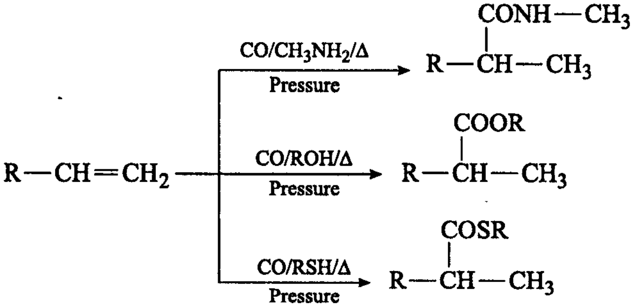
Alkenes undergo hydrocarboxylation reaction with carbon monoxide and water at high temperature (300°C) and high pressure (500 atm) in the presence of H_2SO_4.

This reaction is also known as **Koch-Haaf** reaction. In this reaction carboxylic group adds on the doubly bonded carbon which has lesser number of hydrogen.



$$R\text{—CH=CH}_2 + \text{CO} + \text{H}_2\text{O} \xrightarrow[\overset{\oplus}{\text{or H}}/\text{HCOOH}/\Delta]{\overset{\oplus}{\text{H}},\ 300°\text{C}/500\text{ atm}} R\text{—}\underset{}{\overset{\text{COOH}}{\overset{|}{\text{CH}}}}\text{—CH}_3$$

In this reaction water can be replaced by alcohols, amines (*prim* and *sec*) and thioalcohols.



$$\text{R—CH=CH}_2 \xrightarrow[\text{Pressure}]{\text{CO/CH}_3\text{NH}_2/\Delta} \text{R—}\overset{\text{CONH—CH}_3}{\overset{|}{\text{CH}}}\text{—CH}_3$$

$$\text{R—CH=CH}_2 \xrightarrow[\text{Pressure}]{\text{CO/ROH}/\Delta} \text{R—}\overset{\text{COOR}}{\overset{|}{\text{CH}}}\text{—CH}_3$$

$$\text{R—CH=CH}_2 \xrightarrow[\text{Pressure}]{\text{CO/RSH}/\Delta} \text{R—}\overset{\text{COSR}}{\overset{|}{\text{CH}}}\text{—CH}_3$$

5.9.11 Hydroformylation or Oxo Process

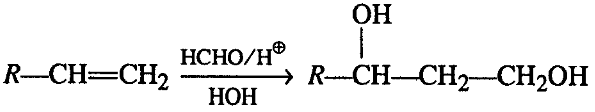
Alkenes undergo hydroformylation with carbon monoxide and hydrogen at high temperature (150°C) and high pressure (300 atm) in the presence of catalyst $\text{Co}_2(\text{CO})_8$.

In this reaction aldehydic group adds on the doubly bonded carbon which has higher number of hydrogens.

$$R\text{—CH=CH}_2 + \text{CO} + \text{H}_2 \xrightarrow{\text{Co}_2(\text{CO})_8} R\text{—CH}_2\text{—CH}_2\text{—CHO}$$

5.9.12 Addition with Aldehydes

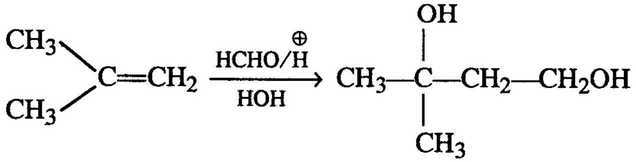
Alkenes gives addition reaction with aldehydes (usually formaldehyde). This reaction takes place in the presence of acid as a catalyst. This addition reaction is known as **Prins** reaction.



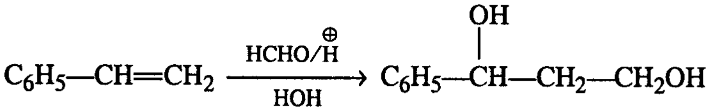
$$R\text{—CH=CH}_2 \xrightarrow[\text{HOH}]{\text{HCHO/H}^{\oplus}} R\text{—}\overset{\text{OH}}{\overset{|}{\text{CH}}}\text{—CH}_2\text{—CH}_2\text{OH}$$

The overall reaction is addition of **—OH** and **—CH_2OH** groups.

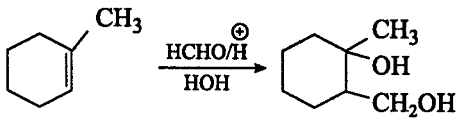
—OH group always adds on doubly bonded carbon which has least number of hydrogen (or doubly bonded carbon which can form stable carbocation). For example :

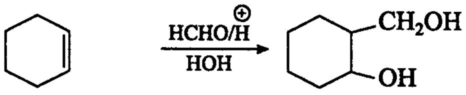


$$(\text{CH}_3)_2\text{C=CH}_2 \xrightarrow[\text{HOH}]{\text{HCHO/}\overset{\oplus}{\text{H}}} \text{CH}_3\text{—}\underset{\text{CH}_3}{\underset{|}{\overset{\text{OH}}{\overset{|}{\text{C}}}}}\text{—CH}_2\text{—CH}_2\text{OH}$$



$$\text{C}_6\text{H}_5\text{—CH=CH}_2 \xrightarrow[\text{HOH}]{\text{HCHO/}\overset{\oplus}{\text{H}}} \text{C}_6\text{H}_5\text{—}\overset{\text{OH}}{\overset{|}{\text{CH}}}\text{—CH}_2\text{—CH}_2\text{OH}$$



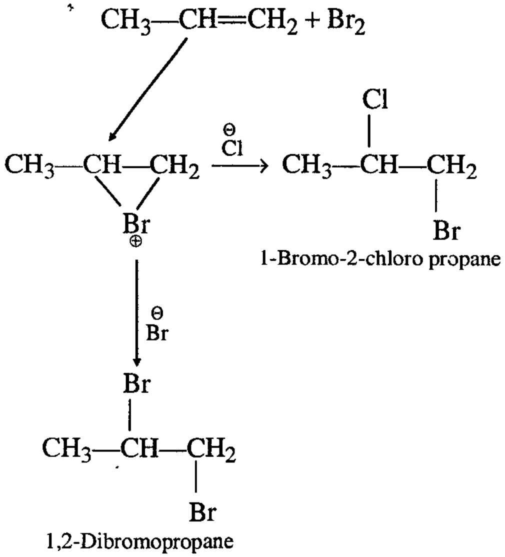


5.9.13 Mixed Additon

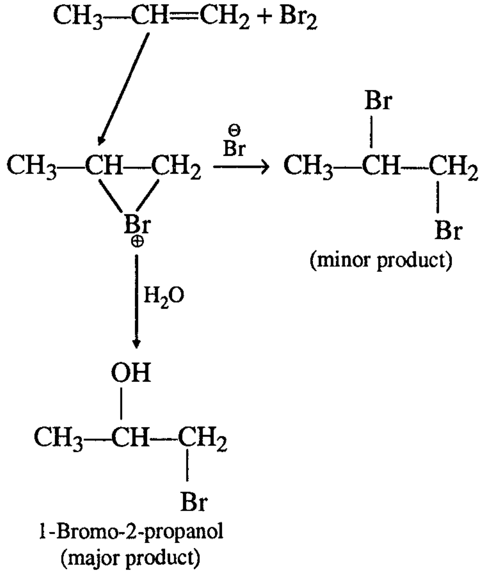
Mixed addition reactions are obtained in those cases where reaction mixture contains only one electrophilic species and two or more than two nucleophilic species.

The main examples are as follows :

(1) Addition of Br_2 in the presence of chloride ion :



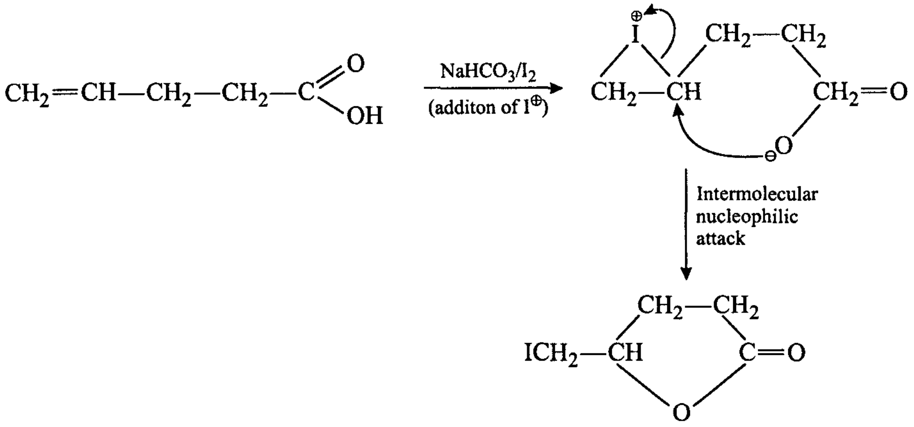
(2) Addition of Halogens and Water : When alkene is treated with a mixture of Cl_2 or Br_2 in water, a, 2,2-halohydrin is formed. This is also an example of mixed addition reaction



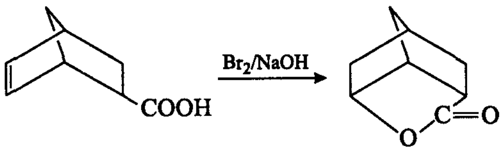
5.9.14 Halolactonisation

γ, δ-Unsaturated acids give halolactonisation reaction with X_2 ($Br_2$and I_2) in the presence of base.

The reaction takes place as follows :

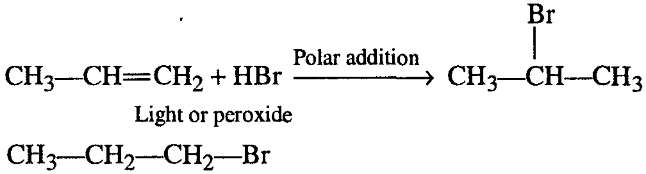


Other example :



5.10 FREE RADICAL ADDITION : (ADDITION OF HBr)

In the absence of peroxides and in polar media, hydrogen bromide undergoes a slow addition to propene to form only 2-bromopropane. This product is in complete accord with Markovnikov's rule. When peroxides, light or other free radical initiators are present, rapid addition occurs to give 1-bromopropane, and the direction of addition is exactly opposite to that found in electrophilic addition.



$$CH_3—CH=CH_2 + HBr \xrightarrow{\text{Polar addition}} CH_3—\overset{\displaystyle Br}{\overset{|}{C}H}—CH_3$$

$$\xrightarrow[\text{Light or peroxide}]{} CH_3—CH_2—CH_2—Br$$

Thus in the presence of light or peroxides, the addition occurs *anti* to the Markovnikov rule. This phenomenon of *anti*-Markovnikov addition caused by the presence of light or peroxide is known as Kharasch Peroxide effect (discovered by M.S. Kharasch). This effect is observed with HBr and not observed with HCl and HI. When peroxide is present or reaction is carried out in the presence of UV light, HBr addition proceeds through a free radical mechanism instead of an ionic one.

The sequence of steps involved in free radical chain addition reaction is shown below :

Initiation Steps :

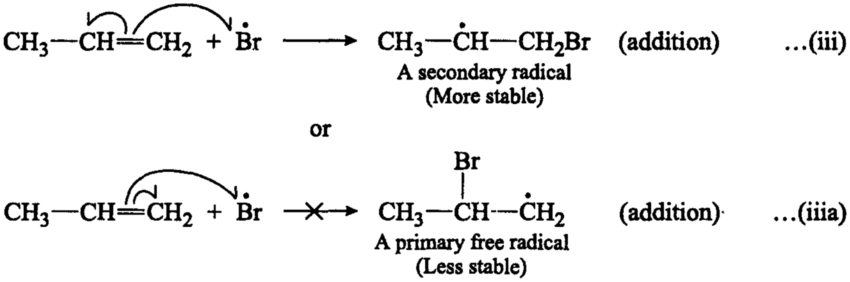
$$R—O—O—R \xrightarrow{\text{Heat}} 2R\dot{O} \qquad ...(i)$$

$$R\dot{O} + HBr \longrightarrow ROH + \dot{B}r \qquad ...(ii)$$

or

$$H—Br \xrightarrow{\text{Light}} \dot{H} + \dot{B}r$$

Propogation Steps :



$$CH_3-CH{=}CH_2 + \dot{B}r \longrightarrow CH_3-\dot{C}H-CH_2Br \quad \text{(addition)} \qquad ...(iii)$$

A secondary radical
(More stable)

or

$$CH_3-CH{=}CH_2 + \dot{B}r \not\longrightarrow CH_3-\underset{}{\overset{Br}{CH}}-\dot{C}H_2 \quad \text{(addition)} \qquad ...(iiia)$$

A primary free radical
(Less stable)

$$CH_3-\dot{C}H-CH_2Br + H-Br \longrightarrow CH_3-CH_2-CH_2-Br + \dot{B}r \qquad (iv)$$

Termination :

$$\dot{R} + \dot{R}' \longrightarrow R-R'$$

$$\dot{B}r + \dot{B}r \longrightarrow Br_2$$

The preferred pathway is determined by the relative stabilities of the intermediate radicals. Clearly, the 1-bromo-2-propyl radical, a secondary radical, is more stable than the primary 2-bromo-1-propyl radical, since the stabilities of alkyl radicals are in the order tertiary > secondary > primary. The product is therefore *n*-propyl bromide.

The peroxide effect is observed only in addition of HBr but not observed in addition of HCl and H—I. This can be explained on the basis of bond dissociation energies of propogation steps (iii) and (iv).

With HBr

$$R-CH{=}CH_2 + \dot{B}r \longrightarrow R-\dot{C}H-CH_2Br \qquad \Delta H = -9 \text{ kcal/mole}$$

$$R-\dot{C}H-CH_2-Br + H-Br \longrightarrow R-CH_2-CH_2Br + \dot{B}r \qquad \Delta H = -7 \text{ kcal/mole}$$

With HI

$$R-CH{=}CH_2 + \dot{I} \longrightarrow R-\dot{C}H-CH_2I \qquad \Delta H = +5 \text{ kcal/mole}$$

$$R-\dot{C}H-CH_2I + H-I \longrightarrow R-CH_2-CH_2I + \dot{I} \qquad \Delta H = -24 \text{ kcal/mole}$$

With HCl

$$R-CH{=}CH_2 + \dot{C}l \longrightarrow R-\dot{C}H-CH_2Cl \qquad \Delta H = -22 \text{ kcal/mole}$$

$$R-\dot{C}H-CH_2Cl + HCl \longrightarrow R-CH_2-CH_2Cl + \dot{C}l \qquad \Delta H = +8 \text{ kcal/mole}$$

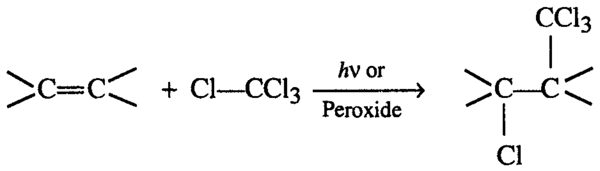
Free radical chain reactions work best when both propogation steps (iii) and (iv) are exothermic. An endothermic step correspond to slow and reversible reaction that breaks the chain.

In case of HI, C—I bond equation (iii) is so weak that the addition of iodine atoms to double bonds is endothermic. It becomes exothermic only at elevated temperatures.

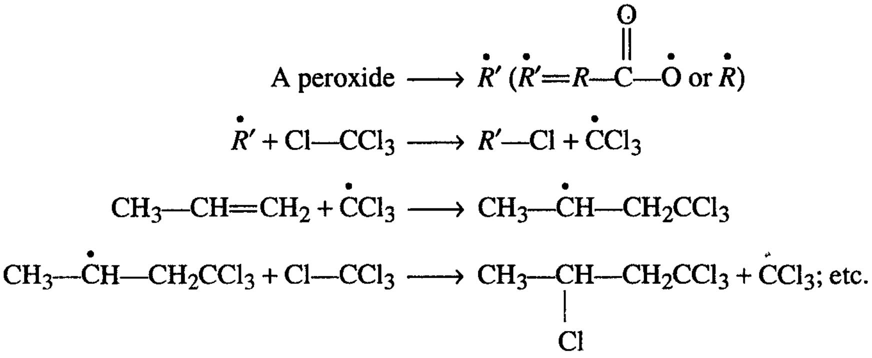
In case of HCl, the H—Cl bond is so strong that the second step in propogation equation (iv) is endothermic and slow.

5.10.1 Other Free Radical Additions

Besides HBr, there are other compounds which may also add to carbon-carbon double bond in the presence of peroxides. The following is the most common example of such reaction :



The mechanism of this reaction is similar to that of free radical addition of HBr. Thus,



$$\text{A peroxide} \longrightarrow \dot{R}' \; (R' = R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}\dot{O} \text{ or } \dot{R})$$

$$\dot{R}' + Cl\text{—}CCl_3 \longrightarrow R'\text{—}Cl + \dot{C}Cl_3$$

$$CH_3\text{—}CH{=}CH_2 + \dot{C}Cl_3 \longrightarrow CH_3\text{—}\dot{C}H\text{—}CH_2CCl_3$$

$$CH_3\text{—}\dot{C}H\text{—}CH_2CCl_3 + Cl\text{—}CCl_3 \longrightarrow CH_3\text{—}\underset{\underset{\displaystyle Cl}{|}}{C}H\text{—}CH_2CCl_3 + \dot{C}Cl_3\text{; etc.}$$

5.11 NUCLEOPHILIC ADDITIONS TO ALKENES

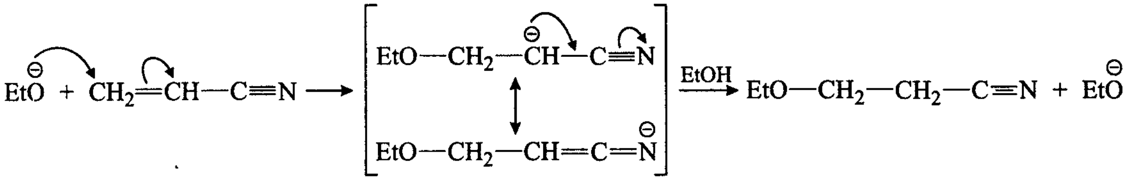
Alkenes undergo nucleophilic additions only when an electron-withdrawing group is attached to the double bonded carbon. This electron-withdrawing group stabilises the intermediate carbanion by dispersing the negative charge. The common examples of such additions are the reactions of nucleophiles with α, β-unsaturated nitriles, aldehydes, ketones and esters.

5.11.1 Addition to Acrylonitrile (Cyanoethylation)

This is a 1, 4-addition (conjugate addition).

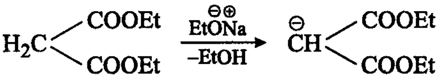
$$CH_2{=}CH\text{—}CN \xrightarrow[\text{EtOH}]{\overset{\ominus\oplus}{\text{EtONa}}} EtO\text{—}CH_2\text{—}CH_2\text{—}CN$$

Mechanism :

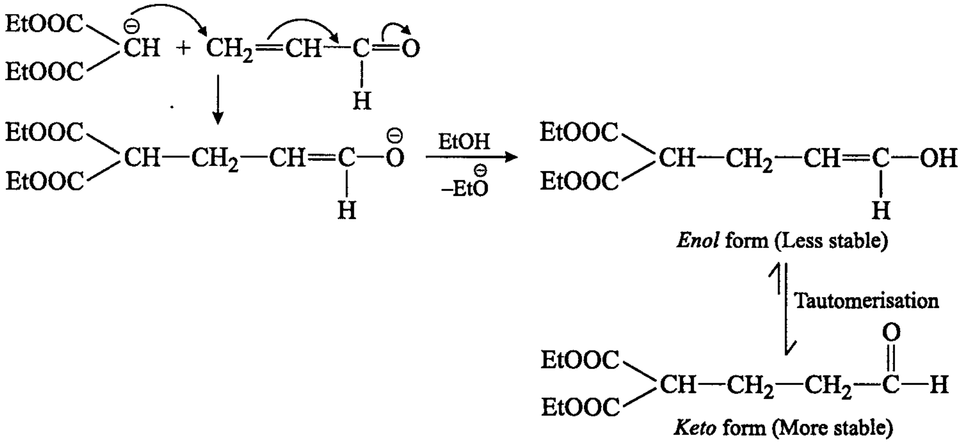


5.11.2 Addition to α, β-unsaturated Carbonyl Compounds (Michael Addition)

Probably the most important addition reaction of α, β-unsaturated carbonyl compounds is the nucleophilic addition of enolate anions to the carbon-carbon double bond. This process in which a carbon-carbon bond is formed is called **Michael addition**. Enolate anions are commonly produced from malonic ester, ethyl cyanoacetate and ethyl acetoacetate.



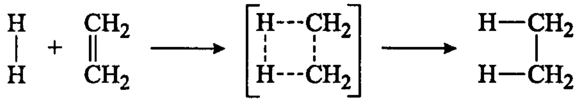
Malonic ester



5.12 ADDITION OF HYDROGEN (CATALYTIC HYDROGENATION)

$$CH_2{=}CH_2 + H_2 \longrightarrow CH_3CH_3 \qquad \Delta H^\circ = -\,32{\cdot}7 \text{ kcal/mole}$$

Addition of hydrogen to *pi* bond is an exothermic reaction, even though ethylene does not react with hydrogen at an appreciable rate without an appropriate catalyst. This is because of the high energy of activation associated with the addition. In the absence of catalyst formation of product takes place via the formation of cyclic four membered transition state.



Cyclic four membered transition state

Such four-centred mechanisms are rare because cyclic four-membered transition states shown as above have usually high energy. The high activation energy corresponds to an impractically slow reaction rate. Heating cannot supply the energy needed to get the molecule to the transition state; however reaction proceeds smoothly when a catalyst is added.

Catalysts for hydrogenation include finely divided platinum, palladium, ruthenium, rhodium and nickel. These metals are insoluble in organic solvents and are called heterogeneous catalysts. The most famous of these include Adam's catalyst and Raney nickel. Adam's catalyst consists of finely divided platinum metal, called platinum black. It is used in low pressure (1 to 2 atm) hydrogenations. Raney nickel is also used for low pressure hydrogenations. It is less active than Pt and Pd.

$$R{-}CH{=}CH_2 + H_2 \xrightarrow{\text{Catalyst}} R{-}CH_2{-}CH_3$$

How does a catalyst ease the course of a hydrogenation reactions ? Experimental evidence supports the theory that first the hydrogen molecules are absorbed on to the metallic surface of the catalyst, then the σ-bonds of hydrogen molecules are broken, and metal–H bonds are formed. The alkene is also absorbed on to the metallic surface with its *pi* bond interacting with the empty orbitals of the metal. The alkene molecule moves around on the surface until it collides with a metal bonded hydrogen atom, undergoes reaction, and then leaves as the hydrogenated product.

The overall effect of the catalyst is to provide a surface on which the reaction can occur and to weaken the bonds of both H_2 and the alkene (Fig. 5.5). The result is a lowering of the energy of activation for the reaction (Fig. 5.6).

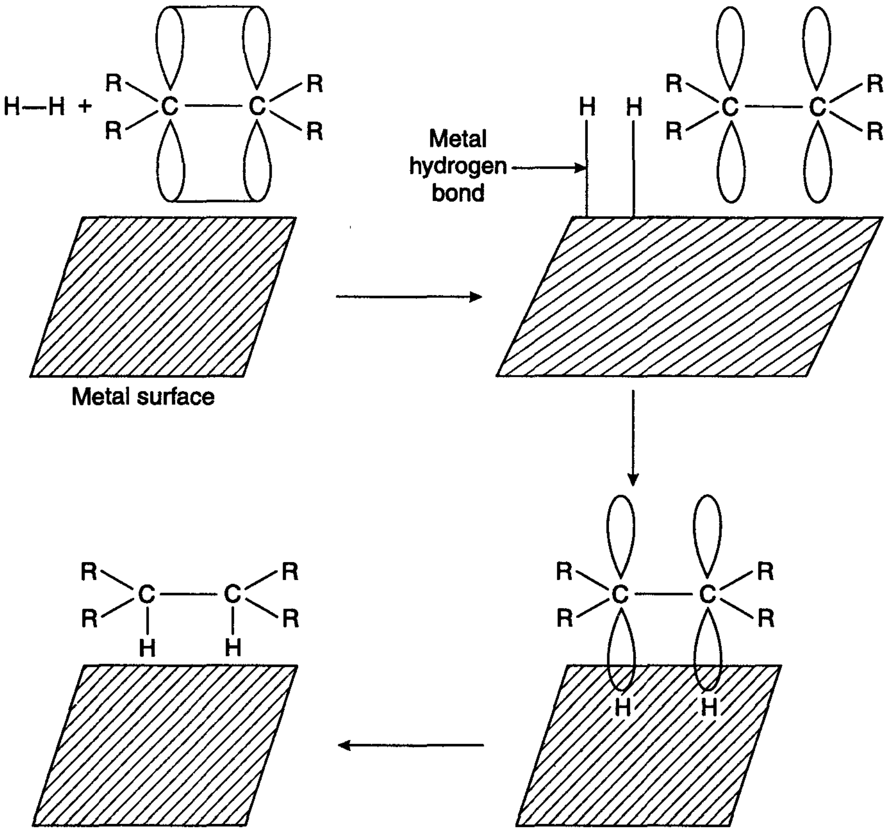


Fig. 5.5. Effect of catalyst on the addition of H_2 to alkenes.

Fig. 5.6 shows energy diagram for a hydrogenation reaction. Note that the catalyst does not affect the energies of reactants and products. The ΔH for the reaction is not changed by catalytic action, only the E_{act} is changed.

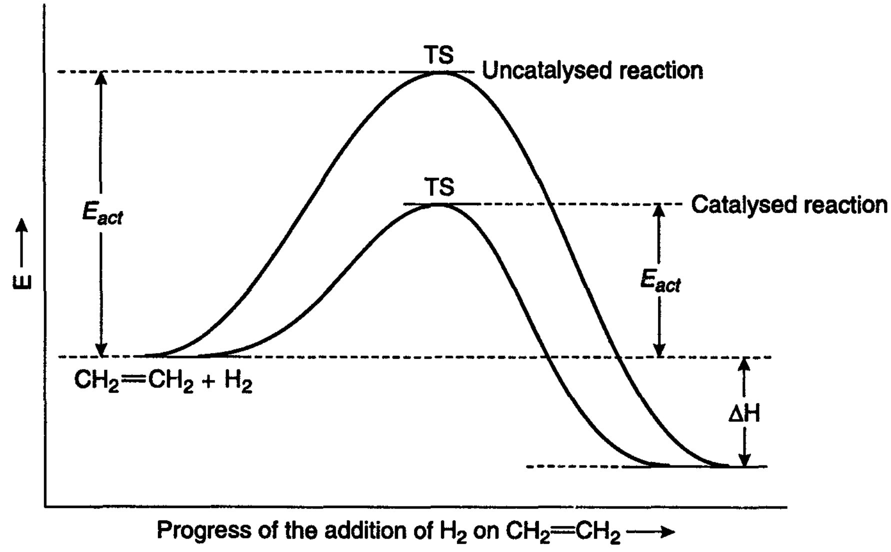
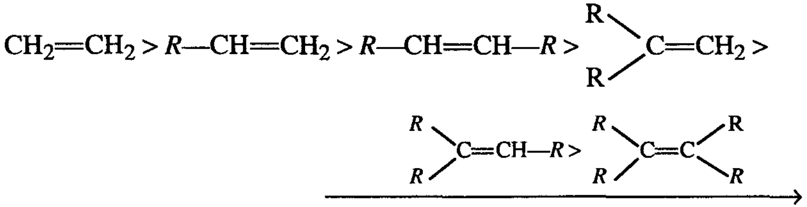


Fig. 5.6. Energy diagram for a hydrogenation reaction.

From the given mechanism the following conclusions can be drawn :

(i) Reduction reaction of alkene is always catalytic reduction and this reaction is ***syn* addition** in which product formation takes place by the formation of transition state (TS). Thus addition of hydrogen is stereospecific reaction.

(ii) Addition takes place by the formation of TS therefore least substituted alkene will be most reactive for this reaction.



Reactivity in decreasing order for addition of H_2

(iii) This reaction is always exothermic reaction

$$CH_2{=}CH_2 + H_2 \xrightarrow{\text{Catalyst}} CH_3{-}CH_3 + \text{heat}$$

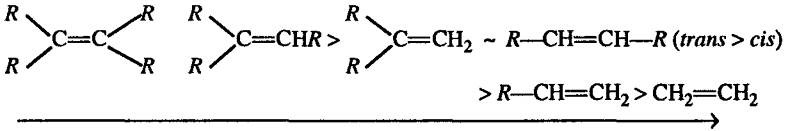
Experimentally it has been found that

(a) Stability of alkene $\propto \dfrac{1}{\text{Heat of hydrogenation}}$

and

Heat of hydrogenation $\propto$ Number of hydrogens on both sp^2 hybrid carbons of alkene

Thus,



(i) Stability of alkenes in decreasing order

(ii) Heat of hydrogenation in increasing order

(iv) Reactivity of alkene for reduction $\propto$ Heat of hydrogenation.

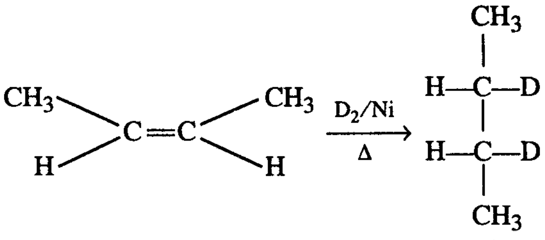
(v) CSM is the word from which stereochemistry of ***syn* addition** reactions can be concluded as follows :

C (means *cis* alkene) on

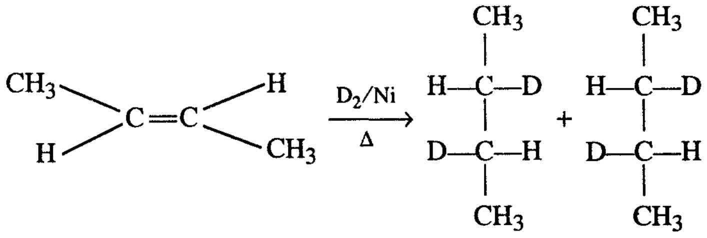
S (means *syn* addition) gives

M (*meso* form)

For example :



meso form



racemic mixture

5.13 OXIDATION OF ALKENES

Reaction involving oxidation of carbon-carbon double bond may be classified into two general groups.

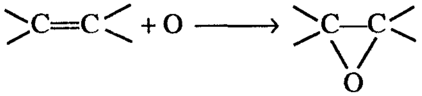
(1) Oxidation of the *pi* bond without cleavage of the *sigma* bond. This oxidation is known as oxidation without cleavage.

(2) Oxidation of the *pi* bond with cleavage of the *sigma* bond. This oxidation is known as **oxidative cleavage of alkenes.**

5.13.1 Oxidation Without Cleavage

This oxidation is given by mild oxidising agents. The products of the oxidation without cleavage are either epoxides or 1, 2 diods.

(A) Formation of epoxides : Formation of epoxide takes place as follows :



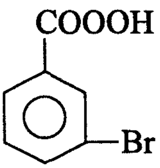
Nascent oxygen obtained from mild oxidising agent

epoxide or oxirane

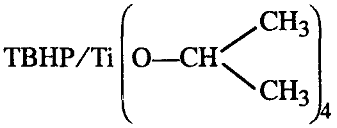
Following four reagents give epoxide formation

(i) $O_2/Ag/\Delta$

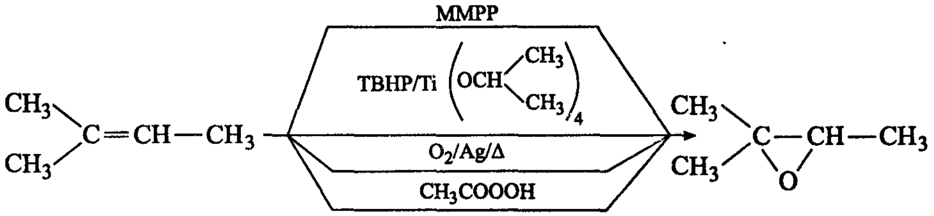
(ii) Organic peracids : RCOOOH, the most common peracid is *meta*-bromo perbenzoic acid.



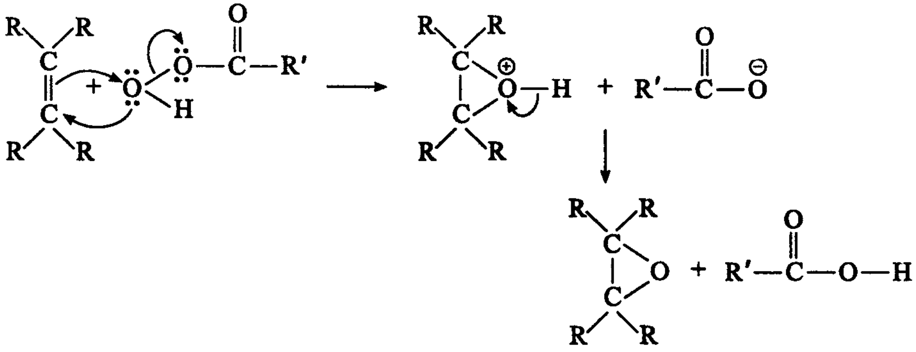
(iii) *Tertiary*butyl hydroperoxide (TBHP) in the presence of titanium isopropoxide.



(iv) Magnesium monoperoxyphthalate (MMPP).

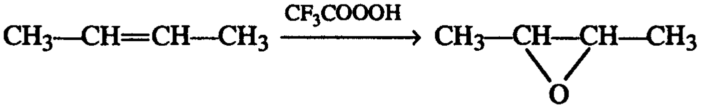


Conversion of alkenes into epoxides with per acids take place as follows :



This reaction is known as **Prilezhaev reaction.**

For epoxidation best result is obtained from CF_3COOOH.



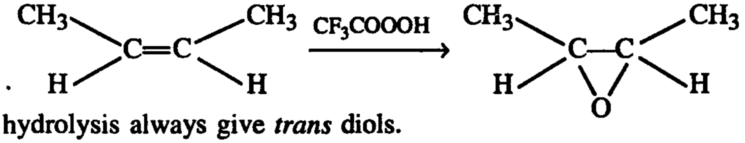
$$CH_3{-}CH{=}CH{-}CH_3 \xrightarrow{CF_3COOOH} CH_3{-}\underset{O}{CH{-}CH}{-}CH_3$$

Alkene in which double bond is conjugated with strong electron withdrawing group does not give epoxidation reaction.

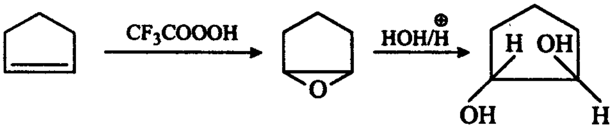
$$CH_2{=}CH{-}COOC_2H_5 \xrightarrow{CF_3COOOH} \text{No reaction; epoxide does not form}$$

$$C_6H_5{-}CH{=}CH{-}CHO \xrightarrow{CF_3COOOH} \text{Epoxide does not form}$$

The epoxidation reaction is stereospecific and addition of oxygen atom across double bond is always *syn*.



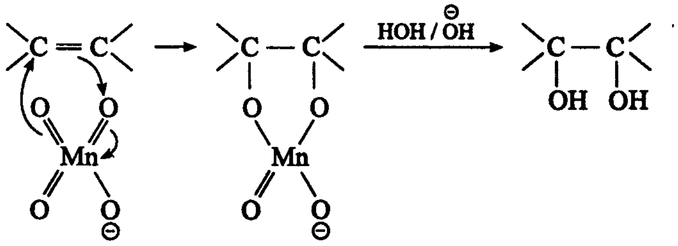
Epoxides on hydrolysis always give *trans* diols.

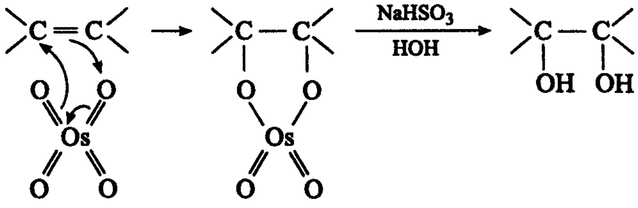


trans diol

This epoxidation followed by hydrolysis can be used for the preparation of *trans* diols from the alkenes.

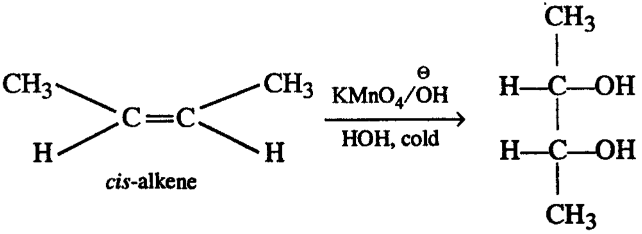
(B) Diol Formation : The most popular reagent used to convert an alkene to a 1, 2-diol is a cold alkaline aqueous solution of potassium permanganate (known as Baeyer's reagent). Osmium tetraoxide (OsO_4) is also used for the same purpose but the use of this reagent is limited because it is both expensive and toxic. Both of these reagents form cyclic inorganic esters with alkenes which yield *vicinal* diol on hydrolysis catalysed by base.





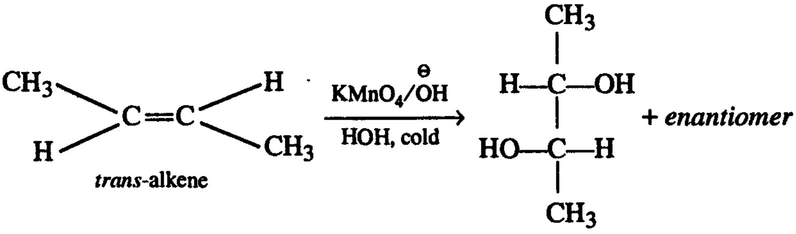
Osmate ester

(i) Thus the overall reaction is addition of OH group on both the doubly bonded carbons and addition is *syn*. Thus *cis* alkenes will give *meso* form whereas *trans* will give *dl* mixture.



cis-alkene

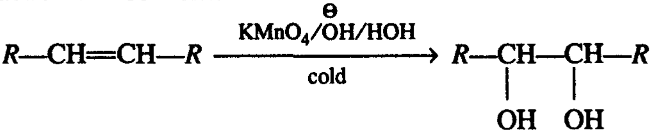
Meso form



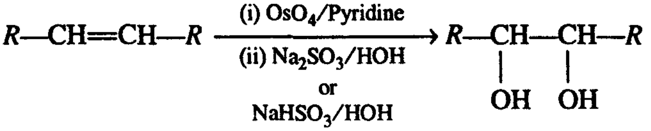
trans-alkene

dl mixture

(ii) The net reaction can be written as :

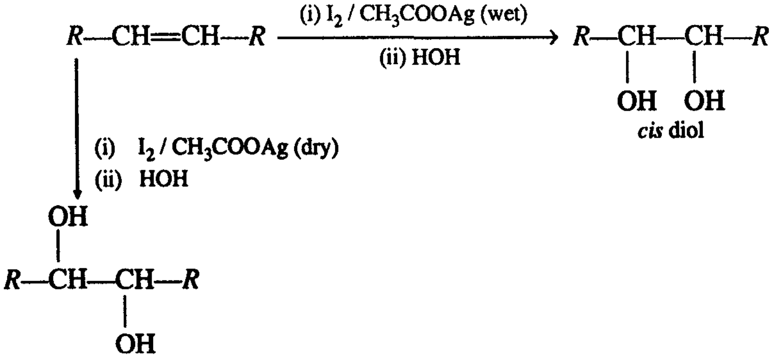


$$R{-}CH{=}CH{-}R \xrightarrow[\text{cold}]{KMnO_4/\overset{\ominus}{O}H/HOH} R{-}\underset{OH}{CH}{-}\underset{OH}{CH}{-}R$$



$$R{-}CH{=}CH{-}R \xrightarrow[\text{(ii) } Na_2SO_3/HOH \text{ or } NaHSO_3/HOH]{\text{(i) } OsO_4/\text{Pyridine}} R{-}\underset{OH}{CH}{-}\underset{OH}{CH}{-}R$$

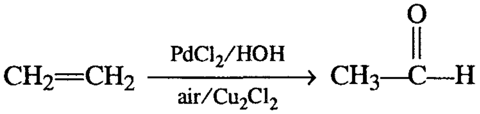
(iii) I_2/CH_3COOAg also gives 1, 2-diol formation with alkenes. Stereochemistry of the product depends on nature of CH_3COOAg.



cis diol

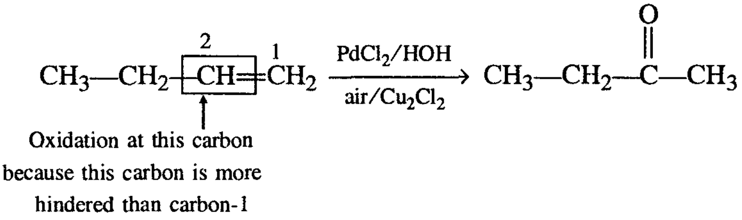
trans diol

(c) Oxidation of alkenes into carbonyl compounds : Wacker Process : Oxidation of ethylene, mono substituted and 1, 2-disubstituted alkenes into carbonyl compound in the presence of $PdCl_2$, HOH, air and CuCl is known as Wacker process.



$$CH_2{=}CH_2 \xrightarrow[\text{air}/Cu_2Cl_2]{PdCl_2/HOH} CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H$$

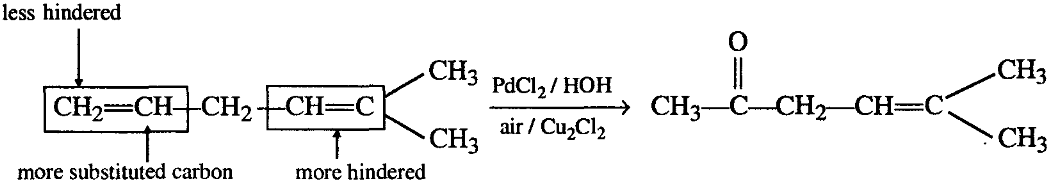
In the case of unsymmetrical alkenes more hindered olefinic carbon converts into carbonyl group.



$$CH_3{-}CH_2{-}\overset{2}{CH}{=}\overset{1}{CH_2} \xrightarrow[\text{air}/Cu_2Cl_2]{PdCl_2/HOH} CH_3{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$$

Oxidation at this carbon
because this carbon is more
hindered than carbon-1

If compound has more than one double bond then oxidation takes place on that double bond which is less hindered.



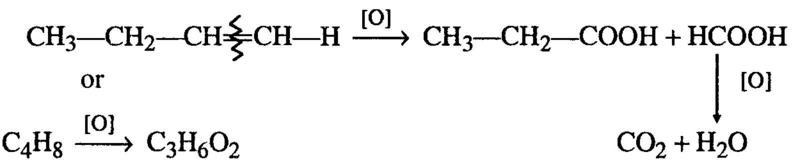
5.13.2 Oxidation with cleavage : Oxidative cleavage

(A) Cleavage with hot basic $KMnO_4$: The product of oxidation reaction depends upon the structure of the alkene.

(1) Mono substituted vinylic carbon converts into carboxylic group by $KMnO_4/\overset{\ominus}{O}H/\Delta$.

$$CH_3{-}CH{=}CH{-}CH_3 \xrightarrow{KMnO_4/\overset{\ominus}{O}H/\Delta} CH_3{-}COOH + CH_3{-}COOH$$

Note : Terminal alkene gives formic acid as of one of the products which further undergoes oxidation into CO_2 and H_2O. This reaction takes place only under drastic conditions.



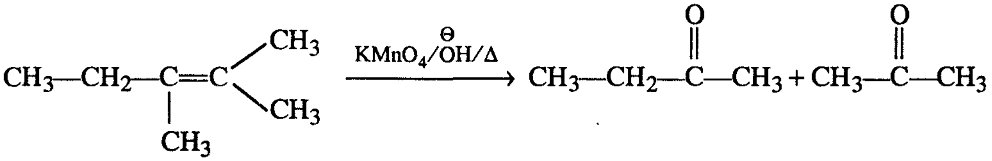
$$CH_3{-}CH_2{-}CH{=}CH{-}H \xrightarrow{[O]} CH_3{-}CH_2{-}COOH + HCOOH \xrightarrow{[O]} CO_2 + H_2O$$

or

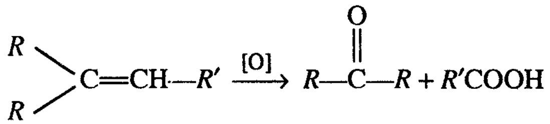
$$C_4H_8 \xrightarrow{[O]} C_3H_6O_2$$

Thus loss of one carbon in this reaction indicates that alkene is a terminal alkene.

(2) Disubstituted vinylic carbon converts into keto group by the reagent.

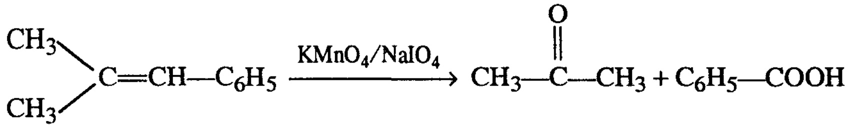


Note : If one vinylic carbon is monosubstituted and other is disubstituted then product will be mixture of ketone and monobasic acid.

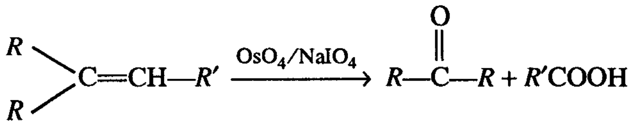


(B) Cleavage with $NaIO_4/KMnO_4$ (known as Lemieux reagent) : The results obtained by this reagent is identical to the results obtained by $KMnO_4/\overset{\ominus}{O}H/\Delta$

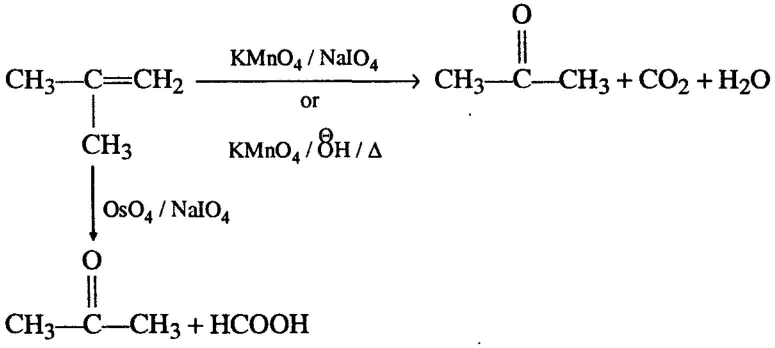
$$CH_3-CH=CH-CH_2-CH_3 \xrightarrow{KMnO_4/NaIO_4} CH_3-COOH + CH_3-CH_2-COOH$$



(C) Cleavage with $OsO_4/NaIO_4$ (This is also known as Lemieux reagent) : In this case also monosubstituted vinylic carbon converts into carboxylic group and disubstituted vinylic carbon into keto group.



Note : HCOOH does not undergo further oxidation by this reagent.



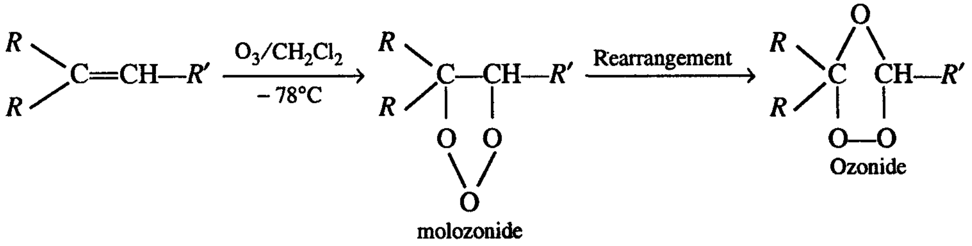
$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 \xrightarrow[\text{or}\ KMnO_4/\overset{\ominus}{O}H/\Delta]{KMnO_4/NaIO_4} CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + CO_2 + H_2O$$

$$\downarrow OsO_4/NaIO_4$$

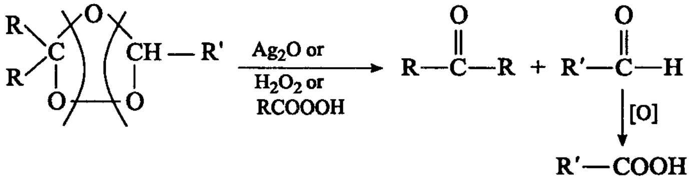
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + HCOOH$$

5.14 ADDITION OF OZONE AND OZONOLYSIS

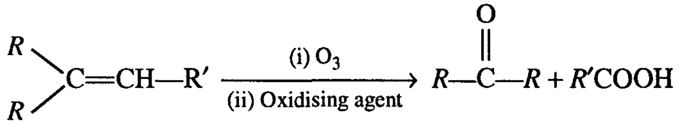
Ozone gives 1, 3-dipolar addition reaction with alkenes. Product of the addition reaction is molozonide which undergoes rearrangement to give ozonide. The reaction takes place in the presence of solvent at – 78°C. Ozonides are unstable compounds and they are explosive in nature.



Ozonide converts into carbonyl compound by the addition of oxidising as well as reducing agents.
(a) Reaction with oxidising agents.

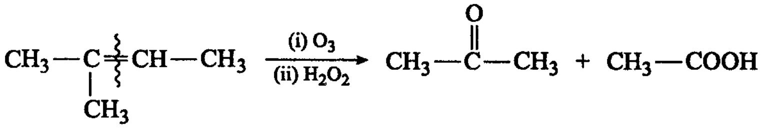


Overall reaction can be represented as follows :



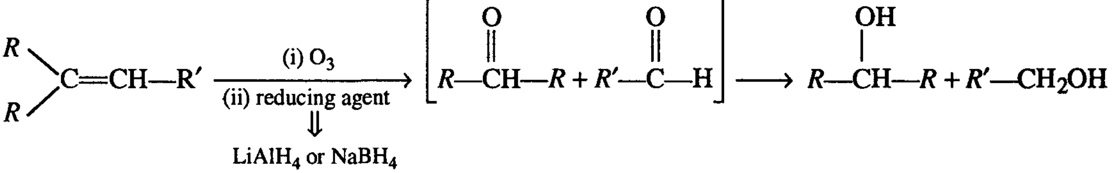
$$R_2C{=}CH{-}R' \xrightarrow[\text{(ii) Oxidising agent}]{\text{(i) O}_3} R{-}\overset{\overset{\large O}{\|}}{C}{-}R + R'COOH$$

In this sequence of reactions doubly bonded carbon having no hydrogen converts into keto group and doubly bonded carbon having hydrogens converts into carboxylic group, *e.g.*,



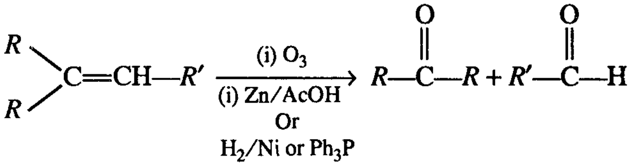
$$CH_3{-}\underset{\underset{CH_3}{|}}{C}{=}CH{-}CH_3 \xrightarrow[\text{(ii) H}_2\text{O}_2]{\text{(i) O}_3} CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}CH_3 + CH_3{-}COOH$$

Reduction of ozonide : In the presence of reducing agents such as $LiAlH_4$ and $NaBH_4$ ozonide first converts into carbonyl compounds which further undergo reduction to give alcohols.



$$R_2C{=}CH{-}R' \xrightarrow[\substack{\text{(ii) reducing agent} \\ \Downarrow \\ LiAlH_4 \text{ or } NaBH_4}]{\text{(i) O}_3} \left[R{-}\overset{\overset{\large O}{\|}}{CH}{-}R + R'{-}\overset{\overset{\large O}{\|}}{C}{-}H\right] \longrightarrow R{-}\overset{\overset{\large OH}{|}}{CH}{-}R + R'{-}CH_2OH$$

When reducing agent is Zn/CH_3COOH, H_2/Ni or triphenylphosphine, products are carbonyl compounds. In this case carbonyl compounds do not convert into corresponding alcohols.

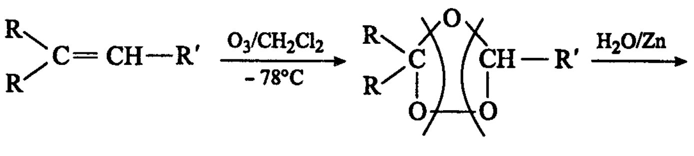


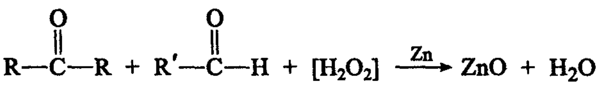
$$R_2C{=}CH{-}R' \xrightarrow[\substack{\text{(i) Zn/AcOH} \\ \text{Or} \\ H_2/Ni \text{ or } Ph_3P}]{\text{(i) O}_3} R{-}\overset{\overset{\large O}{\|}}{C}{-}R + R'{-}\overset{\overset{\large O}{\|}}{C}{-}H$$

Ozonolysis : Ozonolysis reaction is two step reaction. First step is formation of ozonide. Second step is hydrolysis of ozonide, either in the presence of reducing agents (Zn dust or $CH_3{-}S{-}CH_3$) or in the absence of reducing agents. Thus ozonolysis is of two types :

5.14.1 Reductive Ozonolysis or Reductive Work up

Addition of ozone followed by hydrolysis in the presence of reducing agent is known as reductive ozonolysis. This type of ozonolysis is mainly used in alkenes.

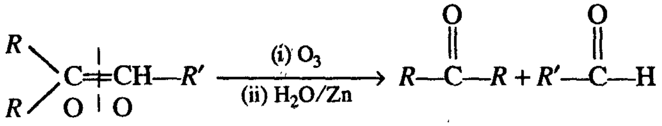




$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R + R'-\overset{\overset{\displaystyle O}{\|}}{C}-H + [H_2O_2] \xrightarrow{Zn} ZnO + H_2O$$

In reductive ozonolysis by-product H_2O_2 which is an oxidising agent is reduced by reducing agent and hence carbonyl compounds do not undergo further oxidation.

In reductive ozonolysis unsubstituted or monosubstituted olefinic carbon converts into aldehyde and disubstituted carbon converts into ketone. Thus overall reaction can be represented as follows :



Ozonolysis reaction is used to know the number and position of double bonds in alkenes and polyenes.

Follow the following points for the determination of structure of an alkene from the ozonolysis products :

(i) Number of carbons in alkene and products should be the same, *e.g.*,

$$\underset{6C}{C_6H_{12}} \xrightarrow{\text{Ozonolysis}} \underset{3C}{CH_3-CH_2-CHO}$$

$$\Downarrow$$

$$C_6H_{12} \longrightarrow \underset{3\times 2=6C}{2CH_3-CH_2-CHO}$$

(ii) Connect both carbonyl carbons by double bond with the removal of oxygen.

$$CH_3-CH_2-CHO + CHO-CH_2-CH_3$$

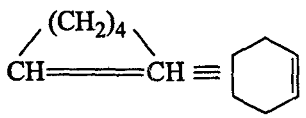
$$\Downarrow$$

$$\underset{C_6H_{12}}{CH_3-CH_2-CH{=}CH-CH_2-CH_3}$$

(iii) If product is dicarbonyl compound and number of carbons in reactant and product is the same then reactant will be cycloalkene.

$$\underset{\substack{6C\\\text{cycloalkene}}}{C_6H_{10}} \xrightarrow{\text{Ozonolysis}} \underset{6C}{CHO-(CH_2)_4-CHO}$$

connect these two C's by double bond



(iv) Number of product in polyenes = $n+1$

where, n = number of double bonds whose value may be 2, 3, 4, 5, 6, ...

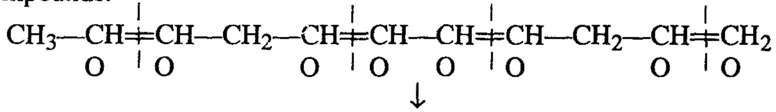
Out of $n+1$ products, two products will always be monocarbonyl compounds and remaining products will be dicarbonyl compounds. This result is applicable in those polyenes whose double bonds are present in the main chain. For example :

$$CH_3-CH{=}CH-CH_2-CH{=}CH-CH{=}CH-CH_2-CH{=}CH_2$$

Number of double bonds = 4

Hence number of products = 5

Out of 5 products two products will be monocarbonyl compounds and the remaining three will be dicarbonyl compounds.

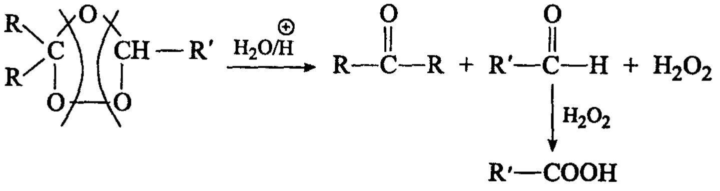


$$CH_3—CHO + OHC—CH_2—CHO + OHC—CHO + OHC—CH_2—CHO + CH_2O$$

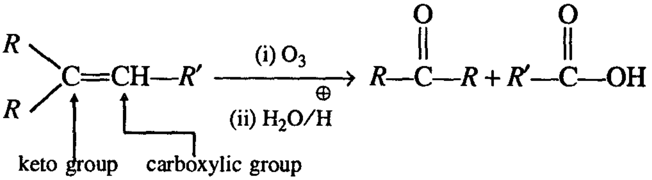
5.14.2 Oxidative Ozonolysis

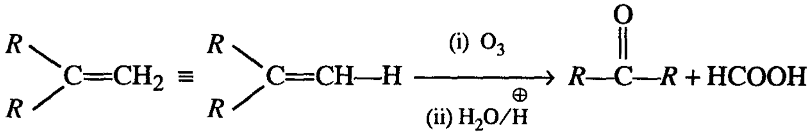
Addition of ozone followed by hydrolysis in the absence of reducing agent is known as oxidative ozonolysis. This ozonolysis is mainly carried out in alkynes.

In this ozonolysis, by product, hydrogen peroxide oxidises aldehyde into carboxylic acid.



Thus in oxidative ozonolysis unsubstituted and monosubstituted olefinic carbon converts into carboxylic group (*i.e.*, =CH ⟶ COOH) and disubstituted olefinic carbon converts into keto group.





Thus if alkene is terminal then terminal carbon converts into formic acid.

Note :

(i) In oxidative ozonolysis formic acid does not undergo oxidation into CO_2 and H_2O.

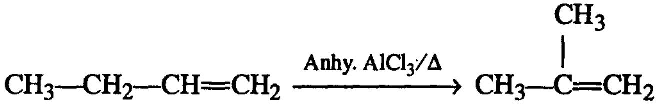
(ii) For determining structure of alkene from products of oxidative ozonolysis ketones are written as such but carboxylic acids are written as corresponding aldehydes rest process is same as in reductive ozonolysis.

5.15 ISOMERISATION

Alkenes isomerise either at higher temperature (500°–700°C), or at lower temperature in the presence of anhydrous aluminium chloride. In most of the cases terminal alkenes convert into non-terminal alkenes.

$$\underset{\text{less stable}}{CH_3—CH_2—CH=CH_2} \xrightarrow{\text{Anhy. AlCl}_3/\Delta} \underset{\text{more stable}}{CH_3—CH=CH—CH_3}$$

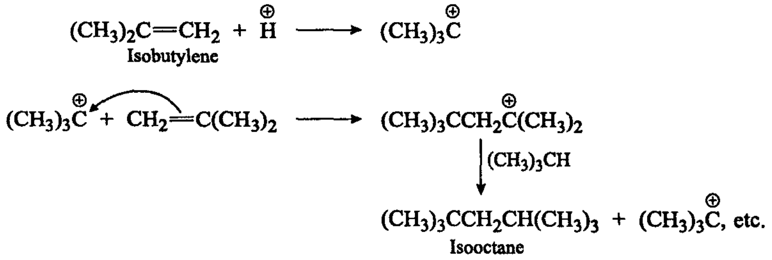
In this reaction linear alkene also converts into branched chain alkenes.



$$CH_3—CH_2—CH=CH_2 \xrightarrow{\text{Anhy. AlCl}_3/\Delta} CH_3—\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2$$

5.16 ALKYLATION OF ALKENES

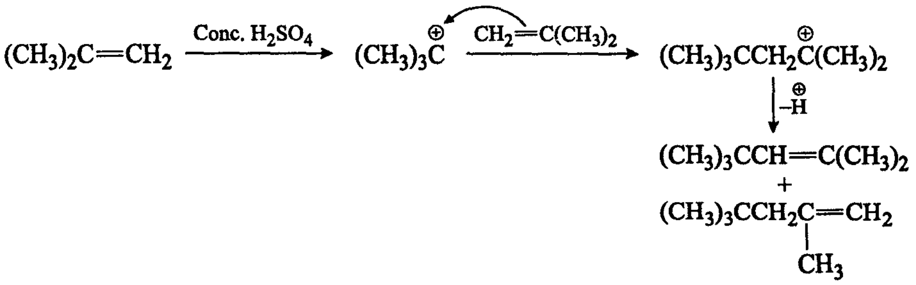
Higher alkenes are obtained by addition of branched chain alkanes to alkenes in the presence of an acid catalyst. For example, addition of isobutane to isobutylene yields 2, 2, 4-trimethylpentane (isooctane) in the presence of conc. H_2SO_4 at 0°C.



$$\underset{\text{Isobutylene}}{(CH_3)_2C{=}CH_2} + \overset{\oplus}{H} \longrightarrow (CH_3)_3\overset{\oplus}{C}$$

$$(CH_3)_3\overset{\oplus}{C} + CH_2{=}C(CH_3)_2 \longrightarrow (CH_3)_3CCH_2\overset{\oplus}{C}(CH_3)_2 \xrightarrow{(CH_3)_3CH} \underset{\text{Isooctane}}{(CH_3)_3CCH_2CH(CH_3)_3} + (CH_3)_3\overset{\oplus}{C}, \text{ etc.}$$

Various alkenes may also dimerise under the influence of suitable catalysts, *e.g.*,



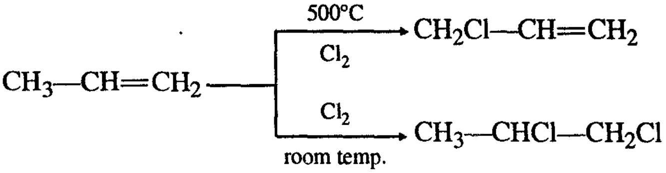
$$(CH_3)_2C{=}CH_2 \xrightarrow{\text{Conc. } H_2SO_4} (CH_3)_3\overset{\oplus}{C} \xrightarrow{CH_2=C(CH_3)_2} (CH_3)_3CCH_2\overset{\oplus}{C}(CH_3)_2 \xrightarrow{-\overset{\oplus}{H}} (CH_3)_3CCH{=}C(CH_3)_2 + (CH_3)_3CCH_2\underset{CH_3}{\underset{|}{C}}{=}CH_2$$

5.17 SUBSTITUTION REACTIONS

Besides addition reactions, there are reactions in which alkenes give substitution reactions mainly at allylic carbon. In some cases substitution also takes place at vinylic carbon.

5.17.1 Allylic Substitution

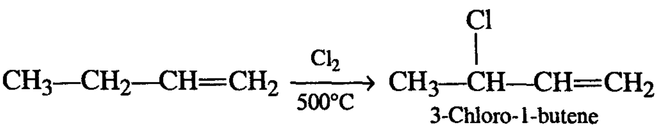
(i) Allylic Halogenation : The alkyl group of alkenes undergo substitution reactions at higher temperature. Thus at very high temperature, propene reacts with chlorine to give allyl chloride.



$$CH_3{-}CH{=}CH_2 \xrightarrow[Cl_2]{500°C} CH_2Cl{-}CH{=}CH_2$$

$$CH_3{-}CH{=}CH_2 \xrightarrow[\text{room temp.}]{Cl_2} CH_3{-}CHCl{-}CH_2Cl$$

If the alkyl group contains more than one carbon atom, even then the substitution occurs at the carbon α to the double bond or at allylic carbon atom. Due to this the substitution reaction is also known as allylic substitution reactions.



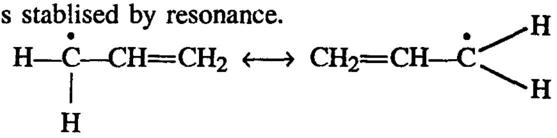
$$CH_3{-}CH_2{-}CH{=}CH_2 \xrightarrow[500°C]{Cl_2} \underset{\text{3-Chloro-1-butene}}{CH_3{-}\overset{Cl}{\overset{|}{C}H}{-}CH{=}CH_2}$$

The substitution reaction proceeds by a free radical mechanism. After initiation, abstraction of a hydrogen from the methyl group of alkene forms a stable, allylic radical.

$$Cl_2 \longrightarrow \dot{Cl} + \dot{Cl}$$

$$CH_3—CH{=}CH_2 + \dot{Cl} \longrightarrow \dot{C}H_2—CH{=}CH_2 + HCl$$

This allylic radical is stablised by resonance.



(Stabilisation of the allyl radical by resonance, delocalisation of the odd electron)

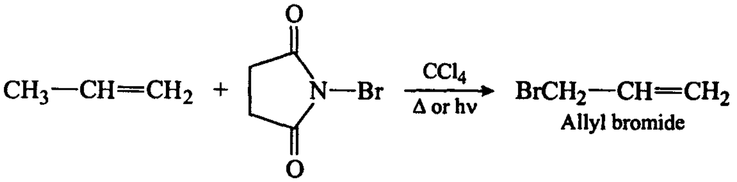
This allylic radical survives long enough to be able to collide with a chlorine molecule to abstract Cl from Cl_2 and form the allyl chloride.

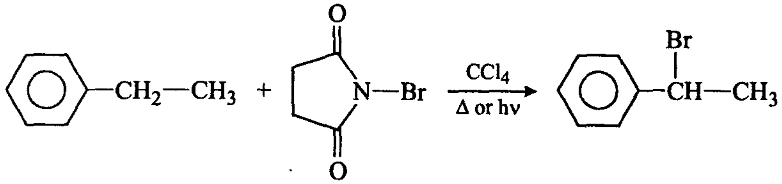
$$\dot{C}H_2—CH{=}CH_2 + Cl_2 \longrightarrow CH_2Cl—CH{=}CH_2 + \dot{Cl}$$

At higher temperatures the normal addition of chlorine atom to the double bond becomes unfavourable. Addition of chlorine free radical leads to the formation of secondary free radical and this radical is very reactive and unstable. This free radical is not able to survive long enough to be able to collide with a chlorine molecule. Due to this Cl is ejected. Thus the double bond survives the reaction conditions, while the allylic position is halogenated.

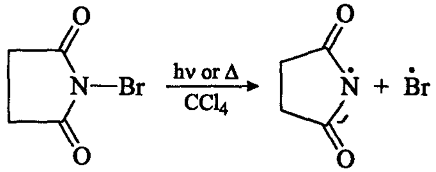
$$CH_3—CH{=}CH_2 + Cl_2 \longrightarrow CH_3—\dot{C}H—CH_2Cl \xrightarrow{-\dot{Cl}} CH_3—CH{=}CH_2$$

Allylic substitutions are brought about by *N*-bromosuccinimide (NBS) at room temperature in the presence of nonpolar solvents. This reagent introduces bromine at the allylic and benzylic positions, but not at other positions. This reaction is (catalysed by) light or by some source of free radicals.

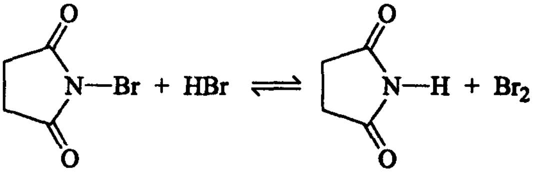




Mechanism :



$$CH_2{=}CH—CH_3 + \dot{Br} \longrightarrow CH_2{=}CH—\dot{C}H_2 + HBr$$



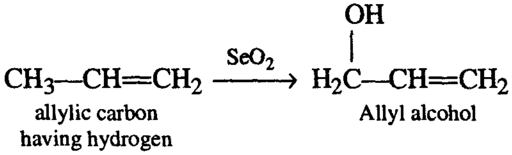
$$CH_2{=}CH—\dot{C}H_2 + Br—Br \longrightarrow CH_2{=}CH—CH_2—Br + \dot{Br}$$

The selective action of NBS depends partly on its ability to provide a low but constant concentration of Br_2. This bromine is the halogenating agent. The Br_2 is generated by the reaction of HBr and NBS as shown above.

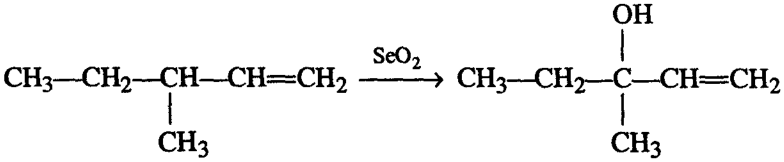
Under these conditions of high dilution on significant addition of bromine to the double bond occurs. Formation of addition product always takes place when a high concentration of bromine is used.

In allylic halogenation reaction tertiary allylic carbon is more reactive than secondary which is more reactive than primary allylic carbon.

(ii) Allylic oxidation : Alkene having at least one hydrogen on allylic carbon is oxidised by SeO_2. In this oxidation the allylic C—H converts into —C—OH.



$$\underset{\text{allylic carbon having hydrogen}}{CH_3-CH=CH_2} \xrightarrow{SeO_2} \underset{\text{Allyl alcohol}}{H_2\overset{\overset{OH}{|}}{C}-CH=CH_2}$$



$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2 \xrightarrow{SeO_2} CH_3-CH_2-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH=CH_2$$

In this reaction also tertiary allylic carbon is more reactive than secondary which is more reactive than primary allylic carbon, *i.e.*,

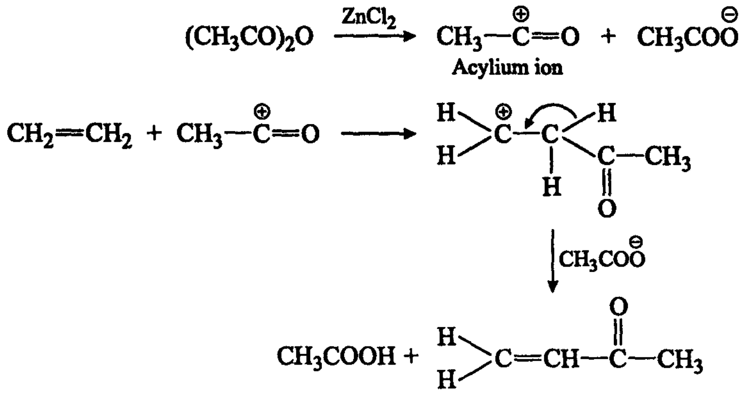
$$-\overset{|}{C}H- > -CH_2- > -CH_3$$

5.17.2 Substitution at Vinylic Position

In certain cases alkenes undergo substitution at the vinylic carbon. For example, ethylene forms methyl vinyl ketone with acetic anhydride in the presence of zinc chloride. This is an example of *SE*1 reaction (Substitution Electrophilic Unimolecular).

$$CH_2=CH_2 + (CH_3COO)_2O \xrightarrow{ZnCl_2} CH_2=CHCOCH_3 + CH_3COOH$$

Mechanism:

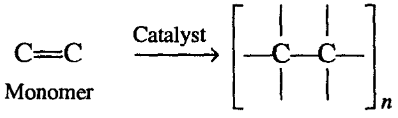


5.18 POLYMERISATION REACTION

An important application of addition reactions is the formation of addition polymers. The word polymer comes from two segments **poly** meaning "many" and **mer** meaning "unit". Polymers are giant molecules composed of recurring structural units called monomers (single units).

$$\underset{\text{Monomer}}{n\text{M}} \longrightarrow \underset{\text{Polymer}}{\text{—M—M—M—M—} \text{ or } (\text{M})_n}$$

Polymers produced by the addition of alkene molecules to one another are called addition polymers



$$\underset{\text{Monomer}}{\text{C}=\text{C}} \xrightarrow{\text{Catalyst}} \left[-\overset{|}{\underset{|}{\text{C}}}-\overset{|}{\underset{|}{\text{C}}}- \right]_n$$

Polymer

In addition polymerisation reaction all the monomers are added up and in that case the product and the starting units have the same empirical formula. Addition polymerisation may follow either the free radical pathway or the ionic pathway. Free radical polymerisation may be catalysed by peroxides, UV light whereas ionic polymerisation may be catalysed by Lewis acid or Lewis base. For example :

$$n\text{CH}_2=\text{CH}_2 \xrightarrow{\text{Peroxide}} [\text{CH}_2\text{—CH}_2]_n$$

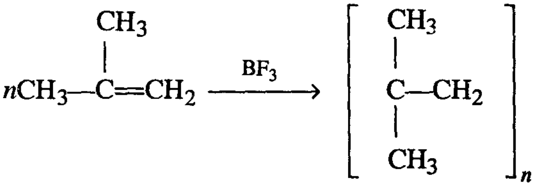
Polyethylene or polythene

(Free radical polymerisation)

$$n\text{CF}_2=\text{CF}_2 \xrightarrow{\text{RLi}} [\text{CF}_2\text{—CF}_2]_n$$

Polytetrafluoroethylene

(Anionic polymerisation)



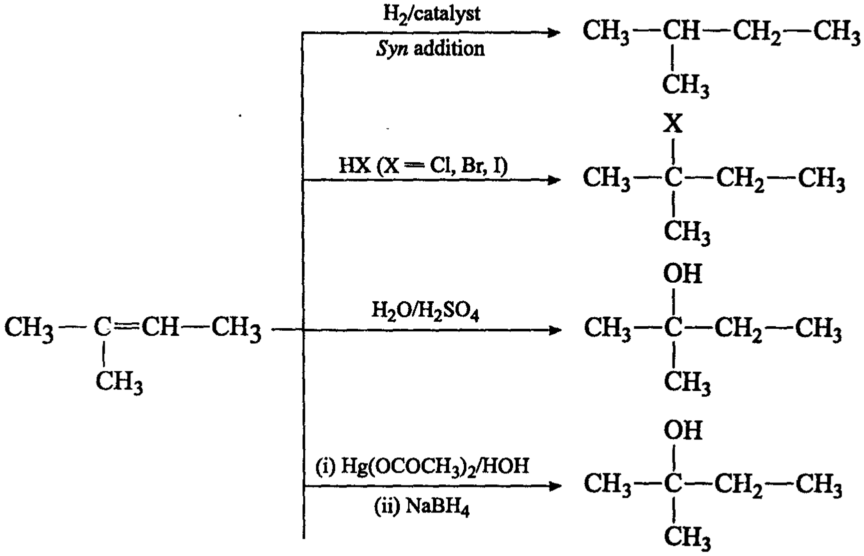
$$n\text{CH}_3-\overset{\overset{\text{CH}_3}{|}}{\text{C}}=\text{CH}_2 \xrightarrow{\text{BF}_3} \left[\begin{array}{l} \text{CH}_3 \\ | \\ \text{C—CH}_2 \\ | \\ \text{CH}_3 \end{array} \right]_n$$

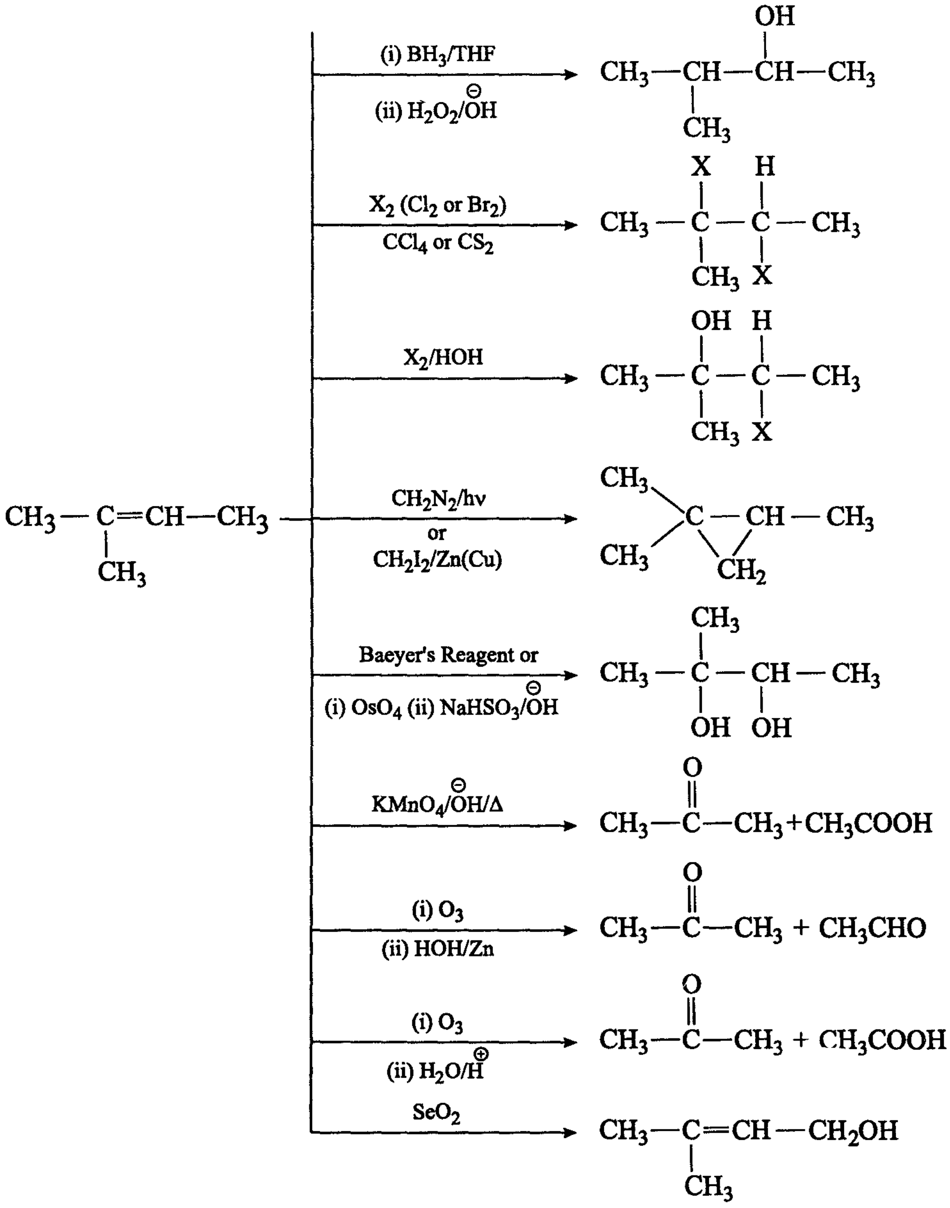
Polyisobutene

Cationic polymerisation

5.19 SUMMARY OF KEY REACTIONS OF ALKENES

The starting material for all reactions is **2-methyl-2-butene.**





5.20 INDUSTRIAL APPLICATIONS OF ETHYLENE AND PROPENE

Ethylene is used in the manufacture of many industrially important polymers, *e.g.*, polythene (a plastic), EPR (ethylene-propylene rubbers), etc. These polymers are used in the manufacture of floor tiles, shoe soles, synthetic fibres, raincoats, purses, pipes and packaging materials. Ethylene is also used for the manufacture of mustard gas and in the preparation of various solvents such as glycol, dioxane, etc.

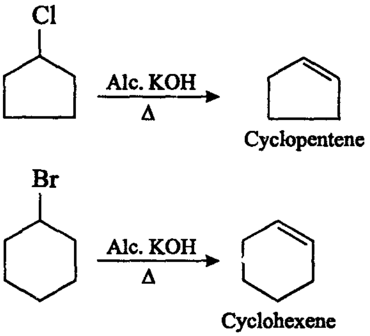
Propylene is used in the manufacture of EPR, polypropylene (a plastic), acetone, isopropyl alcohol, *n*-propyl alcohol, glycerol, etc.

5.21 CYCLOALKENES

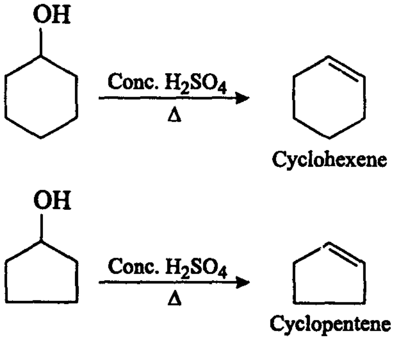
Alicyclic hydrocarbons containing a double bond in the ring are called cycloalkenes.

5.21.1 Methods of Preparation of Cycloalkenes

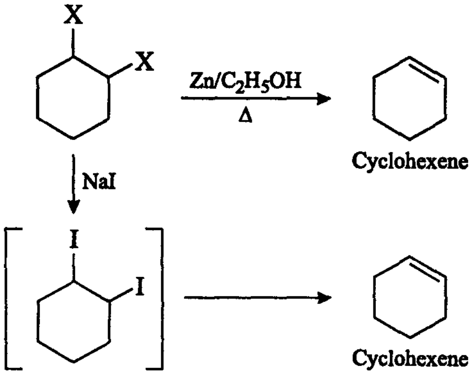
(i) Dehydrohalogenation of halocycloalkanes : Halocycloalkanes give cycloalkene when treated with alc. NaOH or KOH.



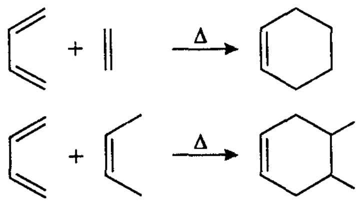
(ii) Dehydration of cycloalkanol : Cycloalkanols on dehydration with dehydrating agents give cycloalkenes.



(iii) Dehalogenation of *vic*-dihalocycloalkanes : *Vicinal*-dihalocycloalkanes on dehalogenation with Zn/C_2H_5OH or with NaI give cycloalkenes.



(iv) From Diels-Alder Reaction : This reaction is the most common reaction for the preparation of cyclohexenes.

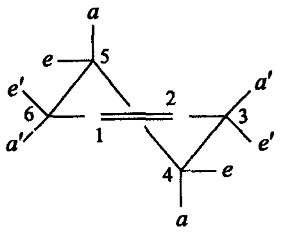


5.21.2 Conformation of Cycloalkenes

Cyclopropene, cyclobutene and cyclopentene are planar due to the presence of ethylenic carbons (*i.e.*, sp^2 hybrid carbons).

In contrast, the higher cycloalkenes are not planar.

Conformation of Cyclohexene : When cyclohexane ring contains trigonal carbon atoms (sp^2 hybridised carbon atoms), its shape is distorted from that of a normal chair. The double bonded carbons and the two adjacent allylic carbons (3 and 6) are in a plane, whereas the atoms on the other sides (4 and 5) are normally staggered as in cyclohexene.

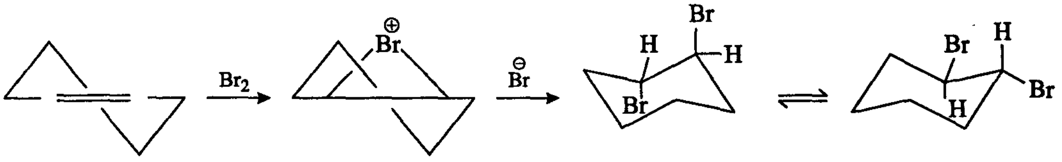


The hydrogen atoms attached to atoms 4 and 5 occupy normal axial and equatorial positions but those attached to atoms 3 and 6 are imperfectly staggered and do not take up the normal equatorial and axial positions. These atoms are said to occupy pseudoaxial (*a*′) and pseudoequational (*e*′) positions. This geometry has been confirmed by *X*-ray diffraction. It has also been found that substituents in the *e* and *e*′ positions is more stable than those in *a* and *a*′.

5.21.3 Chemical Reactions of Cycloalkenes

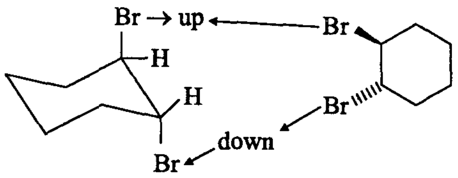
The most important chemical reactions of cycloalkenes are the chemical reactions of cyclohexene. It gives chemical reactions similar to the chemical reactions of alkenes.

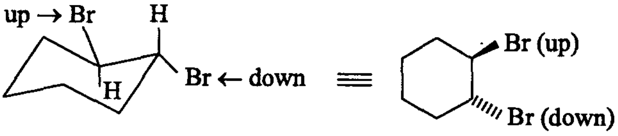
(i) Addition of Bromine : Reagent will attack perpendicular to the double bond, *i.e.*, perpendicular to carbon 1, 2, 3 and 6. Thus in addition to cyclohexene the initial product is the **diaxial** dibromide, which immediately undergoes ring flip to give the more stable diequatorial conformer.

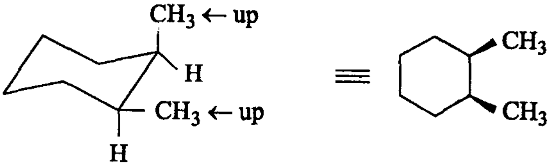


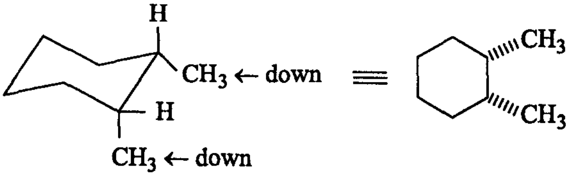
It is not always necessary to draw the chair form in chemical reactions of cyclohexene. Sometimes planar projections of cyclic compounds convey adequate information for the given chemical reaction. We can represent the structures of nonplanar cyclic compounds by using planar polygons with the stereochemistry of the substituents indicated by **dashed** lines or **wedges**. If the substituent is up (axial or equatorial). It is represented with a wedge; if it is down, it is represented with a dashed line.

For example :

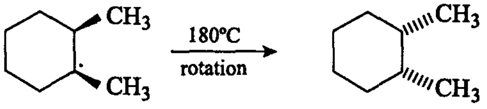








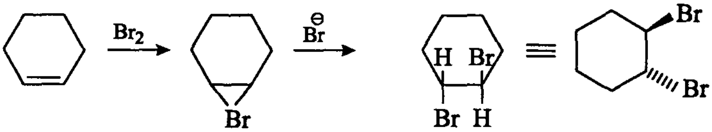
The two methyl groups in *cis*-1, 2-dimethylcyclohexane can be represented with either two wedges or two dashed lines.



cis-1, 2-Dimethylcyclohexane (A)

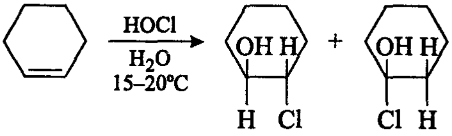
cis-1, 2-Dimethylcyclohexane (B)

Bromination of cyclohexene thus can be represented as follows :



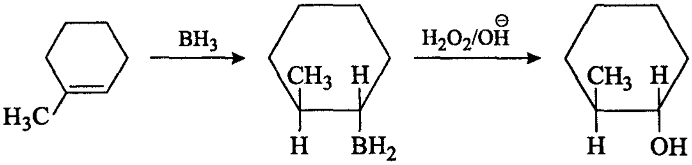
trans-1, 2-dibromocyclohexane

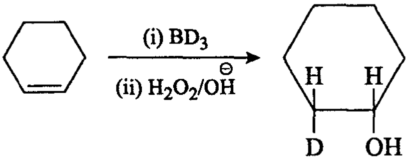
(ii) Addition of Hypochlorous Acid : Hypochlorous acid gives *trans* addition reaction with alkenes. Thus cyclohexene will give *trans* chlorohydrin.



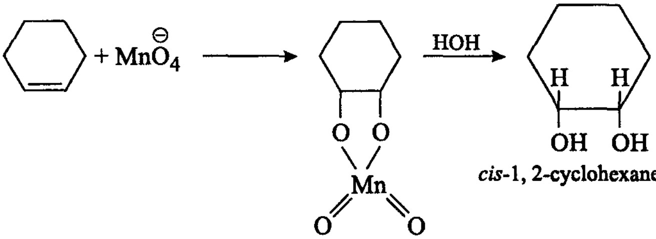
trans-2-chlorocyclohexanol (racemic mixture)

(iii) Hydroboration Oxidation Reaction : This reaction is *syn* addition reaction.



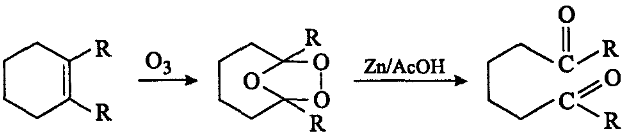


(iv) Oxidation with Baeyer's Reagent : Alkenes give *syn* addition reaction with Baeyer's reagent. Product formation takes place by formation of cyclic ester.

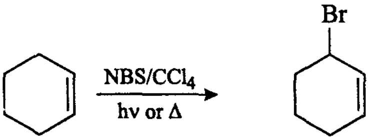


cis-1, 2-cyclohexanediol

(v) Ozonization : Ozonolysis of cycloalkenes results in the rupture of the ring at the double bond to give a bicarbonyl derivative having the same number of carbon atoms as in the parent cycloalkene. Thus, as in the case of alkenes, this is a very good method for locating the position of a double bond in cycloalkenes.

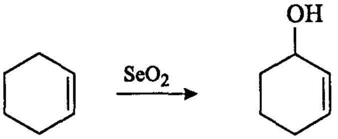


(vi) Allylic Bromination : Cyclohexene gives allylic bromination reaction with NBS.



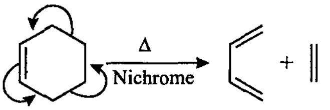
3-Bromocyclohexene

(vii) Allylic Oxidation : Cyclohexene on oxidation with SeO_2 gives allylic oxidation. In this reaction oxidation takes place at allylic carbon.



2-Cyclohexenol

(viii) Pyrolysis (*retro* Diels-Alder reaction) : When vapours of cyclohexene are passed over heated *nichrome* (Ni—Cr—Fe) alloy, 1, 3-butadiene and ethylene are formed. The reaction is reversal of Diels-Alder reaction and is called *retro* Diels-Alder reaction.



5.22 DIENES

Hydrocarbons containing two double bonds are called dienes or alkadienes whereas those with more than two double bonds are called polyenes. Dienes have the general formula C_nH_{2n-2} and are isomeric with alkynes. For example, butadiene, allene, isoprene, etc.

5.22.1 Nomenclature and Classification

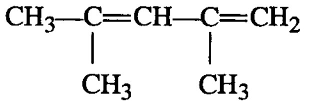
According to IUPAC nomenclature, the longest chain containing the maximum number of double bond is selected and the compound is given the parent name by replacing the suffix "ne" of the corresponding alkane by "diene", "triene", etc. The carbon atoms of the longest selected chain are numbered from one end to the other in such a way that the doubly bonded carbon atoms get the lowest possible numbers. The position of the double bonds are indicated by the number of the first carbon atoms involved in the double bonds. The positions of the substituents are indicated by the number of the carbon atom to which they are attached. The following examples are illustrative (some compounds have common names, which are given in brackets) :

$\overset{4}{CH_3}—\overset{3}{HC}=\overset{2}{C}=\overset{1}{CH_2}$

1, 2-butadiene

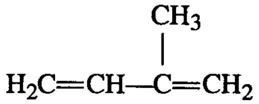
$H_2C=CH—CH=CH_2$

1, 3-butadiene



$CH_3—C(CH_3)=CH—C(CH_3)=CH_2$

2, 4-dimethyl-1, 3-pentadiene



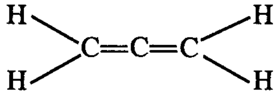
$H_2C=CH—C(CH_3)=CH_2$

2-methyl-1, 3-butadiene

(Isoprene)

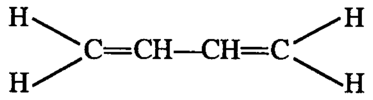
Dienes are classified into the following three groups depending on the relative positions of double bonds :

1. If the double bonds are adjacent to each other, the dienes are called cumulated dienes (cumulenes or allenes), *e.g.*,



Propadiene (allene)

2. If the double bonds are separated by one single bond, the dienes are called conjugated dienes, *e.g.*,

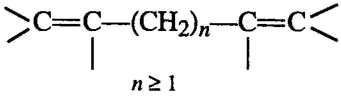


1, 3-butadiene

$CH_3—CH=CH—CH=CH_2$

1, 3-pentadiene

3. If the double bonds are separated by more than one single bond, dienes are called isolated or non-conjugated dienes, *e.g.*,



$CH_2=CH—CH_2—CH=CH_2$

1, 4-pentadiene

5.22.2 Methods of Preparation of Conjugated Dienes

The simplest conjugated diene is 1, 3-butadiene. This may be prepared by the following methods :

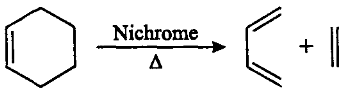
(1) Dehydration of 1, 4-butanediol

$$HOH_2C—CH_2—CH_2—CH_2OH \xrightarrow[\text{or } H_2SO_4]{P_2O_5} CH_2{=}CH—CH{=}CH_2$$

(2) Dehydrohalogenation of 1, 4-dichlorobutane

$$CH_2Cl—CH_2—CH_2—CH_2Cl \xrightarrow[EtOH]{NaOH} CH_2{=}CH—CH{=}CH_2$$

Pyrolysis of cycloalkenes (*retro* Diels-Alder reaction) : 1, 3-Butadiene is produced by passing vapours of cyclohexene over heated nichrome (Ni—Cr—Fe) alloy.



5.22.3 Structure and Stability of 1, 3-Butadiene :

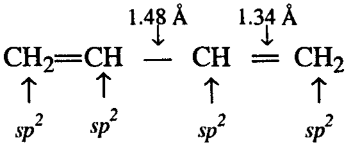
The heat of hydrogenation of alkenes are approximately 30 kcal/mole. Heat of hydrogenation of alkadienes in which the double bonds are separated by one or more carbon atoms is generally double the heat of hydrogenation of alkenes. Heat of hydrogenation of some alkenes and butadiene are given in Table 5.1.

Table 5.1 *Heat of hydrogenation of some alkenes*

	ΔH hydrogenation in kcal/mole
$CH_3—CH_2—CH{=}CH_2$	-30.2
$CH_3—CH_2—CH_2—CH{=}CH_2$	-29.8
$CH_2{=}CH—CH_2—CH{=}CH_2$	-60.6
$CH_2{=}CH—CH_2—CH_2—CH{=}CH_2$	-60.6
$CH_2{=}CH—CH{=}CH_2$	-56.5

The above values show that the heat of hydrogenation of 1, 3-butadiene is about 4 kcal/mole less than other non-conjugated dienes. Thus conjugated dienes are significantly more stable than non-conjugated dienes. This relatively small but significant difference is attributed to two factors.

The two double bonds are normal but the $C_2—C_3$ single bond is shorter than 1.54 Å.



$$\underset{\overset{\uparrow}{sp^2}}{CH_2}{=}\underset{\overset{\uparrow}{sp^2}}{CH} \overset{\overset{1.48\,Å}{\downarrow}}{—} \underset{\overset{\uparrow}{sp^2}}{CH} \overset{\overset{1.34\,Å}{\downarrow}}{=} \underset{\overset{\uparrow}{sp^2}}{CH_2}$$

$sp^2—sp^2$ hybridisation makes the $C_2—C_3$ bond of butadiene short, σ bond length order is as follows :

$$C_{sp^3}—C_{sp^3} > C_{sp^3}—C_{sp^2} > C_{sp^2}—C_{sp^2}$$

This shorter bond having more *s* character is stronger than the normal C—C bond having less *s*-character. This, then, should make 1, 3-butadiene more stable than expected. Secondly, all four carbon atoms in butadiene are sp^2 hybridised (Fig. 5.7a). The parallel to axes overlaping of the *p*-orbitals of C_1 and of C_2, and C_3 and C_4 gives rise to two localised π bonds (Fig. 5.7b).

The p-orbitals on carbon C_2 and C_3 can also overlap to give some double bond character to the $C_2—C_3$ single bond (Fig. 5.7c).

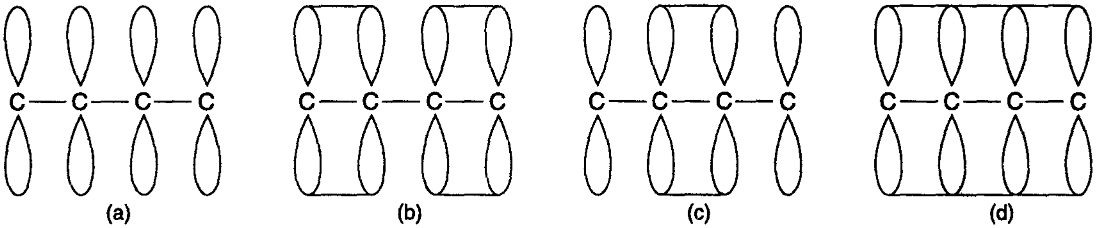


Fig. 5.7. *p*-orbitals in butadiene and their overlapping.

The overlap of p-orbitals of C_2 and C_3 in both directions (C_2 with C_1 and C_3, C_3 with C_2 and C_4) allows the π-electrons to be delocalised (Fig. 5.5d). This delocalisation of the π-electrons imparts greater stability to 1, 3-butadiene. However, the overlap between the C_2 and C_3 is much less than those between C_1 and C_2 and between C_3 and C_4 because of the greater distance between the C_2 and C_3 p-orbitals.

5.22.4 Chemical Reactions of Dienes

(i) Reduction Reaction : Dienes undergo addition reaction with hydrogen in the presence of catalyst.

$$CH_3—CH{=}C{=}CH—CH_3 + 2H_2 \xrightarrow{Pt} n\text{-pentane} \qquad \Delta H = -70.5 \text{ kcal/mole}$$

$$CH_2{=}CH—CH_2—CH{=}CH_2 + 2H_2 \xrightarrow{Pt} n\text{-pentane} \qquad \Delta H = -60.2 \text{ kcal/mole}$$

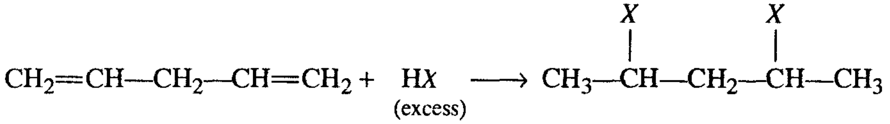
$$CH_2{=}CH—CH{=}CH—CH_3 + 2H_2 \xrightarrow{Pt} n\text{-pentane} \qquad \Delta H = -54.1 \text{ kcal/mole}$$

From the above results we can conclude the order of stability of dienes, which is as follows :

$$\xrightarrow[\text{Stability in decreasing order}]{\text{Conjugated dienes > Isolated dienes > Cumulated dienes}}$$

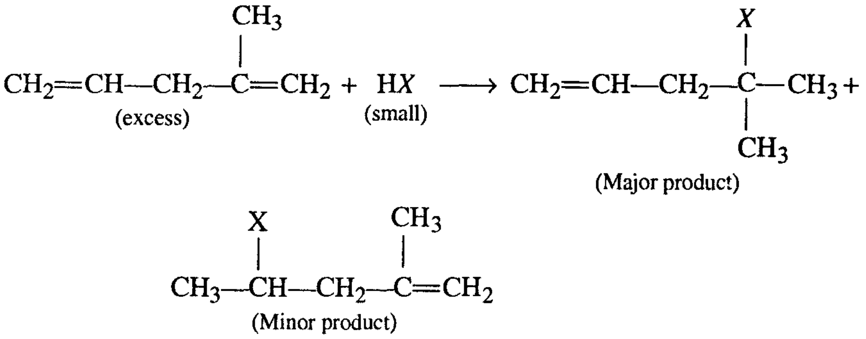
(ii) Electrophilic Addition Reactions of Dienes

(A) Isolated dienes : The reactions of isolated dienes are same as the reactions of alkenes. If an excess of the electrophilic reagent is present, two independent addition reactions will occur, each following Markovnikov's rule.



$$CH_2{=}CH—CH_2—CH{=}CH_2 + \underset{\text{(excess)}}{HX} \longrightarrow CH_3—\overset{\overset{X}{|}}{C}H—CH_2—\overset{\overset{X}{|}}{C}H—CH_3$$

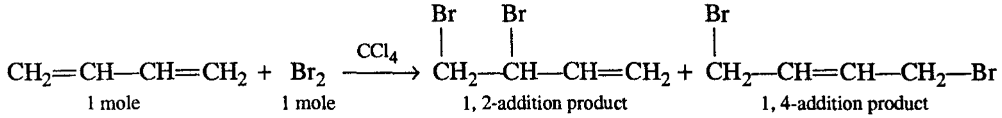
If amount of substrate is more and electrophilic reagent is less, then addition takes place on that double bond which *is more reactive* for electrophilic addition reaction.



$$\underset{\text{(excess)}}{CH_2{=}CH—CH_2—\overset{\overset{CH_3}{|}}{C}{=}CH_2} + \underset{\text{(small)}}{HX} \longrightarrow \underset{\text{(Major product)}}{CH_2{=}CH—CH_2—\overset{\overset{X}{|}}{\underset{\underset{CH_3}{|}}{C}}—CH_3} +$$

$$\underset{\text{(Minor product)}}{CH_3—\overset{\overset{X}{|}}{C}H—CH_2—\overset{\overset{CH_3}{|}}{C}{=}CH_2}$$

(B) Conjugated dienes : If conjugated dienes react with a limited amount of electrophilic reagent, so that addition can occur at only one double bond, two addition products are formed. One is a 1, 2-addition product which is a result of addition at the 1- and 2-positions. The other is a 1, 4-addition product, the result of addition at the 1- and 4-positions.



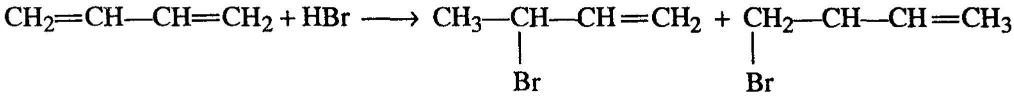
$$\underset{\text{1 mole}}{CH_2{=}CH{-}CH{=}CH_2} + \underset{\text{1 mole}}{Br_2} \xrightarrow{CCl_4} \underset{\text{1, 2-addition product}}{\overset{Br}{\overset{|}{CH_2}}{-}\overset{Br}{\overset{|}{CH}}{-}CH{=}CH_2} + \underset{\text{1, 4-addition product}}{\overset{Br}{\overset{|}{CH_2}}{-}CH{=}CH{-}CH_2{-}Br}$$

Addition at 1- and 2-positions is called 1, 2-addition or **direct addition.** Addition at 1- and 4- is called 1, 4-addition or **conjugate addition.**

When we refer to addition at the 1- and 2-positions or at the 1- and 4-positions, we mean that addition occurs at the 1- and 2- or 1- and 4-positions of the four carbon conjugated system, *i.e.*,

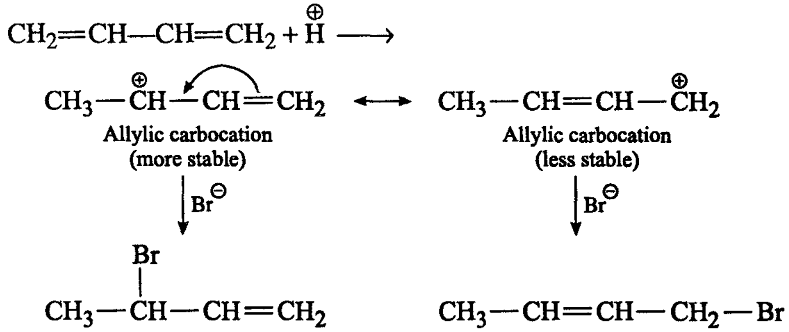
$$CH_3{-}CH_2{-}CH_2{-}\underset{1}{CH}{=}\underset{2}{CH}{-}\underset{3}{CH}{=}\underset{4}{CH}{-}CH_3$$

Mechanism of the Reaction

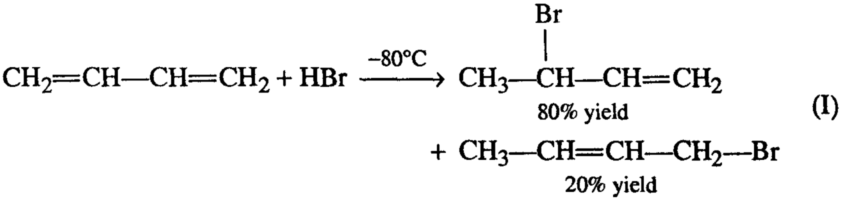


$$CH_2{=}CH{-}CH{=}CH_2 + HBr \longrightarrow CH_3{-}\underset{\underset{Br}{|}}{CH}{-}CH{=}CH_2 + \underset{\underset{Br}{|}}{CH_2}{-}CH{-}CH{=}CH_3$$

Step I.

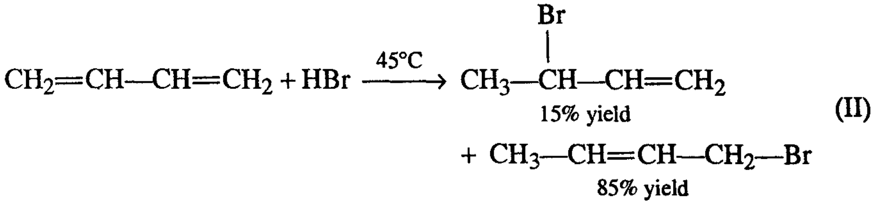


Formation of two products is due to the formation of allylic carbocation as reaction intermediate. When reaction is carried out **at low temperature** 1, 2-addition product is the major product.



$$CH_2{=}CH{-}CH{=}CH_2 + HBr \xrightarrow{-80°C} \underset{\text{80\% yield}}{CH_3{-}\overset{Br}{\overset{|}{CH}}{-}CH{=}CH_2} + \underset{\text{20\% yield}}{CH_3{-}CH{=}CH{-}CH_2{-}Br} \qquad (I)$$

In contrast, when reaction is carried out **at higher temperature,** the major product is 1, 4-addition product.



$$CH_2{=}CH{-}CH{=}CH_2 + HBr \xrightarrow{45°C} \underset{\text{15\% yield}}{CH_3{-}\overset{Br}{\overset{|}{CH}}{-}CH{=}CH_2} + \underset{\text{85\% yield}}{CH_3{-}CH{=}CH{-}CH_2{-}Br} \qquad (II)$$

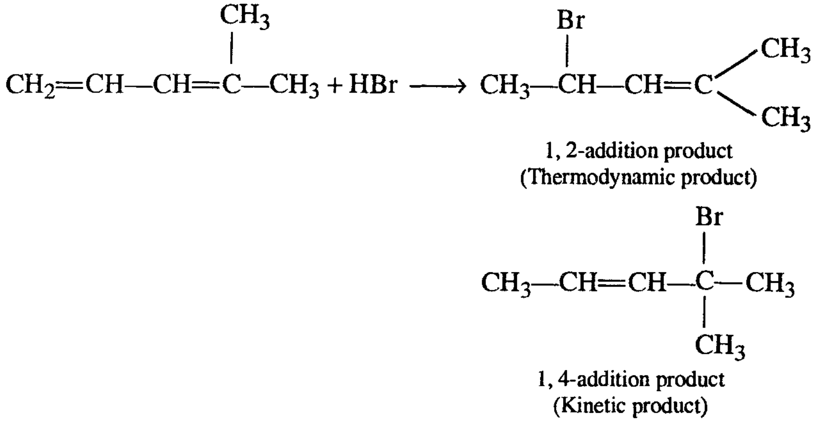
When a reaction produces more than one product, through common intermediate, the product that is formed the most rapidly is called the **kinetic product.** The most stable product is called the **thermodynamic product.**

The reaction that produces the kinetic product as the major product is called kinetically controlled reaction (reaction–(I)).

The reaction that produces the thermodynamic product as the major product is called thermodynamically controlled reaction (reaction II).

The thermodynamic product predominates when the reaction is reversible while the kinetic product predominates when reaction is not reversible.

Product which is formed by more stable allylic carbocation (or RI) is always kinetic product and product which is formed by less stable carbocation (or RI) is thermodynamic product.

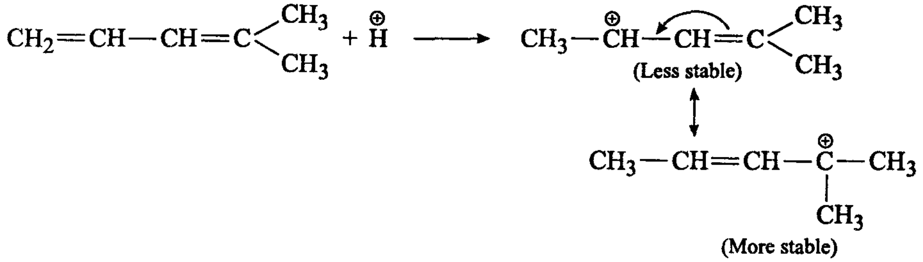


$$CH_2{=}CH{-}CH{=}\overset{\overset{CH_3}{|}}{C}{-}CH_3 + HBr \longrightarrow CH_3{-}\overset{\overset{Br}{|}}{C}H{-}CH{=}C(CH_3)_2$$

1, 2-addition product
(Thermodynamic product)

$$CH_3{-}CH{=}CH{-}\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}}{-}CH_3$$

1, 4-addition product
(Kinetic product)

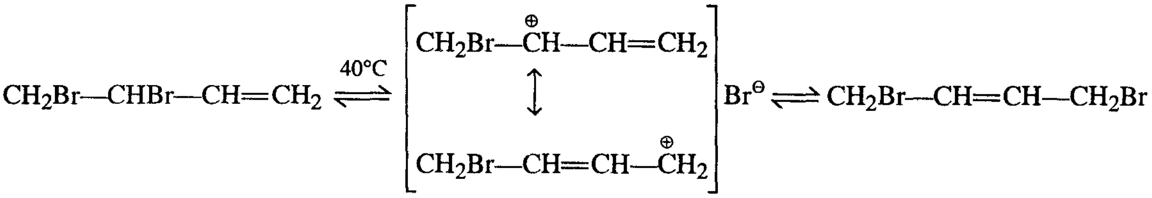


$$CH_2{=}CH{-}CH{=}C(CH_3)_2 + \overset{\oplus}{H} \longrightarrow CH_3{-}\overset{\oplus}{C}H{-}CH{=}C(CH_3)_2 \longleftrightarrow CH_3{-}CH{=}CH{-}\underset{\underset{CH_3}{|}}{\overset{\oplus}{C}}{-}CH_3$$

(Less stable)

(More stable)

While elevated temperatures increase the rate of formation of 1, 2-addition product, they also increase its rate of decomposition. The 1, 4-addition product is also an allylic halide and should ionise to an allylic carbocation. While this does happen at + 40°C, it is harder to remove (by ionisation) bromide ion from the 1, 4-addition product than from 1, 2-addition product because 1, 4-addition product has an internal double bond (more substituted) whereas 1, 2-addition product has terminal double bond (less substituted). Due to this 1, 4-addition product is more stable than 1, 2-addition product. At higher temperatures, the relative stabilities of the products control the product ratio, and the reaction is under equilibrium or thermodynamic control.



$$CH_2Br{-}CHBr{-}CH{=}CH_2 \xrightleftharpoons{40^\circ C} \left[\begin{array}{c} CH_2Br{-}\overset{\oplus}{C}H{-}CH{=}CH_2 \\ \updownarrow \\ CH_2Br{-}CH{=}CH{-}\overset{\oplus}{C}H_2 \end{array}\right] Br^{\ominus} \rightleftharpoons CH_2Br{-}CH{=}CH{-}CH_2Br$$

Fig. 5.8 shows the energy diagram for the equilibrium. From the energy profile diagram it is clear that the allylic cation is the intermediate which is involved in the equilibrium of the two products.

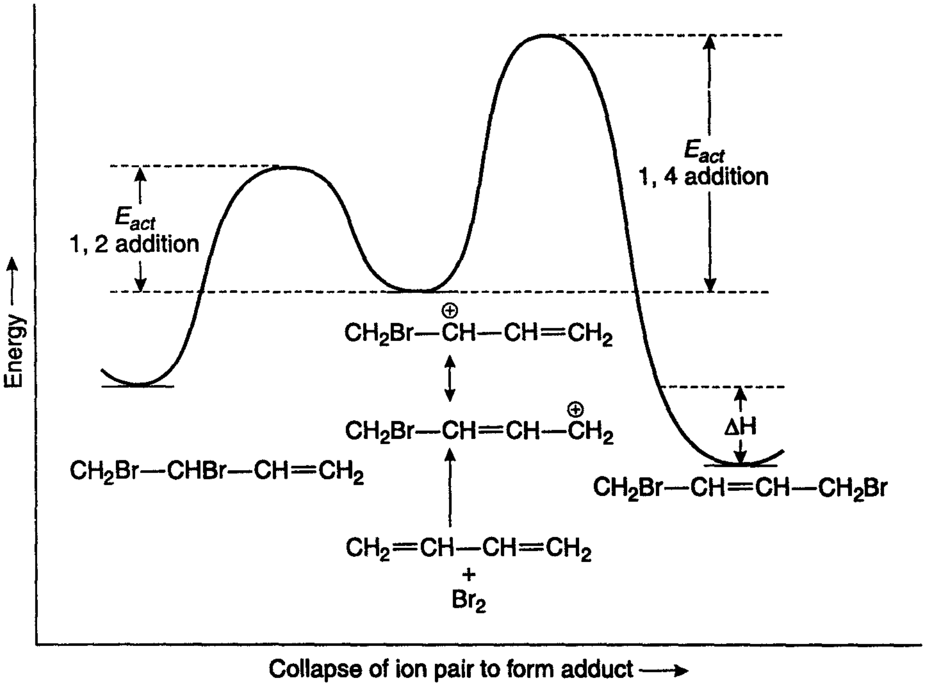
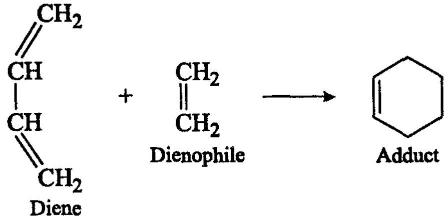


Fig. 5.8. Energy diagram for 1, 2 and 1, 4 addition of Br_2 to 1, 3-butadiene.

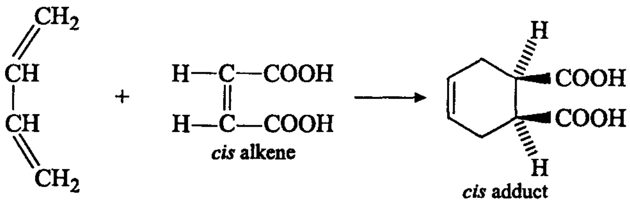
In this reaction two products are obtained; one of them (1, 2-addition product) is formed more rapidly (E_{act} of 1, 2 addition is less) than the other (1, 4-addition product). This one is called the kinetic product or kinetically controlled product. The other product (1, 4 addition product) is formed more slowly (E_{act} of 1, 4-addition product is more) but is more stable. This product is called the thermodynamic product or thermodynamically controlled product.

(iii) Diels-Alder Reaction : Conjugated dienes add to alkenes by 1, 4-addition to form cyclic compounds. The alkene is called dienophile and the product is **Adduct**. The reaction is usually exothermic.

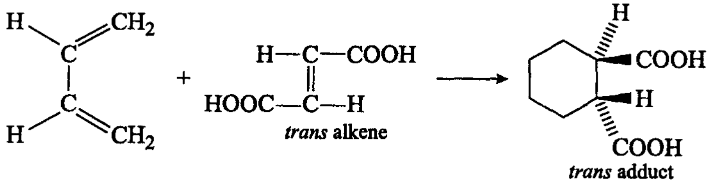


This reaction which is very useful for preparing six membered rings, is called the Diels-Alder reaction. In this reaction, two *pi* bonds are lost while two σ bonds are gained. Since σ bonds are more stable than *pi* bonds, the Diels-Alder reaction is usually exothermic.

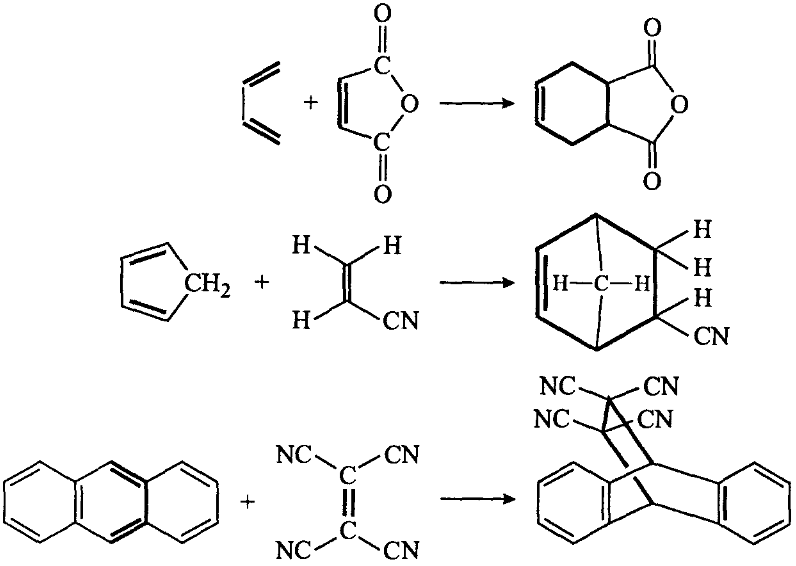
The Diels-Alder reaction is highly stereospecific. The stereochemistry of the diene and dienophile are preserved during adduct formation. This can be seen when *cis* and *trans* disubstituted alkenes are used as dienophile. If the dienophile is a *cis*-disubstituted alkene, then these substituents will be *cis* to each another in the product. It should be noted that only a *cisoid* (*s-cis*) and not a *transoid* diene takes part in Diels-Alder reaction.



Similarly, if the dienophile is *trans* disubstituted, then these substituents will be *trans* to each another in the product.

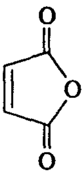


The Diels-Alder reaction is very useful for the synthesis of complex system. This can be seen from the examples given below. In each of these the diene, dienophile and the product-ring are shown by thick line.

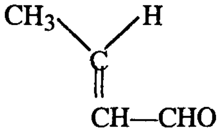


In general, the most reactive dienophiles have the alkene double bond conjugated to some electron-withdrawing group. The most common dienophiles of this type include the following compounds.

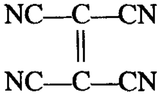
Maleic anhydride



Crotonaldehyde

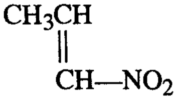


tetracyanoethylene



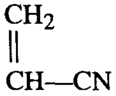
$$\begin{array}{c}\mathrm{NC{-}C{-}CN}\\ \|\\ \mathrm{NC{-}C{-}CN}\end{array}$$

1-nitropropene



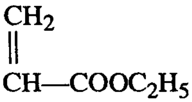
$$\begin{array}{l}\mathrm{CH_3CH}\\ \quad\ \|\\ \quad\ \mathrm{CH{-}NO_2}\end{array}$$

acrylonitrile



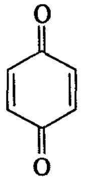
$$\begin{array}{l}\mathrm{CH_2}\\ \|\\ \mathrm{CH{-}CN}\end{array}$$

ethyl acrylate



$$\begin{array}{l}\mathrm{CH_2}\\ \|\\ \mathrm{CH{-}COOC_2H_5}\end{array}$$

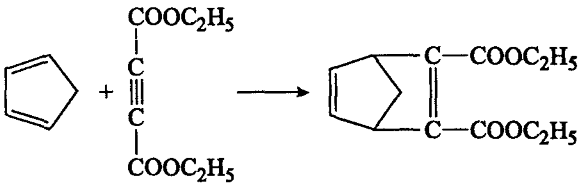
Benzoquinone



While the most common reactive dienophiles have electron withdrawing groups on double bond, the more common reactive dienes have electron donating alkyl groups bonded to the double bonds.

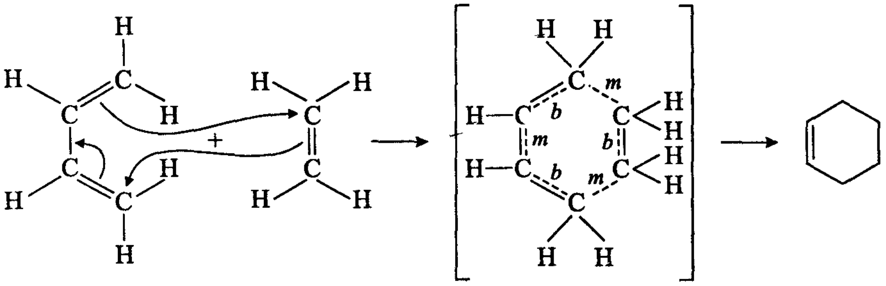
Most Diels-Alder reactions involve electron rich dienes and electron poor dienophiles. However, it is now believed that what is essential for the reaction to occur is that the diene and dienophile have complementary electronic nature. Diels-Alder reaction can also occur between electron-rich dienophiles and electron-poor dienes.

In addition to alkenes, the reactive dienophile may also be an alkyne as shown below :



Similarly, the diene in Diels-Alder reaction may also be a conjugated polyene, enyne or diyne.

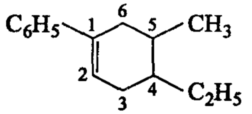
The Diels-Alder reaction does not involve ionic or free radical intermediates. It proceeds in a concerted manner involving cyclic transition state with simultaneous making and breaking of bonds. Three bonds are being made in the activated complex. Two of these are σ bonds which will lie together the diene and dienophile. The third bond being made is a *pi* bond. It will appear in the product, where there was a single bond in the diene. Three bonds are being broken in the activated complex. All three of these are π bonds.



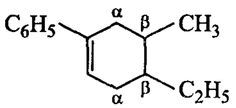
Activated complex
m = bond being made
b = bond being broken

From the structure of the adduct we can know the structure of diene and dienophile as follows :

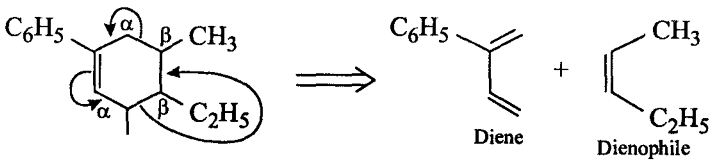
Suppose adduct has the following structure :



(1) Assign α and β positions with respect to the multiple bond of the adduct.



(2) Deduce the starting materials by drawing the curved arrow for the reverse of Diels-Alder reaction (*i.e.*, curved arrow started from bond between α and β-reaction)



5.23 ALKYNES

Hydrocarbons having triple bond between carbon atoms are called alkynes. They have the general formula C_nH_{2n-2}. The first and the most important member of this series of hydrocabons is acetylene and hence these are also called the acetylenes or substituted acetylenes and the triple bond is known as acetylenic bond.

5.23.1 Nomenclature

The IUPAC nomenclature of alkyne is directly analogous to that of the alkene. The suffix for an alkyne is *yne*. The position of a triple bond is indicated by a number when necessary. If the triple bond can take up more than one position in the molecule then the carbon chain is numbered in such a way so as to assign minimum number to carbon preceding the triple bond. The monovalent groups (alkynyl groups) derived from alkynes are named by deleting the *e* of the corresponding alkyne by *yl*. Some names are given below in Table 5.2.

Table 5.2. Names of some alkynes and alkynyl groups

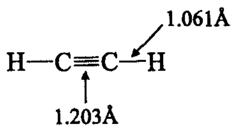
Formula	Alkyne	Alkynyl group
$CH{\equiv}CH$	Ethyne	Ethynyl
$CH_3{-}C{\equiv}C{-}CH_3$	2-Butyne	2-Butynyl
$CH_3{-}CH_2{-}C{\equiv}C{-}CH_3$	2-Pentyne	2-Pentynyl

When both a double and triple bond are present, the hydrocarbon is named an alkenyne with number as low as possible given to the multiple bonds. In case of a choice, the double bond gets the lower number.

$CH_3{-}CH{=}CH{-}C{\equiv}CH$
3-Penten-1-*yne*
not
2-Penten-4-*yne*

$CH{\equiv}C{-}CH_2{-}CH{=}CH_2$
1-Penten-4-*yne*
not
4-Penten-1-*yne*

Acetylene is known experimentally to have a linear structure. Its C≡C bond distance is 1.20 Å. This is the shortest C—C bond distance. The C—H bond distance is 1.06 Å. This C—H bond distance is shorter than C—H bond distance in ethylene (1.08 Å) or in ethane (1.10 Å).



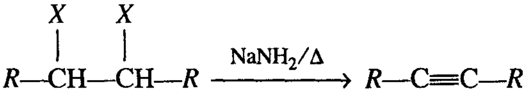
$$\mathrm{H{-}\underset{\underset{1.203\,Å}{\uparrow}}{C{\equiv}C}{-}\overset{\swarrow 1.061\,Å}{H}}$$

A triple bond carbon is in *sp* hybrid state. The *sp* hybrid orbital is one half *s* character while an sp^2 orbital is one third *s* and sp^3 orbital is only one fourth *s* character. The greater the *s* character a hybrid orbital has, the shorter will be the bond formed by it. Acetylene is a linear molecule. Both carbon-hydrogen and carbon-carbon bonds are cylindrically symmetrical about the line joining the nuclei, *i.e.*, acetylene molecule has a compact barlike structure.

5.23.2 Methods of Preparation of Alkynes

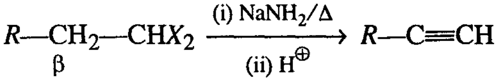
Alkynes are prepared by elimination reactions.

(i) Dehydrohalogenation of *vic* dihalides : *Vicinal* dihalides having hydrogens on α-carbons give alkyne with strong bases.

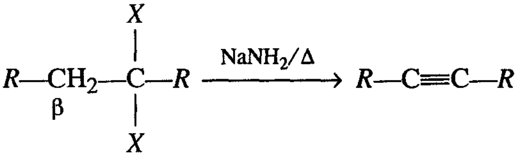


$$R{-}\overset{\overset{X}{|}}{\mathrm{C}}\mathrm{H}{-}\overset{\overset{X}{|}}{\mathrm{C}}\mathrm{H}{-}R \xrightarrow{\mathrm{NaNH_2}/\Delta} R{-}\mathrm{C{\equiv}C}{-}R$$

(ii) Dehydrohalogenation of *gem* dihalides having two β-hydrogens : Such type of compounds give alkyne with strong bases.

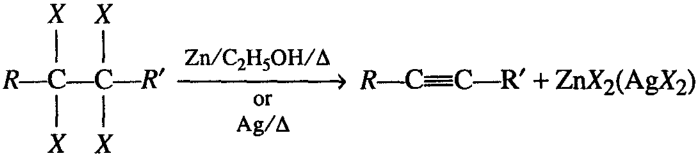


$$R{-}\underset{\beta}{\mathrm{CH_2}}{-}\mathrm{CH}X_2 \xrightarrow[\text{(ii) H}^{\oplus}]{\text{(i) NaNH}_2/\Delta} R{-}\mathrm{C{\equiv}CH}$$



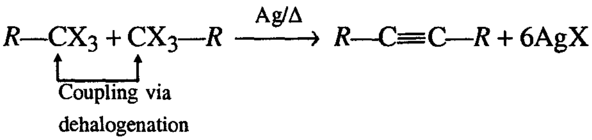
$$R{-}\underset{\beta}{\mathrm{CH_2}}{-}\underset{\underset{X}{|}}{\overset{\overset{X}{|}}{\mathrm{C}}}{-}R \xrightarrow{\mathrm{NaNH_2}/\Delta} R{-}\mathrm{C{\equiv}C}{-}R$$

(iii) Dehalogenation of α, α, β, β-tetrahaloalkanes : α, α, β, β-Tetrahaloalkanes give alkyne with Zn/C_2H_5OH or Ag/Δ.



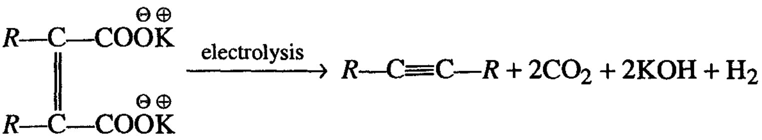
$$R{-}\underset{\underset{X}{|}}{\overset{\overset{X}{|}}{\mathrm{C}}}{-}\underset{\underset{X}{|}}{\overset{\overset{X}{|}}{\mathrm{C}}}{-}R' \xrightarrow[\substack{\text{or}\\ \mathrm{Ag}/\Delta}]{\mathrm{Zn/C_2H_5OH}/\Delta} R{-}\mathrm{C{\equiv}C}{-}\mathrm{R'} + \mathrm{Zn}X_2(\mathrm{Ag}X_2)$$

(iv) Dehalogenation and coupling of *gem* trihalides : *Gem* trihalides undergo coupling reaction *via* dehalogenation in the presence of Ag/Δ to give alkynes.



$$\underbrace{R{-}\mathrm{CX_3} + \mathrm{CX_3}}_{\substack{\text{Coupling via}\\ \text{dehalogenation}}}{-}R \xrightarrow{\mathrm{Ag}/\Delta} R{-}\mathrm{C{\equiv}C}{-}R + 6\mathrm{AgX}$$

(v) Kolbe hydrocarbon synthesis : Potassium salt of maleic acid and its alkyl derivatives give alkynes on electrolysis.



$$\begin{array}{l} R{-}\mathrm{C}{-}\overset{\ominus\oplus}{\mathrm{COOK}} \\ \quad\| \\ R{-}\mathrm{C}{-}\overset{\ominus\oplus}{\mathrm{COOK}} \end{array} \xrightarrow{\text{electrolysis}} R{-}\mathrm{C{\equiv}C}{-}R + 2\mathrm{CO_2} + 2\mathrm{KOH} + \mathrm{H_2}$$

5.23.3 Acidity of Alkynes

The hydrogens in terminal alkynes are relatively acidic because they readily donate proton to strong bases.

$$R{-}C{\equiv}C{-}H + \text{Base (B)} \longrightarrow R{-}C{\equiv}\overset{\ominus}{C} + \overset{\oplus}{B}H$$

When terminal alkynes are treated with sodamide in liquid ammonia or passed over molten sodium they convert into the corresponding carbanions.

$$\underset{\text{Strong acid}}{R{-}C{\equiv}C{-}H} + \underset{\text{Strong base}}{NaNH_2} \longrightarrow \underset{\text{Weak base}}{R{-}C{\equiv}\overset{\ominus\oplus}{CNa}} + \underset{\text{Weak acid}}{NH_3}$$

$$R{-}C{\equiv}C{-}H + Na \longrightarrow R{-}C{\equiv}\overset{\ominus\oplus}{CNa} + \frac{1}{2}H_2$$

The above two reactions suggest the acidic character of hydrogen in 1-alkynes. From the above reactions it is also clear that 1-alkynes are stronger acid than ammonia because we know that a stronger acid displaces a weak acid from its salt.

On the other hand, sodium acetylides on treatment with water afford alkynes, thus 1-alkynes are weaker acid than water.

$$\underset{\text{Strong base}}{R{-}C{\equiv}\overset{\ominus\oplus}{CNa}} + \underset{\text{Strong acid}}{HOH} \longrightarrow \underset{\text{Weak acid}}{R{-}C{\equiv}CH} + \underset{\text{Weak base}}{NaOH}$$

The acidity of some compounds is given in Table 5.3.

Table 5.3

Compound	Formula	*Ka*
Acetic acid	CH_3COOH	10^{-5}
Ethanol	CH_3CH_2OH	10^{-16}
Acetylene	$CH{\equiv}CH$	10^{-26}
Ammonia	NH_2H	10^{-35}
Ethylene	$CH_2{=}CH_2$	10^{-44}
Methane	CH_4	10^{-50}

When ethylene or methane is treated with $NaNH_2$ the reaction does not occur. From Table 5.3 it is clear that there is a vast difference in the acidity of acetylene, ethene and methane. In other words, there is vast difference in the stability of the carbanions $RC{\equiv}\overset{\ominus}{C}$, $CH_2{=}\overset{\ominus}{C}H$ and $\overset{\ominus}{C}H_3$. Thus alkynes differ from alkenes and alkanes in that they exhibit acidic character. What special feature is responsible for the acidity of 1-alkynes? The strength of acid depends on the stability of an anion after the removal of proton. In other words, the strength of an acid depends upon the ease with which it can lose a proton.

$$R{-}C{\equiv}C{-}H \rightleftharpoons R{-}C{\equiv}\overset{\ominus}{C} + \overset{\oplus}{H}$$

$$CH_2{=}CH_2 \rightleftharpoons CH_2{=}\overset{\ominus}{C}H + \overset{\oplus}{H}$$

$$CH_4 \rightleftharpoons \overset{\ominus}{C}H_3 + \overset{\oplus}{H}$$

Carbon atoms in acetylene or 1-alkynes are *sp* hydridised, hence have more *s* character than in ethylene and ethane. As *s* electrons are closer to the nucleus than *p* electrons, *s* orbitals are more electronegative than *p* orbitals Therefore, increasing the *s* character of a hybrid orbital makes the orbital more electronegative. For carbon the order of orbital electronegativity is $s > p > sp > sp^2 > sp^3$. This means that C—H bond in 1-alkyne is slightly more polar than C—H bond in ethylene and other alkanes. Alternatively since the greater the electronegativity of an atom the more readily it can accommodate a negative charge.

5.23.4 Chemical Reactions of Alkynes

Alkynes give two types of chemical reactions :

(1) Reaction due to acidic hydrogen and (2) Reaction due to π-bonds:

5.24 REACTIONS DUE TO ACIDIC HYDROGEN

Relative acidities of some compounds are as follows in decreasing order

$$HOH > ROH > CH{\equiv}CH > NH_3 > CH_2{=}CH_2$$

Thus alkyne is very weak acid. Acetylene and terminal alkynes are acidic in character. Acetylene is more acidic than other terminal alkynes. Reactions due to acidic hydrogen will be given only by acetylene and terminal alkynes.

5.24.1 Salt Formation

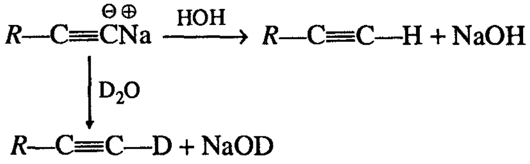
Terminal alkyne is very weak acid, it forms salt with very strong base such as $NaNH_2$ and molten sodium metal.

$$R{-}C{\equiv}C{-}H \xrightarrow[NH_3(l)]{NaNH_2} R{-}C{\equiv}\overset{\ominus\oplus}{CNa} + \frac{1}{2}H_2$$

$$H{-}C{\equiv}C{-}H \xrightarrow[NH_3(l)]{Na} \overset{\oplus\ \ominus}{NaC}{\equiv}\overset{\ominus\oplus}{CNa} + H_2$$

Sodium salt of alkyne is known as sodium alkynide.

(a) Sodium alkynide is hydrolysed with water because it is salt.



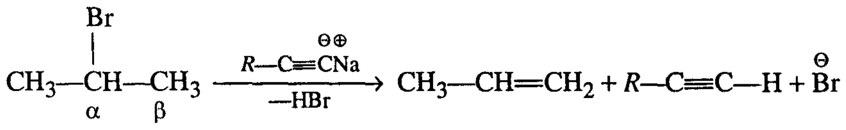
$$\begin{tikzcd} R{-}C{\equiv}\overset{\ominus\oplus}{CNa} \arrow[r, "HOH"] \arrow[d, "D_2O"] & R{-}C{\equiv}C{-}H + NaOH \\ R{-}C{\equiv}C{-}D + NaOD & \end{tikzcd}$$

(b) $$\underset{\text{Weak acid}}{R{-}C{\equiv}C{-}H} \xrightarrow[NH_3(l)]{NaNH_2} \underset{\text{Strong base}}{R{-}C{\equiv}\overset{\ominus\oplus}{CNa}}$$

Sodium salt behaves as nucleophile as well as strong base. For *prim*-alkyl halides it behaves as nucleophile. Thus primary alkyl halides give SN reaction with this salt.

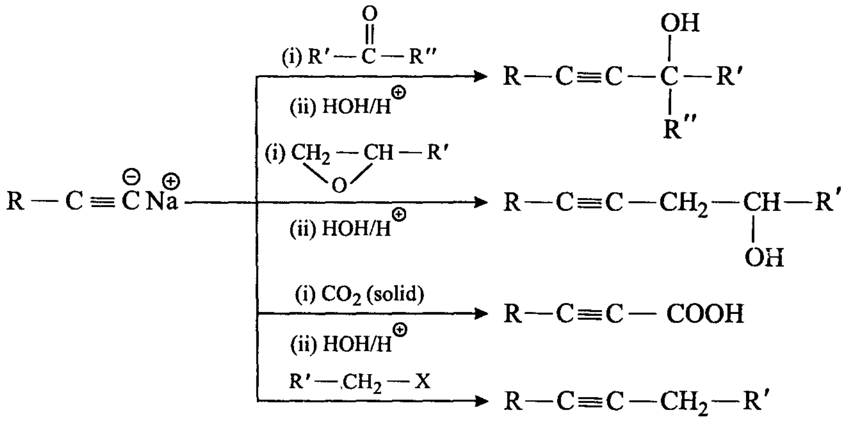
For secondary and tertiary alkyl halides it behaves as strong base hence they undergo elimination reaction.

$$R{-}C{\equiv}\overset{\ominus\oplus}{CNa} \xrightarrow[SN]{R'{-}CH_2{-}Br} R{-}C{\equiv}C{-}CH_2{-}R'$$

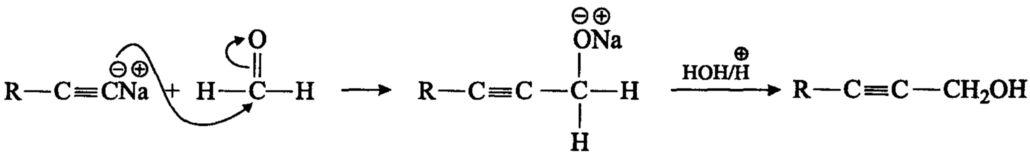


$$\underset{\alpha}{CH_3{-}\overset{\overset{Br}{|}}{CH}}{-}\underset{\beta}{CH_3} \xrightarrow[-HBr]{R{-}C{\equiv}\overset{\ominus\oplus}{CNa}} CH_3{-}CH{=}CH_2 + R{-}C{\equiv}C{-}H + \overset{\ominus}{Br}$$

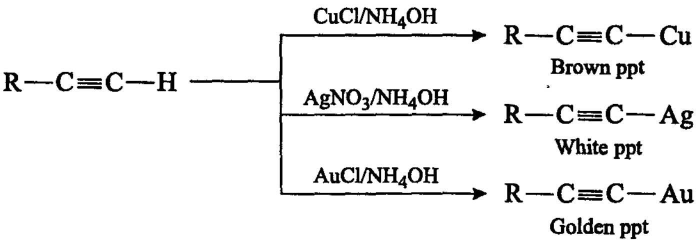
Metal alkynides (specially sodium alkynides) are very important starting material for the preparation of different organic compounds. Some of the reactions of metal alkynides are as follows :



Note : Reaction between sodium alkynide and formaldehyde is known as **ethinylation** reaction which takes place as follows :



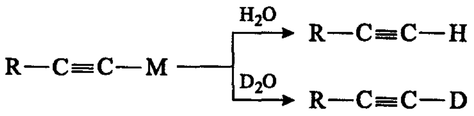
5.24.2 Formation of Metal Alkynide



Alkyne forms metal alkynide with Cu_2Cl_2, $AgNO_3$ and AuCl in the presence of NH_4OH.

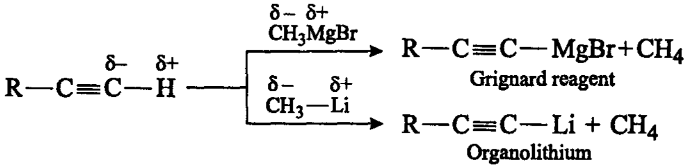
(a) These metal alkynides are obtained as precipitate, hence this reaction can be used for the identification of terminal alkynes.

(b) Metal alkynide reacts with water to give alkyne.



5.24.3 Reaction with Grignard Reagent and Alkyllithium

These two reagents react with terminal alkyne to form hydrocarbon and new organometallic compounds, respectively.



5.24.4 Electrophilic Substitution with $X_2/\overset{\ominus}{O}H$ or NaOX

Terminal alkyne gives electrophilic substitution reaction in which acidic hydrogen is replaced by electrophilic part of the reagent ($NaOX \rightarrow Na\overset{\ominus}{O} + \overset{\oplus}{X}$), *i.e.*, with $\overset{\oplus}{X}$.

$$R{-}C{\equiv}C{-}H \xrightarrow{NaOCl} R{-}C{\equiv}C{-}Cl$$

$$H{-}C{\equiv}C{-}H \xrightarrow{NaOCl} Cl{-}C{\equiv}C{-}Cl$$

Iodine gives above reaction in the presence of NH_3

$$H{-}C{\equiv}C{-}H \xrightarrow{I_2/NH_3} \underset{\text{Diiodoacetylene}}{I{-}C{\equiv}C{-}I}$$

5.25 REACTIONS DUE TO π-BONDS

Alkynes undergo addition as well as oxidation reactions due to the presence of π-bonds. Alkynes give two types of addition reactions.

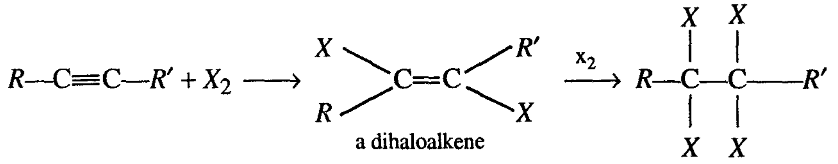
(1) Electrophilic addition reactions. (2) Nucleophilic addition reactions

In addition reactions, alkynes can react with one mole as well as with two moles of the reagent depending on the reaction conditions and number of moles of the substrate and reagent.

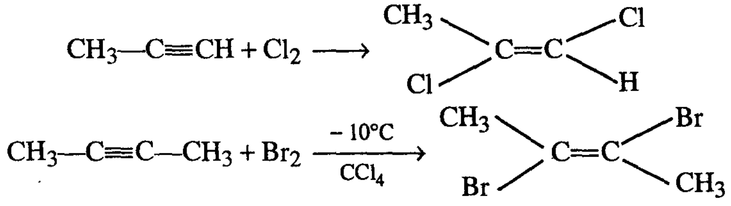
5.26 ELECTROPHILIC ADDITION REACTIONS

5.26.1 Addition of Halogens

Alkynes undergo the same kind of addition reactions with chlorine and bromine that alkenes undergo. The major difference is that an alkyne reacts with two molecules of halogen while an alkene reacts with only one.



A dihaloalkene is an intermediate in this reaction. It often is possible to prepare dihaloalkenes by adding calculated amount of halogen (1 mole) to the alkyne at low temperatures. This addtion of halogen to an alkyne is predominately an *anti* addition.

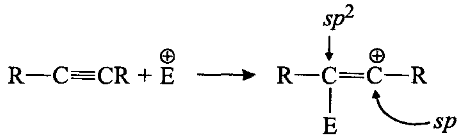


Alkynes undergo addition of halogens, as well as other electrophilic additions, more slowly than do alkenes.

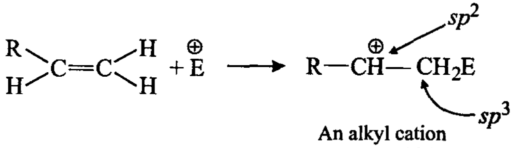
$$CH{\equiv}C{-}CH_2{-}CH{=}CH_2 \xrightarrow[CCl_4\,-\,20°C]{Br_2\,(1\text{ mole})} \underset{90\%}{CH{\equiv}C{-}CH_2{-}CHBr{-}CH_2Br}$$

Formation of the above product is due to addition of bromine across double bond and not the triple bond. The above reaction clearly shows that alkynes are less reactive than alkenes toward electrophilic reagent.

Since alkynes are more unsaturated than alkenes, it somehow seems wrong for them to be less ractive than alkenes. This apparent anomaly is rationalised by examining the intermediates that are formed when alkynes and alkenes react with an electrophile $\overset{\oplus}{E}$.



A vinyl cation
(less stable)

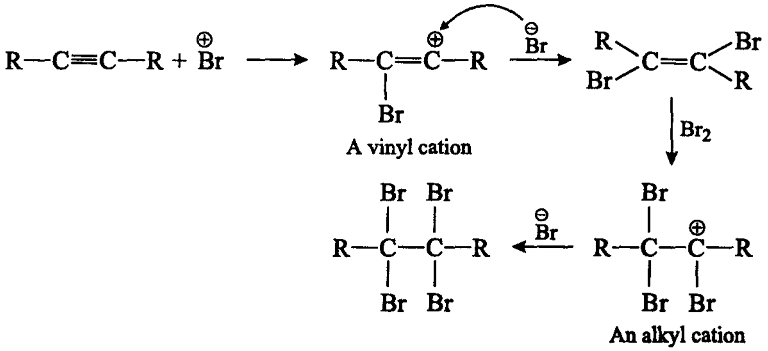


An alkyl cation
(more stable)

The carbocation produced from an alkyne is a vinyl cation with a more electronegative *sp* hybridised carbon which is less tolerant of the positive charge than the alkyl cation with sp^2 carbon produced from an alkene. Thus addition of electrophile to an alkyne forms a much less stable intermediate than that in the case of an alkene.

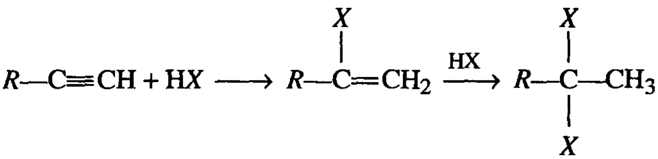
We know that reactivity of a substance depends on the stability of reaction intermediate. Higher is the stability of reaction intermediate, more will be the reactivity of the substrate. Therefore, alkenes are more reactive than alkynes in electrophilic addition reactions.

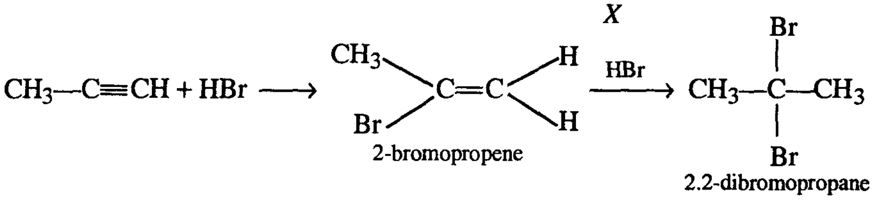
The mechanism of addition of halogen to an alkyne can be represented as follows :

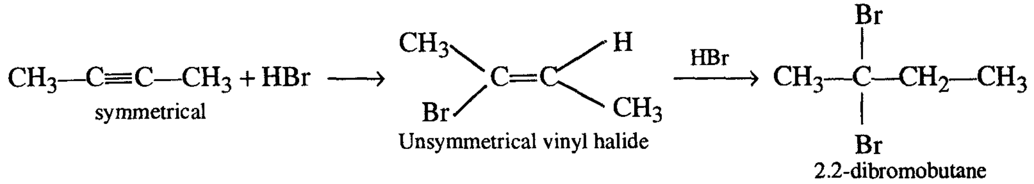


5.26.2 Addition of Hydrogen Halides to Alkynes

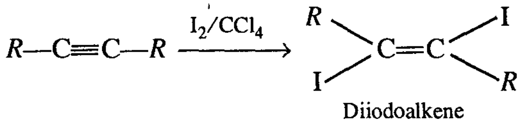
Halogen acids add to alkyne in two stages. Addition of one molecule of halogen acid gives an unsaturated halide which then adds another molecule of *HX* to form *gem* dihaloalkane. The addition of *HX* in both the steps follow the Markovnikov rule.







Chlorine and bromine form di- as well as tetrahalo derivatives but iodine forms only diiodo derivative.



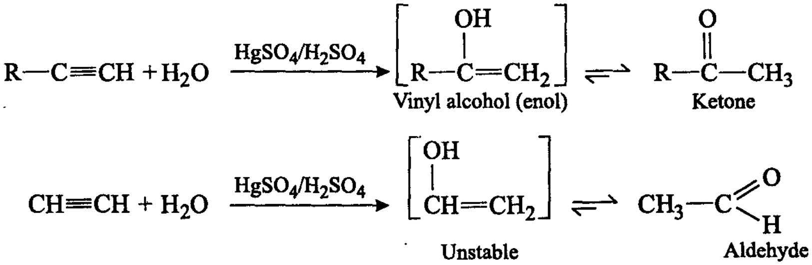
Hydrogen bromide adds to alkenes in an *anti* Markovnikov manner in the presence of free radical initiators. Hydrogen bromide also adds in an *anti*-Markovnikov manner to alkynes in the presence of radical sources.

$$CH_3—CH_2—CH_2—C{\equiv}CH \xrightarrow[\text{Peroxide}]{\text{HBr}} \underset{\text{Vinyl halide}}{CH_3—CH_2—CH_2—CH{=}CH—Br}$$

$$CH_3—C{\equiv}CH + HBr \xrightarrow[\text{Peroxide}]{\text{HBr}} \underset{\text{Vinyl halide}}{CH_3—CH{=}CH—Br}$$

5.26.3 Addition of Water

Water adds to carbon-carbon triple bond in the presence of mercuric sulphate and sulphuric acid to form a vinyl alcohol (enol) which readily tautomerises to the corresponding carbonyl compound.

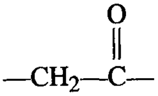


$$R—C{\equiv}CH + H_2O \xrightarrow{HgSO_4/H_2SO_4} \underset{\text{Vinyl alcohol (enol)}}{\left[R—\overset{\overset{\displaystyle OH}{|}}{C}{=}CH_2\right]} \rightleftharpoons \underset{\text{Ketone}}{R—\overset{\overset{\displaystyle O}{\|}}{C}—CH_3}$$

$$CH{\equiv}CH + H_2O \xrightarrow{HgSO_4/H_2SO_4} \underset{\text{Unstable}}{\left[\overset{\overset{\displaystyle OH}{|}}{CH}{=}CH_2\right]} \rightleftharpoons \underset{\text{Aldehyde}}{CH_3—C\!\begin{smallmatrix}{\nearrow}O\\ {\searrow}H\end{smallmatrix}}$$

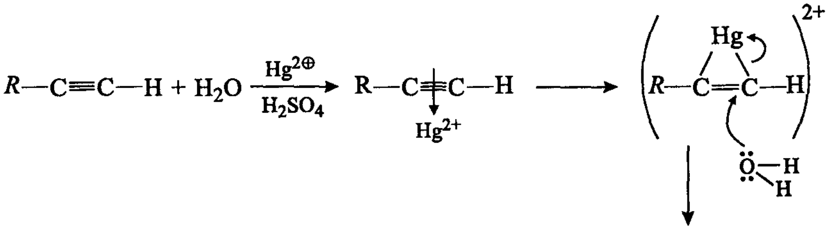
Since the addition follows Markovnikov rule acetylene itself is the only alkyne that undergoes hydration to give an aldehyde, other alkynes give ketones.

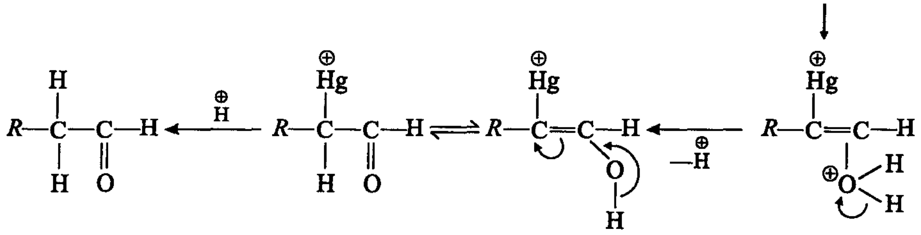
This reaction is useful method for synthesising special kinds of ketones having



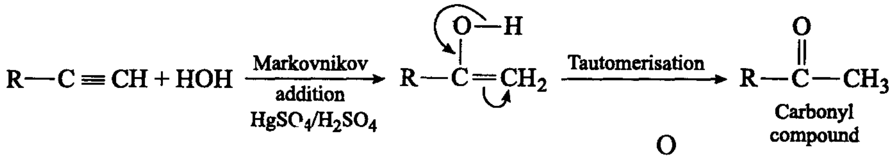
$—CH_2—\overset{\overset{\displaystyle O}{\|}}{C}—$ grouping.

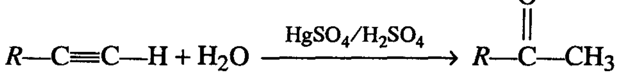
The mechanism of the actual addition of water across the triple bond is complex. It requires the presence of strong acid and also the presence of mercuric ion. Mercuric ion may play several roles in the reaction. One of these is the formation of a simple adduct between $Hg^{2\oplus}$ and the triple bond.





Thus the overall reaction can be represented as follows :



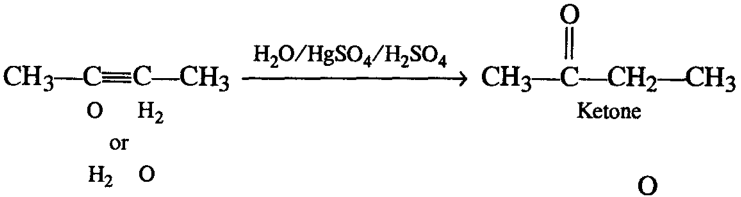


$$R\text{—C}\equiv\text{C—H} + H_2O \xrightarrow{HgSO_4/H_2SO_4} R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}CH_3$$

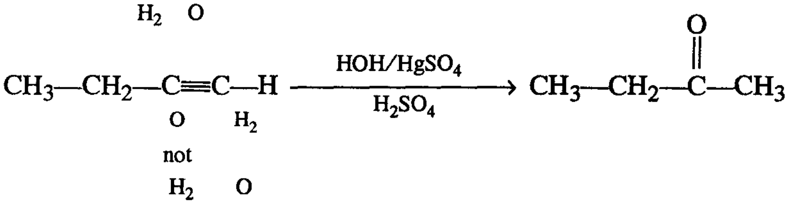
We can make a rule for obtaining product in this reaction and the rule can be formulated as follows :

(i) Add oxygen on one triply bonded carbon and 2H's on other triple bonded carbon.

(ii) In case of terminal alkynes, always add oxygen on triply bonded carbon which has no hydrogen.



$$\underset{\substack{O\quad H_2\\ \text{or}\\ H_2\quad O}}{CH_3\text{—C}\equiv\text{C—}CH_3} \xrightarrow{H_2O/HgSO_4/H_2SO_4} \underset{\text{Ketone}}{CH_3\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}CH_2\text{—}CH_3}$$

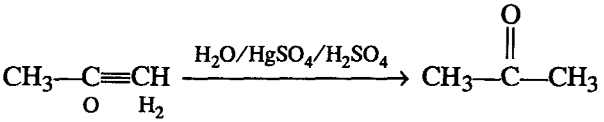


$$\underset{\substack{O\quad H_2\\ \text{not}\\ H_2\quad O}}{CH_3\text{—}CH_2\text{—C}\equiv\text{C—H}} \xrightarrow[H_2SO_4]{HOH/HgSO_4} CH_3\text{—}CH_2\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}CH_3$$

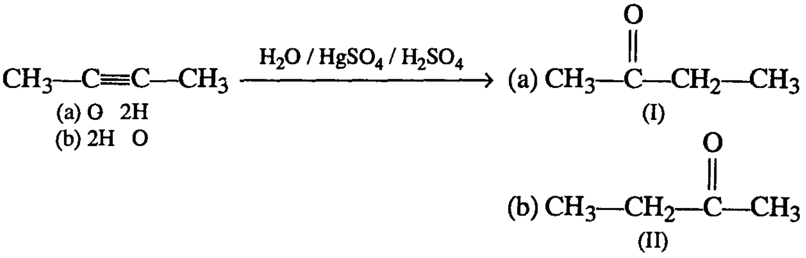
Note :

(1) Only acetylene gives aldehyde and aldehyde is acetaldehyde.

(2) Terminal alkynes and symmetrical internal alkynes form single ketone.



$$\underset{O\quad H_2}{CH_3\text{—C}\equiv\text{CH}} \xrightarrow{H_2O/HgSO_4/H_2SO_4} CH_3\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}CH_3$$

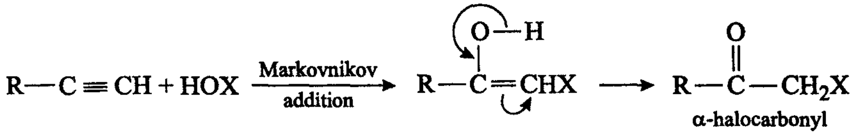


$$\underset{\substack{(a)\,O\quad 2H\\ (b)\,2H\quad O}}{CH_3\text{—C}\equiv\text{C—}CH_3} \xrightarrow{H_2O\,/\,HgSO_4\,/\,H_2SO_4} \begin{array}{l}(a)\ \underset{(I)}{CH_3\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}CH_2\text{—}CH_3}\\ (b)\ \underset{(II)}{CH_3\text{—}CH_2\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}CH_3}\end{array}$$

Both (I) and (II) are the same

5.26.4 Addition of HO*X*

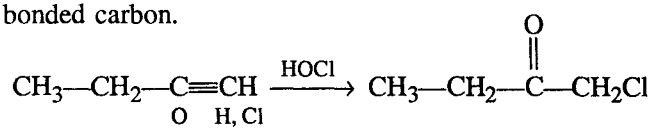
Alkyne reacts with HO*X* to give haloenol. This compound undergoes tautomerisation to give α-halocarbonyl compound.



$$\mathrm{R{-}C{\equiv}CH + HOX \xrightarrow[\text{addition}]{\text{Markovnikov}} R{-}\overset{\overset{\displaystyle O{-}H}{|}}{C}{=}CHX \longrightarrow R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2X}$$

α-halocarbonyl compound

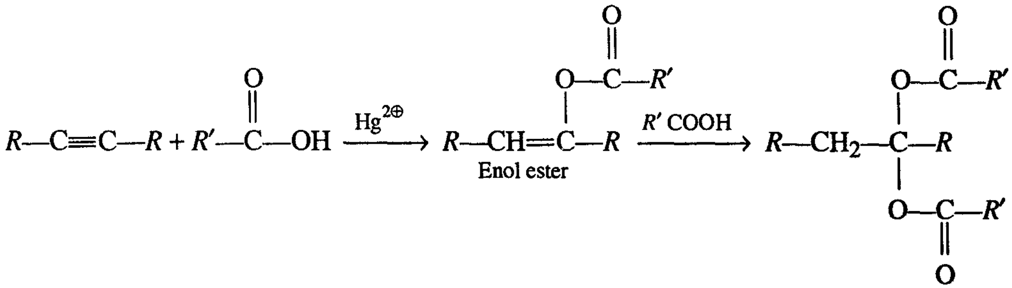
Note : We can make a rule for obtaining product for this reaction and the rule may be as follows : add oxygen on triply bonded carbon of unsymmetrical alkyne having no hydrogen and H and *X* on other triply bonded carbon.



$$\mathrm{CH_3{-}CH_2{-}\underset{O}{C}{\equiv}\underset{H,\,Cl}{CH} \xrightarrow{HOCl} CH_3{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2Cl}$$

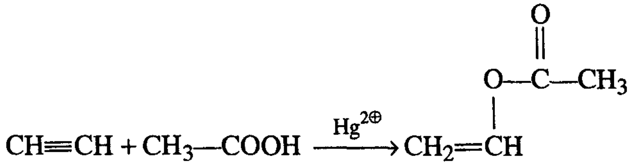
5.26.5 Addition of Acetic Acid

In the presence of mercuric ions, acetic acid adds to alkynes forming either an enol ester or *gem* diester.



$$R{-}C{\equiv}C{-}R + R'{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH \xrightarrow{Hg^{2\oplus}} \underset{\text{Enol ester}}{R{-}CH{=}\overset{\overset{\displaystyle O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R'}{|}}{C}{-}R} \xrightarrow{R'COOH} R{-}CH_2{-}\overset{\overset{\displaystyle O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R'}{|}}{\underset{\underset{\displaystyle O{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}R'}{|}}{C}}{-}R$$

A *gem* diester



$$CH{\equiv}CH + CH_3{-}COOH \xrightarrow{Hg^{2\oplus}} CH_2{=}\overset{\overset{\displaystyle O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3}{|}}{CH}$$

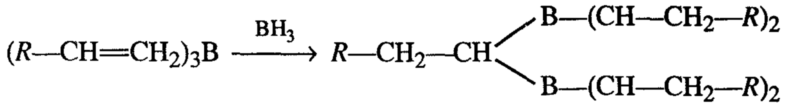
Vinyl acetate

5.26.6 Hydroboration

Addition reaction of alkyne with boron hydride is known as hydroboration. The reaction takes place as follows :

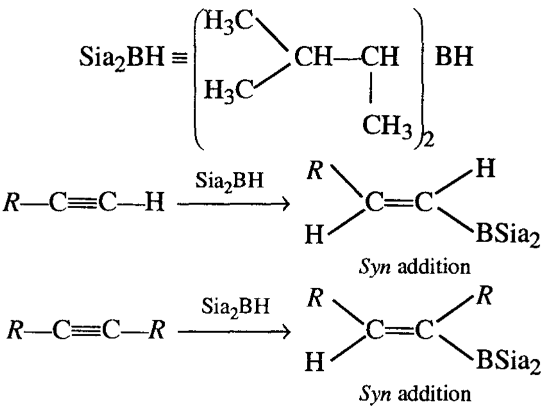
$$3R{-}C{\equiv}C{-}H + BH_3 \longrightarrow \underset{\text{Trivinylborane}}{(R{-}CH{=}CH)_3B}$$

This trivinylborane is very useful compound but this cannot be isolated because it still has *pi* bond and reacts further with BH_3 to give *gem*-diborane.

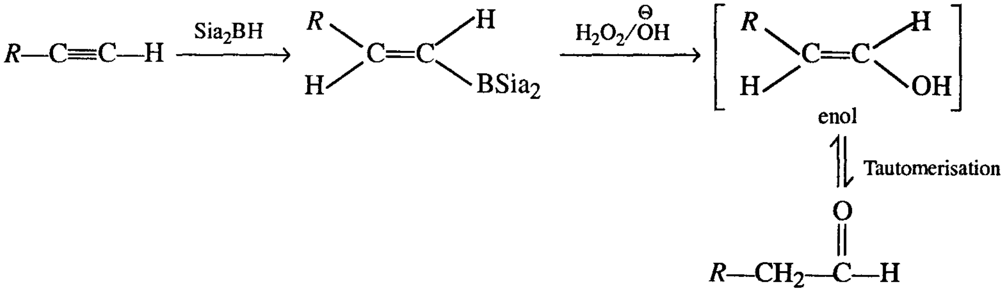


$$(R{-}CH{=}CH_2)_3B \xrightarrow{BH_3} R{-}CH_2{-}CH\begin{cases} B{-}(CH{-}CH_2{-}R)_2 \\ B{-}(CH{-}CH_2{-}R)_2 \end{cases}$$

Because of this, it becomes quite difficult to make vinylboranes in this manner. Vinyl boranes are preapared by selective hydroborating agent known as disiamylborane (abreviated as Sia_2BH). This sterically hindered dialkylborane reacts with alkyne to give only vinylboranes.

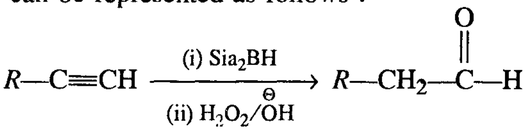


(a) Vinylborane on oxidation with $H_2O_2/\overset{\ominus}{O}H$ gives carbonyl compound. Thus alkyne can be converted into carbonyl compound and the sequence of reaction is known as hydroboration-oxidation.



Carbonyl compound

The overall reaction can be represented as follows :



$$R{-}C{\equiv}CH \xrightarrow[\text{(ii) } H_2O_2/\overset{\ominus}{O}H]{\text{(i) } Sia_2BH} R{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H$$

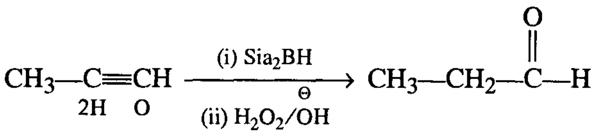
We can formulate rules for this reaction :

Rule 1. Add oxygen on one triply bonded carbon and 2H's on other triply bonded carbon. In case of terminal alkyne add oxygen on terminal carbon.

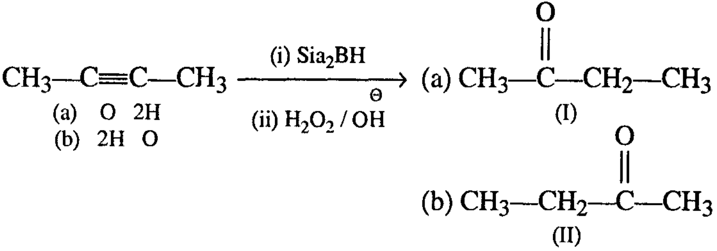
Rule 2. Terminal alkyne always gives aldehyde.

Rule 3. Symmetrical internal alkyne gives only one ketone.

Rule 4. Unsymmetrical internal alkyne gives two ketones which are isomers (positional and metamers).

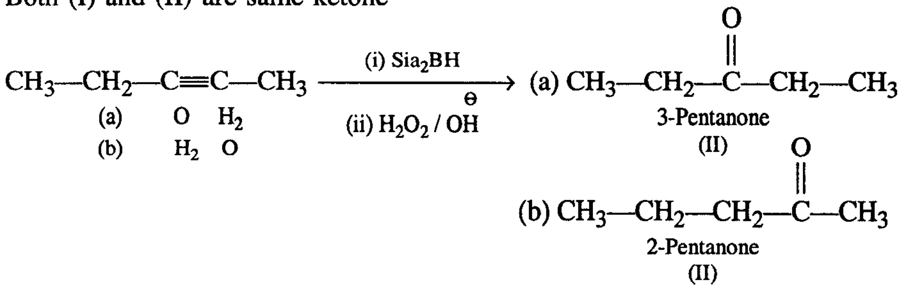


$$\underset{2H\quad O}{CH_3{-}C{\equiv}CH} \xrightarrow[\text{(ii) } H_2O_2/\overset{\ominus}{O}H]{\text{(i) } Sia_2BH} CH_3{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H$$



$$\begin{array}{l}CH_3{-}C{\equiv}C{-}CH_3\\ \text{(a)}\ \ O\ \ 2H\\ \text{(b)}\ \ 2H\ \ O\end{array} \xrightarrow[\text{(ii) } H_2O_2/\overset{\ominus}{O}H]{\text{(i) } Sia_2BH} \begin{array}{l}\text{(a) } CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2{-}CH_3\ \text{(I)}\\ \text{(b) } CH_3{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3\ \text{(II)}\end{array}$$

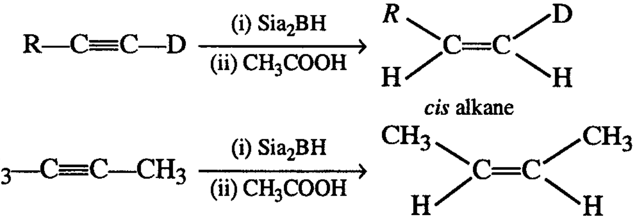
Both (I) and (II) are same ketone



3-Pentanone (II)

2-Pentanone (II)

(b) Vinylborane on acidification with organic acids give alkene (*cis* alkene if geometrical isomerism is possible)



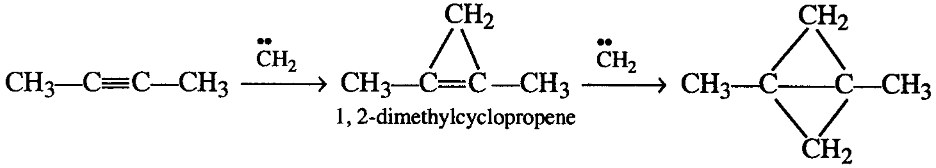
cis alkane

cis alkane

$$CH_3-C\equiv C-H \xrightarrow[\text{(ii) } CH_3COOH]{\text{(i) } Sia_2BH} CH_3-CH=CH_2$$

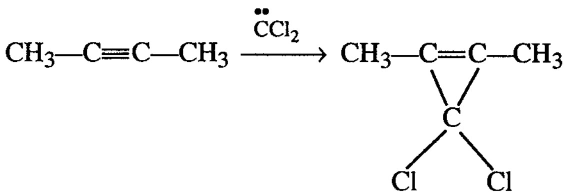
5.26.7 Addition of Carbenes

Alkynes react with carbenes to form addition products. Since alkynes have two π bonds, this addition can occur twice. The first addition gives a cyclopropene system. The second addition convert this cyclopropene into bicyclobutane system.



1, 2-dimethylcyclopropene

1, 3-dimethylbicyclo[1, 1, 0]butane



3, 3-dichloro-1, 2-dimethylcyclopropene

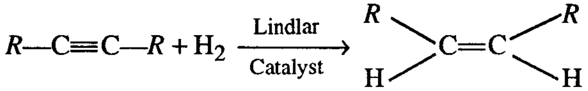
5.27 ADDITION OF HYDROGEN—REDUCTION OF ALKYNES

In the presence of metal catalyst (Ni, Pt, Pd) alkynes add two molecules of hydrogen to form the corresponding alkanes. The reaction takes place in two steps.

$$CH\equiv CH + H_2 \xrightarrow{\text{Catalyst}} CH_2=CH_2 \qquad \Delta H° = -41.9 \text{ kcal/mole}$$

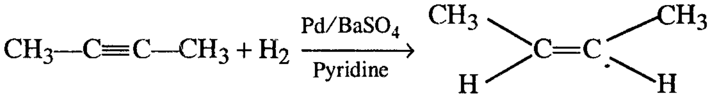
$$CH_2=CH_2 + H_2 \xrightarrow{\text{Catalyst}} CH_3-CH_3 \qquad \Delta H° = -32.7 \text{ kcal/mole}$$

The first step of the reduction is more exothermic than the second. The second step is so facile that with most of the catalyst it is not possible to stop the reduction at the alkene stage. However, the use of Lindlar catalyst (Pd—$CaCO_3$—PbO) allows the reaction to be stopped after the addition of only one molecule of hydrogen to the triple bond. The reduction involves the *syn* addition of hydrogen to the triple bond.

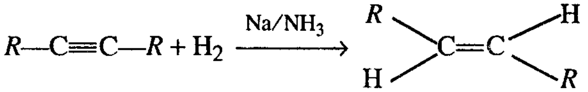


cis alkene

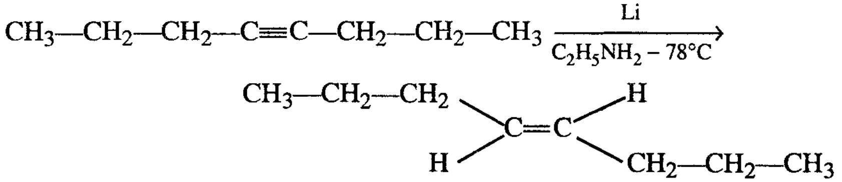
The synthesis of *cis* alkenes may also be achieved by reducing alkynes in a pyridine solution using catalyst Pd supported on $BaSO_4$.



Alkynes are also reduced by sodium or lithium in liquid ammonia or ethylamine. This produces *trans* rather than *cis* alkene.



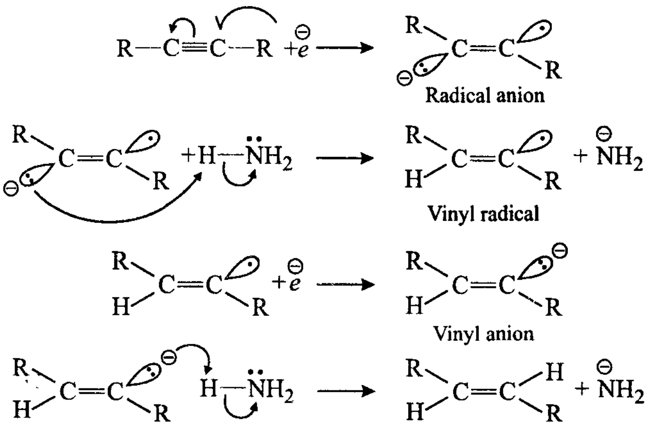
trans alkene



trans product

The mechanism of this reaction involves the reduction of the triple bond by two electrons from sodium atom. The first electron goes into an antibonding π orbital to give a radical anion. This strongly basic species is protonated by ammonia to give a vinyl radical which is reduced by another electron to give a vinyl anion. Final protonation of the vinyl anion by ammonia (acting as an acid) or by a bit of alcohol that is sometimes added as a cosolvent yields the *trans* alkene and amide ion.

$NH_3 + Na \longrightarrow NH_3.e$ (deep blue solution + $\overset{\oplus}{Na}$
solvated electron

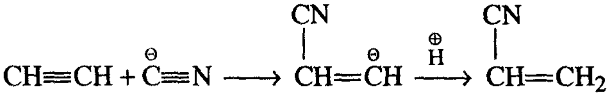


trans alkene

Simple alkenes are not reduced by sodium or potassium in liquid ammonia, so it is easy to perform the reduction of an alkyne to a *trans* alkene. The stereochemistry of the final product is probably established in the reduction of vinly radical. The *trans* anion is more stable than the *cis* anion due to non-bonded interactions.

5.28 NUCLEOPHILIC ADDITION REACTIONS

Unlike simple alkenes, alkynes undergo nucleophilic addition reactions. For example, cyanide ion reacts with acetylene to yield vinyl cyanide.



$$CH{\equiv}CH + \overset{\ominus}{C}{\equiv}N \longrightarrow \overset{\displaystyle CN}{\overset{|}{CH}}{=}\overset{\ominus}{CH} \xrightarrow{\overset{\oplus}{H}} \overset{\displaystyle CN}{\overset{|}{CH}}{=}CH_2$$

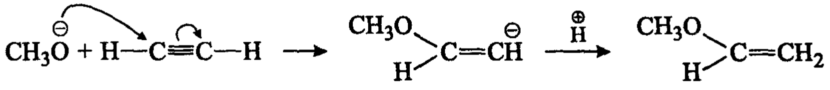
The reaction of stable $\overset{\ominus}{CN}$ to produce a less stable and more basic vinyl anion may seem surprising. However, this addition also involves the formation of a strong C—CN bond at the expense of relatively weak π bond of a triple bond. The net effect of stronger bonding is more than enough to compensate for the creation of a stronger base.

Similarly, alcohols in the presence of a base react with acetylene to form methyl vinyl ether.

$$CH{\equiv}CH + ROH \xrightarrow{KOH} CH_2{=}CHOR$$

$$CH_3OH + KOH \longrightarrow CH_3OK + H_2O$$

$$CH_3OK \rightleftharpoons CH_3\overset{\ominus}{O} + \overset{\oplus}{K}$$



Methyl vinyl ether
(MVE)

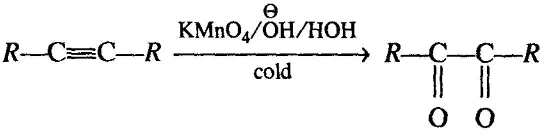
5.29 OXIDATION OF ALKYNES

Like alkenes these also give two types of oxidation reactions :

5.29.1 Oxidation without Cleavage

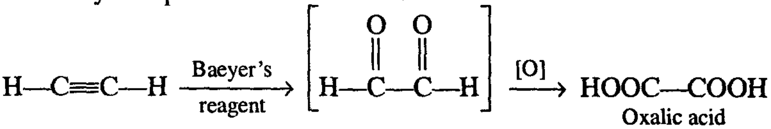
The product of oxidation is *vic* dicarbonyl compound.

(a) Oxidation by Baeyer's Reagent :



$$R{-}C{\equiv}C{-}R \xrightarrow[\text{cold}]{KMnO_4/\overset{\ominus}{O}H/HOH} R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}R$$

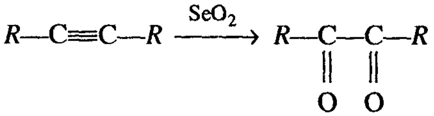
In case of acetylene product is oxalic acid



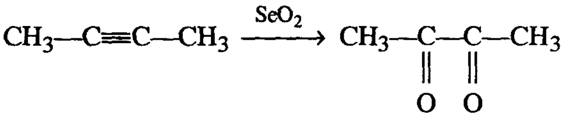
$$H{-}C{\equiv}C{-}H \xrightarrow[\text{reagent}]{\text{Baeyer's}} \left[H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H\right] \xrightarrow{[O]} HOOC{-}COOH$$

Oxalic acid

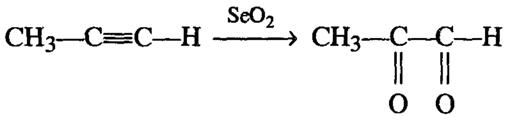
(b) Oxidation by SeO_2 : SeO_2 converts alkyne into *vic* dicarbonyl compound :



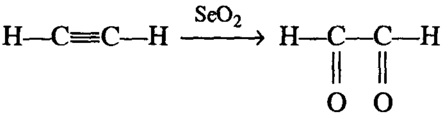
$$R{-}C{\equiv}C{-}R \xrightarrow{SeO_2} R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}R$$



$$CH_3-C\equiv C-CH_3 \xrightarrow{SeO_2} CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3$$



$$CH_3-C\equiv C-H \xrightarrow{SeO_2} CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-H$$



$$H-C\equiv C-H \xrightarrow{SeO_2} H-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-H$$

5.29.2 Oxidative Cleavage

Alkynes undergo oxidative cleavage with hot basic $KMnO_4$. In this oxidation triple bond breaks and both triply bonded carbons convert into carboxylic group.

$$R-C\equiv C-R' \xrightarrow{KMnO_4/\overset{\ominus}{O}H/\Delta} RCOOH + R'COOH$$

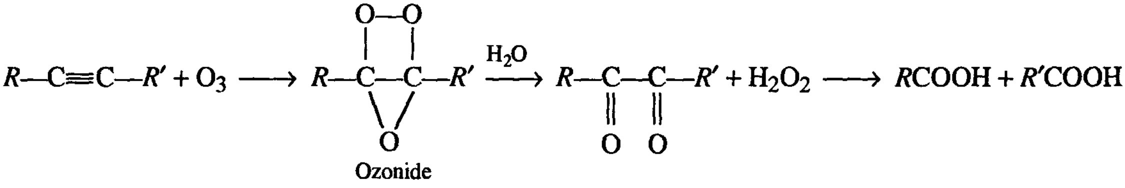
$$CH_3-C\equiv C-C_6H_5 \xrightarrow{KMnO_4/\overset{\ominus}{O}H/\Delta} CH_3COOH + C_6H_5COOH$$

Note : Terminal alkynes give formic acid as one of the oxidation products which further oxidises into CO_2. Thus loss of a carbon in this reaction indicates that alkyne is terminal.

$$\underset{\substack{C_4H_6 \\ (4C)}}{CH_3-CH_2-C\equiv C-H} \xrightarrow{KMnO_4/\overset{\ominus}{O}H/\Delta} \underset{\substack{C_3H_6O_2 \\ (3C)}}{CH_3-CH_2COOH} + CO_2 + H_2O$$

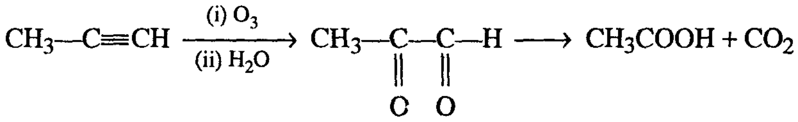
5.30 ADDITION OF OZONE-OZONISATION

Ozone adds to carbon-carbon triple bond forming ozonide. Ozonides are hydrolysed by water to form dicarbonyl compounds and hydrogen peroxide. Dicarbonyls are oxidised by hydrogen peroxide to carboxylic acids by the cleavage of carbon-carbon bond.



$$R-C\equiv C-R' + O_3 \longrightarrow \underset{\text{Ozonide}}{R-\overset{\overset{O-O}{|\quad\ |}}{\underset{\underset{O}{\diagdown\,\diagup}}{C-C}}-R'} \xrightarrow{H_2O} R-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-R' + H_2O_2 \longrightarrow RCOOH + R'COOH$$

$$C_2H_5-C\equiv C-CH_3 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } O_3} C_2H_5COOH + CH_3COOH$$



$$CH_3-C\equiv CH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } O_3} CH_3-\underset{\underset{C}{\|}}{C}-\underset{\underset{O}{\|}}{C}-H \longrightarrow CH_3COOH + CO_2$$

Thus $\equiv C-H$ fragment of terminal alkynes converts into CO_2.

The identification of the acids formed would tell which of the carbons were linked through triple bond in the original alkyne. Thus reaction is particularly useful for elucidating the location of triple bond/bonds in alkynes. Suppose an unknown alkyne with a molecular formula C_5H_8 on ozonolysis gives propionic acid and acetic acid.

$$C_5H_8 \xrightarrow{O_3} \xrightarrow{H_2O} \xrightarrow{H_2O_2} CH_3-CH_2COOH + CH_3COOH$$

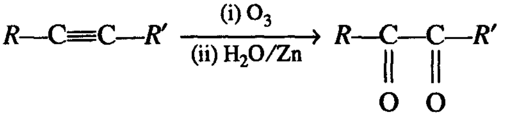
The carboxylic group carbons identify the carbons involved in the alkyne linkage, and hence connecting these two carbons gives structure of unknown alkyne.

$$CH_3-CH_2-COOH \qquad HOOC-CH_3$$

$$\downarrow$$

$$CH_3-CH_2-C\equiv C-CH_3$$

Reductive ozonolysis : Alkyne gives *vic* dicarbonyl compound in reductive ozonolysis.

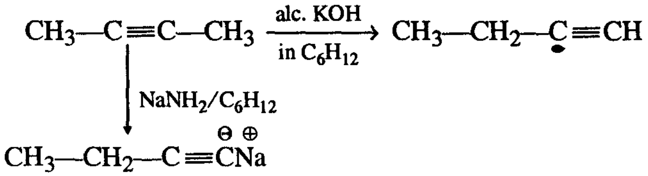


$$R-C\equiv C-R' \xrightarrow[\text{(ii) } H_2O/Zn]{\text{(i) } O_3} R-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-R'$$

5.31 ISOMERISATION

Alkyne undergoes isomerisation either in the presence of alc. KOH or $NaNH_2$

(a) Non-terminal alkyne converts into terminal alkyne.



$$\begin{tikzcd} CH_3-C\equiv C-CH_3 \arrow[r, "\text{alc. KOH}", "\text{in } C_6H_{12}"'] \arrow[d, "NaNH_2/C_6H_{12}"] & CH_3-CH_2-C\equiv CH \\ CH_3-CH_2-C\equiv \overset{\ominus}{C}\overset{\oplus}{Na} & \end{tikzcd}$$

(b) Terminal alkyne having $\alpha-CH_2$ group isomerises into non-terminal alkyne as well as into conjugated diene.

$$CH_3-CH_2-C\equiv CH \xrightarrow[NaNH_2]{\text{alc. KOH or}} CH_3-C\equiv C-CH_3 + CH_2=CH-CH=CH_2$$

$$CH_3-CH_2-CH_2-C\equiv CH \xrightarrow[NaNH_2]{\text{alc. KOH}/\Delta \text{ or}} CH_3-CH=CH-CH=CH_2 +$$

$$CH_3-CH_2-C\equiv C-CH_3$$

5.32 COUPLING OF ALKYNES

(1) Coupling in mild acidic conditions : Terminal alkyne undergoes coupling reaction in the presence of mildy acidic condition to give alkenyne. The reaction is simply addition reaction between two molecules of alkyne. One molecule behaves as substrate and other behaves as reagent and addition takes place according to anti Markovnikov's rule.

$$\underset{\text{Substrate}}{R-C\equiv C-H} + \underset{\text{Reagent}}{\overset{\delta+}{H}-\overset{\delta-}{C}\equiv C-R} \xrightarrow[NH_4Cl]{CuCl} \underset{\text{Alkenyne}}{R-CH=CH-C\equiv C-R}$$

$$CH_3—C{\equiv}C—H + H—C{\equiv}C—CH_3 \xrightarrow[NH_4Cl]{CuCl} \underset{\text{2-Hexen-4-yne}}{CH_3—CH{=}CH—C{\equiv}C—CH_3}$$

$$CH{\equiv}CH + CH{\equiv}CH \xrightarrow[NH_4Cl]{CuCl} \underset{\text{1-Buten-3-yne}}{CH_2{=}CH—C{\equiv}CH}$$

(2) Oxidative coupling : Oxidative coupling takes place by shaking terminal alkyne in a solution of Cu_2Cl_2 in methanol/pyridine (a base) in the presence of oxygen or air. The product of the reaction is alkadiyne.

$$R—C{\equiv}C—\underbrace{H + H}_{\text{coupling}}—C{\equiv}C—R \xrightarrow[CH_3OH/Py/air]{CuCl} \underset{\text{Alkadiyne}}{R—C{\equiv}C—C{\equiv}C—R}$$

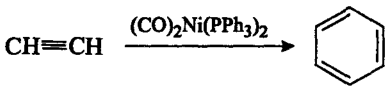
5.33 POLYMERISATION OF ACETYLENE

Under suitable conditions acetylene form a dimer, trimer or tetramer as shown below :

(i) Dimerisation : Two molecules of acetylene, when passed through a solution of Cu_2Cl_2 in NH_4Cl at 70°C, form vinylacetylene.

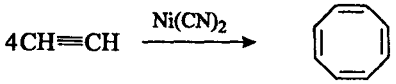
$$CH{\equiv}CH + CH{\equiv}CH \xrightarrow[NH_4Cl\ 70°C]{CuCl} \underset{\text{Vinylacetylene}}{CH_2{=}CH—C{\equiv}CH}$$

(ii) Acetylene trimerises to give benzene when passed through red hot iron tube or in the presence of catalyst dicarbonyl di(triphenylphosphine) nickel.



Benzene

(iii) Tetramerisation : Acetylene tetramerises to form cyclooctatetraene in the presence of Ni $(CN)_2$.



Cyclooctatetraene

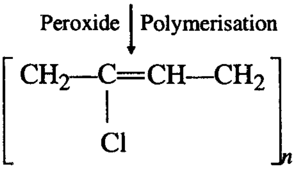
In addition to the above cyclic polymerisation, acetylene undergoes linear polymerisation when passed into a solution of cuprous chloride in ammonium chloride to give vinylacetylene and divinylacetylene.

$$2CH{\equiv}CH \xrightarrow[NH_4Cl]{CuCl} \underset{\text{Vinylacetylene}}{CH_2{=}CH—C{\equiv}CH} \xrightarrow{C_2H_2} \underset{\text{Divinylacetylene}}{CH_2{=}CH—C{\equiv}C—CH{=}CH_2}$$

Vinylacetylene is a useful starting material for the manufacture of a highly solvent-resistant synthetic rubber neoprene. Vinylacetylene adds to a molecule of HCl to form chloroprene (2-chloro-1, 3-butadiene) which readily polymerises to neoprene.

$$CH_2{=}CH—C{\equiv}CH + \text{conc. } HCl \xrightarrow[NH_4Cl]{CuCl} [CH_2Cl—CH{=}C{=}CH_2] \xrightarrow[\text{gement}]{\text{Rearran-}} \underset{\text{Chloroprene}}{CH_2{=}CCl—CH{=}CH_2}$$

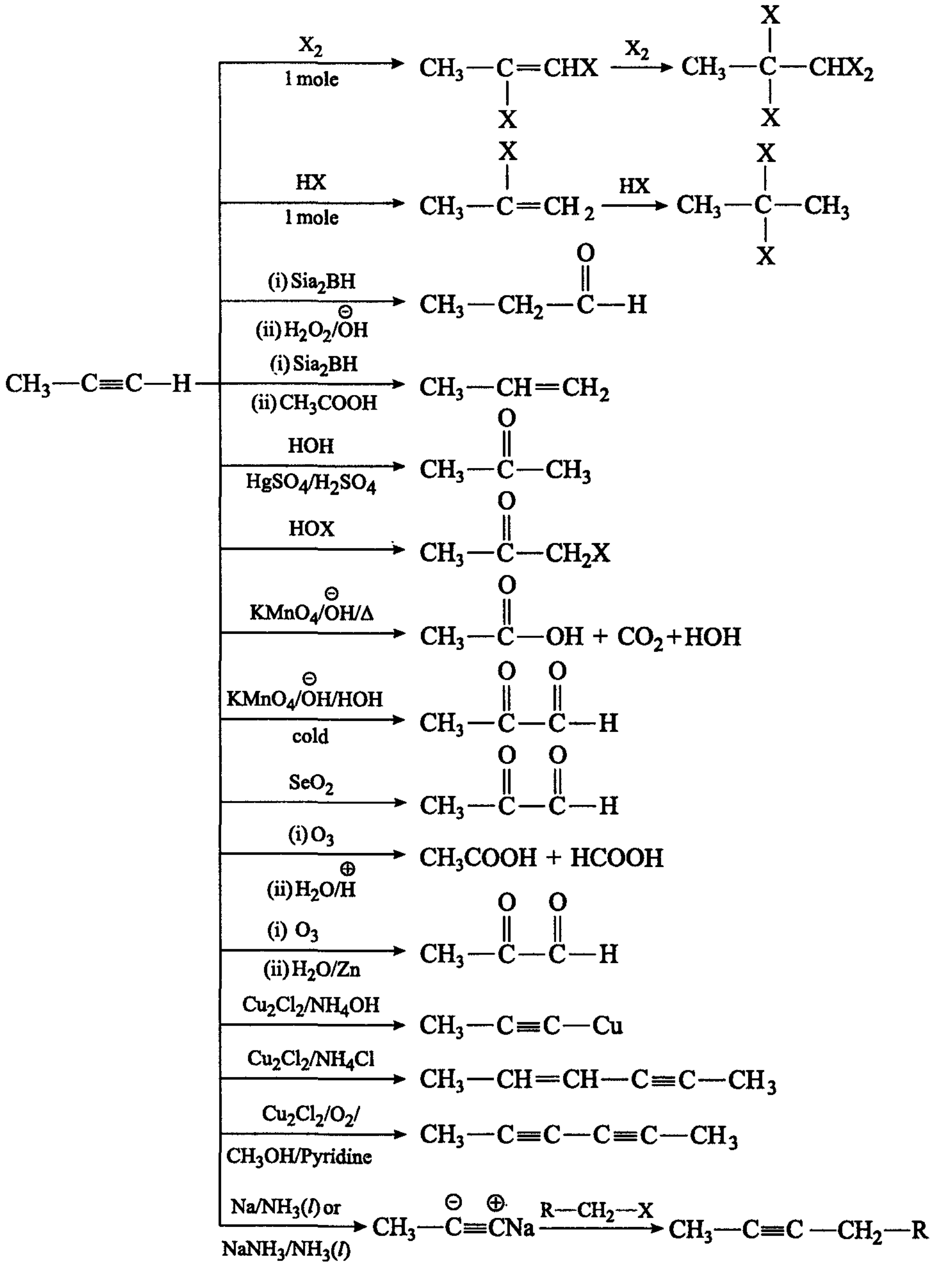
$$\downarrow$$



Neoprene

5.34 SUMMARY OF KEY REACTIONS OF ALKYNES

The starting material for all reactions is **propyne** :

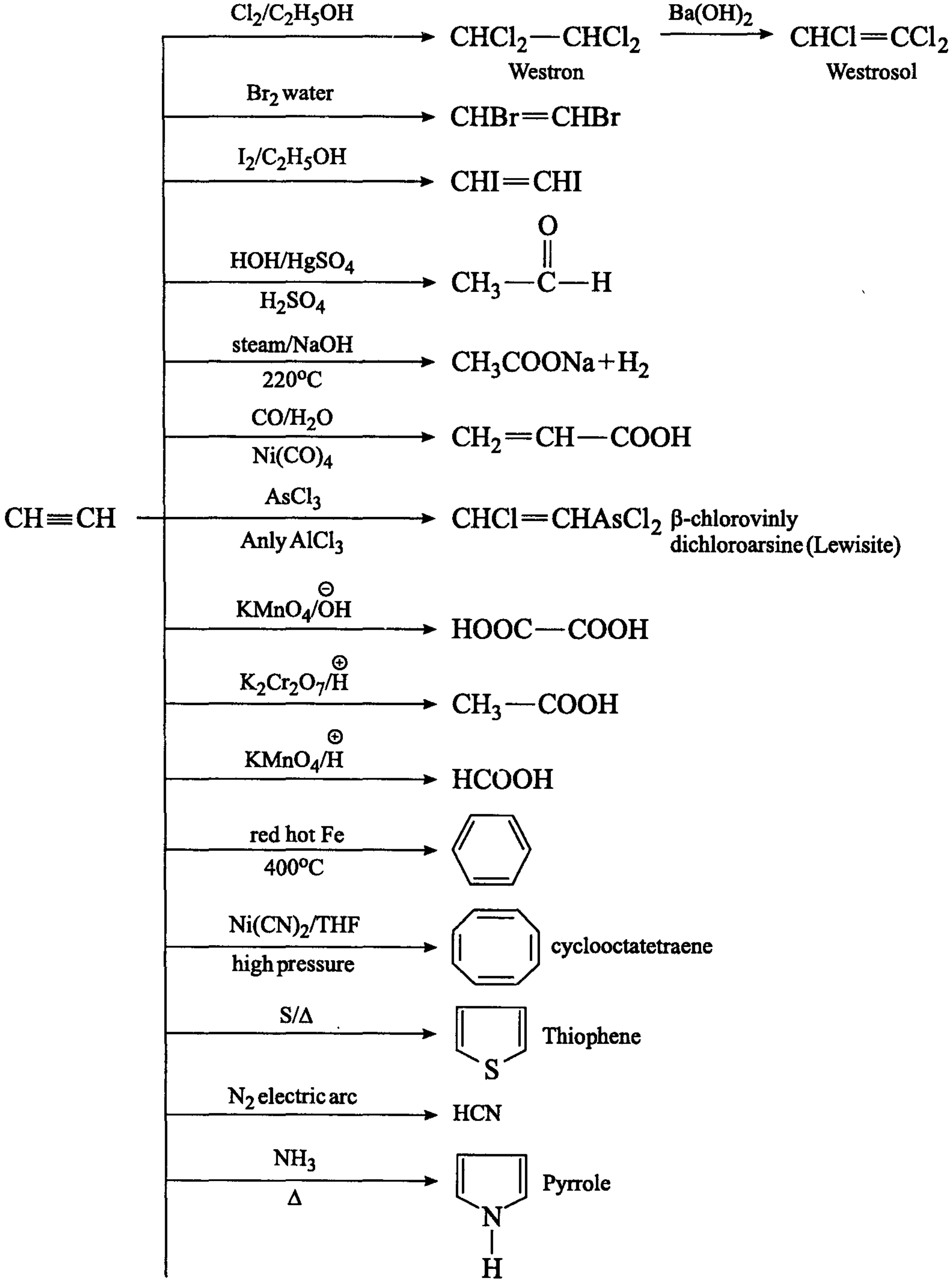


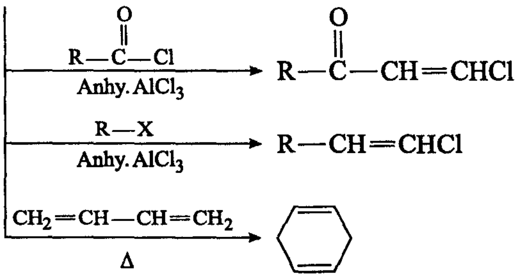
5.35 INDIVIDUAL MEMBER OF ALKYNES

Acetylene : It can be prepared from metal carbide.

$$CaC_2 \xrightarrow{H_2O} C_2H_2 + Ca(OH)_2$$

Properties : Summary of key reactions of acetylene is given below :





Industrial applications of acetylene

On large scale, it is prepared by pyrolysis of methane and ethylene.

$$2CH_4 \xrightarrow[<0{\cdot}1\ \text{sec}]{1500°C} CH{\equiv}CH + 3H_2$$

$$CH_2{=}CH_2 \xrightarrow{>1200°C} CH{\equiv}CH + H_2$$

Most of the acetylene produced commercially is used as a starting material for polymers. Monomers of addition polymer is prepared from acetylene.

(i) $$\underset{\text{(excess)}}{CH{\equiv}CH + HCl} \xrightarrow{HgCl_2} \underset{\substack{\text{Vinyl chloride, colourless gas}\\ \text{bp } -14°C}}{CH_2{=}CHCl}$$

Vinyl chloride is monomer of PVC and Saran.

(ii) $$CH{\equiv}CH \xrightarrow[\text{1 mole}]{HCl} CH_2{=}CHCl \xrightarrow{Cl_2} CH_2Cl{-}CHCl_2 \xrightarrow{Ca(OH)_2} \underset{\substack{\text{vinylidene chloride}\\ \text{Colourless liquid}\\ \text{bp } 32°C}}{CH_2{=}CCl_2}$$

It is monomer of Saran.

(iii) $$\underset{\text{excess}}{CH{\equiv}CH + HCN} \longrightarrow \underset{\text{vinyl cyanide}}{CH_2{=}CH{-}CN}$$

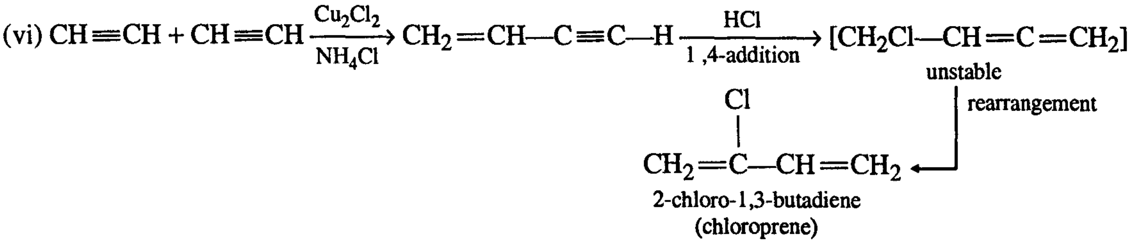
It is monomer of orlon, SAN, ABS and Buna-N.

(iv) $$CH{\equiv}CH + CH_3OH \xrightarrow[180\text{–}200°C]{CH_3ONa} \underset{\text{Methyl vinyl ether}}{CH_2{=}CH{-}OCH_3}$$

(v) $$\underset{\text{(excess)}}{CH{\equiv}CH} \xrightarrow[\substack{Hg(OAc)_2\\ 80°C}]{CH_3COOH} \underset{\text{Vinyl acetate}}{CH_2{=}CH{-}OCOCH_3}$$

$$CH{\equiv}CH \xrightarrow{\substack{Zn(OAc)_2\\ 190-200°C}} CH_2{=}CH{-}OCOCH_3$$

It is monomer of polyvinyl acetate



(vi) $$CH{\equiv}CH + CH{\equiv}CH \xrightarrow[NH_4Cl]{Cu_2Cl_2} CH_2{=}CH{-}C{\equiv}C{-}H \xrightarrow[\text{1,4-addition}]{HCl} \underset{\text{unstable}}{[CH_2Cl{-}CH{=}C{=}CH_2]} \xrightarrow{\text{rearrangement}} CH_2{=}C(Cl){-}CH{=}CH_2$$

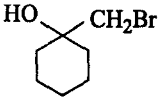
2-chloro-1,3-butadiene
(chloroprene)

It is monomer of chlorinated rubber, Neoprene.

Note : Conversion of acetylene into vinyl derivative ($CH_2=CH—G$) is known as **vinylation.** Thus the above reactions are vinylation.

VERY SHORT ANSWER QUESTIONS

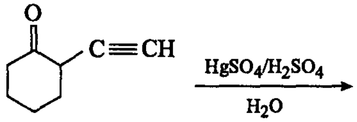
1. Which of the following compounds would undergo facile dehydrobromination?
   trans--2-bromo-2-butene or *cis*-2-bromo-2-butene
2. Give the structure of the alkene which gives *meso*-2, 3-butanediol on hydroxylation with $KMnO_4$.
3. Write the IUPAC name and structure of the six-carbon alkene which could give the same product on reaction with HBr whether in the presence or absence of a peroxide.
4. Give the structure of the alkene which gives the following product on reaction with bromine water :



5. Predict the product of pyrolysis of ethyldimethyl-*n*-propylammonium hydroxide.
6. Which isomer would you expect to obtain from the reaction of cyclohexene and dideuterium in the presence of finely divided platinum?
7. Predict the isomer of 1, 2-dibromocyclohexane which is product when cyclohexene is treated with Br_2.
8. Outline a method for the preparation of 4, 5-dimethylcyclohexene.
9. How will you convert cyclohexene into *cis*-2-deuteriocyclohexanol?
10. Draw the two conformations of 1, 3-butadiene and indicate which is more stable.
11. Write the structure the compound with molecular formula C_6H_{10} which on ozonolysis gives hexanedial.
12. Give the possible prouducts and their IUPAC names when 1, 3-butadiene reacts with one and two moles of HBr.
13. Write the hydroboration-oxidation reaction of propyne.
14. Arrange the following compounds in increasing acid strength :

$$H_2O, NH_3, CH_3OH, HC\equiv CH$$

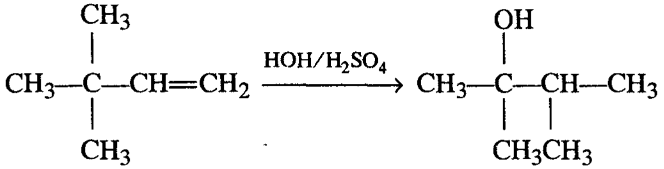
15. Give the product when one mole of $HC\equiv C—CH_2OH$ reacts with one mole of CH_3MgI.
16. Name the product of reductive ozonolysis of 2-butyne.
17. Name the product formed on treatment of 2-butyne with sodium in liquid ammonia.
18. Complete the following reaction :



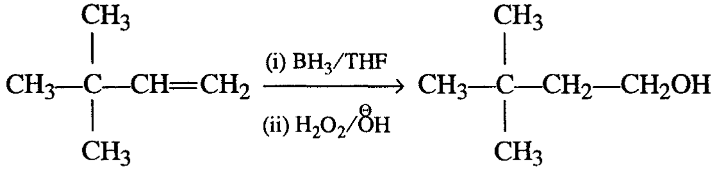
PROBLEMS WITH SOLUTIONS

1. Phenyl group is not an electron donating group but $C_6H_5—CH=CH_2$ reacts very fast with HCl. Explain.
2. Acetylene is allowed to react with HCl. What products do you expect ? Explain why the product is $CH_3—CHCl_2$ and not the $CH_2Cl—CH_2Cl$?

3. Alkynes are less reactive than alkenes for electrophilic addition reactions. Explain.
4. Explain why $CF_3-CH=CH_2$ gives *anti*-Markovnikov addition reaction.
5. Explain why rearranged product is obtained in the first reaction but not in the second reaction ?

(i) 

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=CH_2 \xrightarrow{HOH/H_2SO_4} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

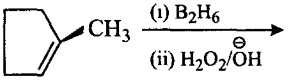
(ii) 

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=CH_2 \xrightarrow[\text{(ii) } H_2O_2/\overset{\ominus}{O}H]{\text{(i) } BH_3/THF} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_2OH$$

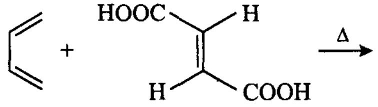
6. Alkynes are more reactive than alkenes for nucleophilic addition reactions. Explain.
7. When bromination of propene is carried out in the presence of added sodium chloride, the major product is 1-bromo-2-chloro propane rather than 2-bromo-1-chloropropane. Explain.
8. Explain why catalytic hydrogenation is an exception to the generalisation that alkenes are more reactive than alkynes toward addition reactions. In other words, alkynes are more reactive than alkenes for hydrogenation reaction.
9. How many products do you expect when propene is treated with bromine in the presence of NaCl and methanol? Discuss the mechanism of formation of the products.
10. A hydrocarbon C_6H_{12} was subjected to ozonolysis to give equimolar amounts of butanone and ethanal. Assign structure and give IUPAC name to the hydrocarbon.
11. Predict the structures of alkenes expected from the dehydrohalogenation of the following alkyl halides. In the case of isomeric alkenes, indicate which will be the major product :
    (a) 2-chloro-3-methylbutane
    (b) 3-chloro-2-methylpentane
    (c) 2-chloro-3-methylpentane
    (d) 2-chloro-3, 3-dimethylpentane
12. Complete the following equations showing the stereochemistry of the products :

(a) $CH_3-C\equiv C-CH_3 \xrightarrow{H_2/Pt}$

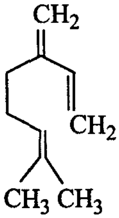
(b) *cis*-2-Butene $\xrightarrow{RCOOOH}$

(c) 

(d) *cis*-2-Butene $\xrightarrow{KMnO_4/\overset{\ominus}{O}H}$

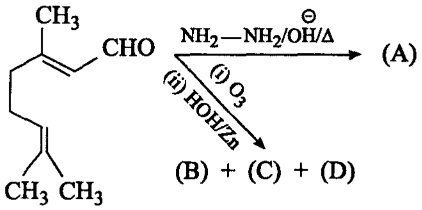
(e) 

13. Myrcene is natural product found in oil of bayberry. Predict the ozonolysis products obtained from myrcene.



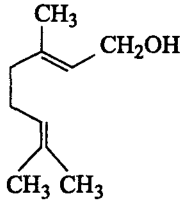
Myrcene

14. Citral is unsaturated aldehyde found in lemon oil. Fragrance of citral leaves and fruits is due to the presence of this compound. Predict the products obtained from this compound in the reactions given below :

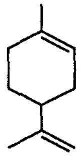


Citral

15. Fragrance of rose is due to the presence of organic compound geraniol. This compound is also known as rose oil. What products will be obtained when this is subjected to (i) reductive ozonolysis and (ii) catalytic reduction.

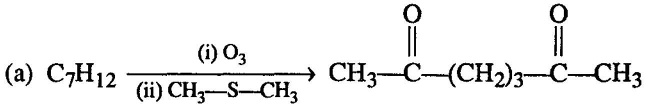


16. Limonnene is an important fragrance found in lemon as well as orange oil. This on ozonolysis will give how many products ? What will be structure of these products ?

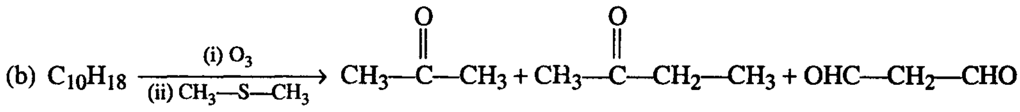


Lemon and orange oil

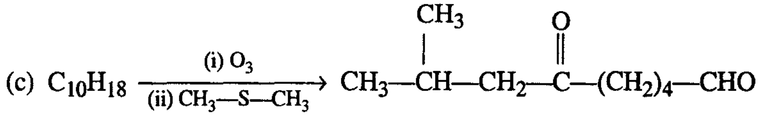
17. Draw the structural formula of the alkene that reacts with ozone followed by dimethyl sulphide to give the following products :



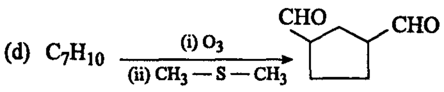
$$\text{(a) } C_7H_{12} \xrightarrow[\text{(ii) } CH_3-S-CH_3]{\text{(i) } O_3} CH_3-\overset{\overset{\large O}{\|}}{C}-(CH_2)_3-\overset{\overset{\large O}{\|}}{C}-CH_3$$



$$\text{(b) } C_{10}H_{18} \xrightarrow[\text{(ii) } CH_3-S-CH_3]{\text{(i) } O_3} CH_3-\overset{\overset{\large O}{\|}}{C}-CH_3 + CH_3-\overset{\overset{\large O}{\|}}{C}-CH_2-CH_3 + OHC-CH_2-CHO$$



$$\text{(c) } C_{10}H_{18} \xrightarrow[\text{(ii) } CH_3-S-CH_3]{\text{(i) } O_3} CH_3-\overset{\overset{\large CH_3}{|}}{CH}-CH_2-\overset{\overset{\large O}{\|}}{C}-(CH_2)_4-CHO$$



18. Give structure of the product(s) from the reaction of 1, 3-butadiene with :

(a) 1 mole of Br_2 at 40°C (b) Excess Br_2 (c) 1 mole of H_2/Pt (d) 1 mole of D_2/Pt

(e) Excess H_2/Pt (f) 1 mole DCl (40°C) (g) Excess DCl

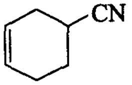
(h) Excess CH_3OH, $Hg(OCOCF_3)_2$ followed by $\overset{\ominus}{B}H_4$

(i) Excess O_3 followed by Zn/CH_3COOH

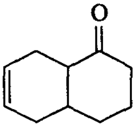
(j) Excess BH_3 followed by CH_3CH_2COOD (reflux)

19. Draw the structures of diene and the dienophile that would give the following products in a Diels-Alder reaction :

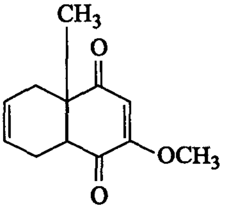
(a)



(b)



(c)



20. Draw the structures of two isomeric alkenes that would yield 1-methycyclohexanol when treated with $Hg(OAc)_2$ in water then $NaBH_4$.

21. Draw the structure of :

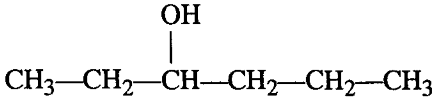
(a) a six carbon alkene that would give the same product with HBr in the presence and absence of peroxide.

(b) a compound C_5H_{10} that would not react with $KMnO_4/\overset{\ominus}{O}H/HOH$.

(c) an alkene that would give the following compound as the only product after ozonolysis followed by H_2O_2.

$$HOOC{-}CH_2{-}CH_2{-}COOH$$

(d) Two alkenes that would give the following alcohol as the major product of hydroboration followed by oxidation :

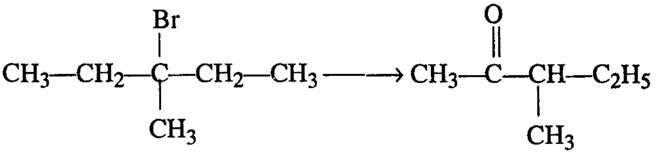


$$CH_3{-}CH_2{-}\underset{}{\overset{\displaystyle OH}{\overset{|}{C}H}}{-}CH_2{-}CH_2{-}CH_3$$

22. Write the product in the mercuration-demercuration of 3, 3-dimethyl-1-butene and compare the product of this reaction from the reaction of 3, 3-dimethyl-1-butene with dil. aqueous HCl.

23. How the following conversions can be performed?

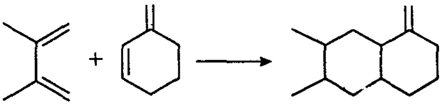
(a)



$$CH_3{-}CH_2{-}\overset{\displaystyle Br}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}CH_2{-}CH_3 \longrightarrow CH_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}{-}C_2H_5$$

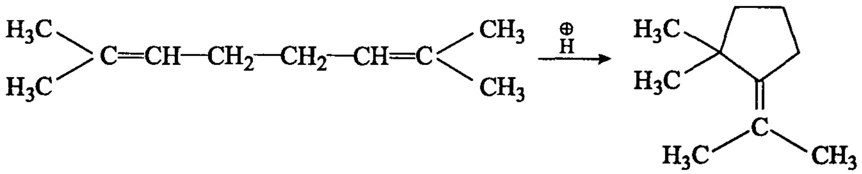
(b) $CH_3{-}CH_2{-}CH{=}CH_2 \longrightarrow CH_3{-}CH_2{-}C{\equiv}CH$

(c)

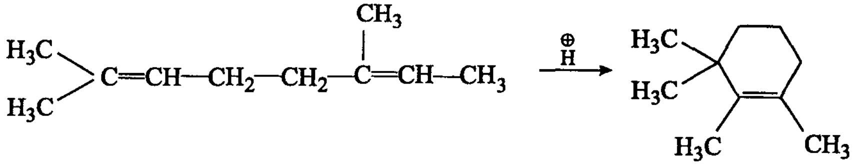


24. Suggest a mechanism for each of the following reactions :

(a)

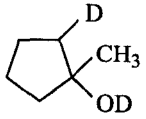


(b)

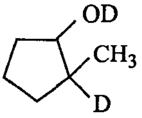


25. (i) How do you prepare the following deuteriated compounds from non-deuteriated 1-methylcyclopentene?

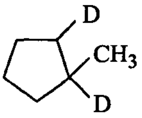
(a)



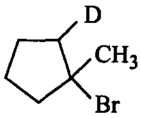
(b)



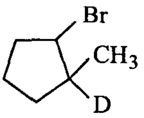
(c)



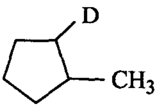
(d)



(e)

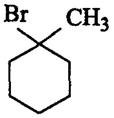


(f)



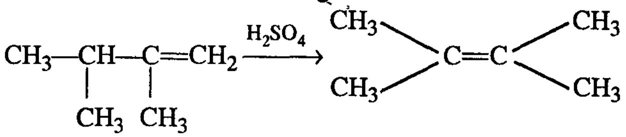
(ii) (a) The following compound can be prepared by the addition of HBr to either of two alkenes; give their structures.

(b) Starting with the same two alkenes, would the products be different if DBr is used? Explain.

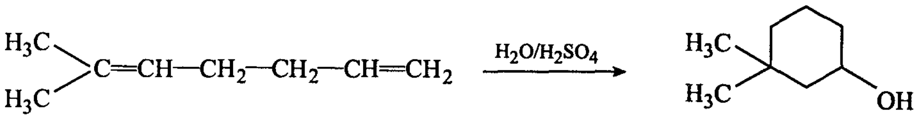


26. Give mechanism of the following transformations :

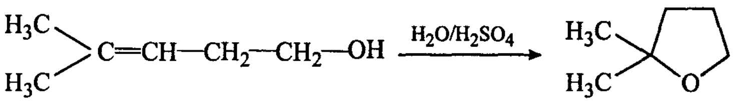
(a)



(b)

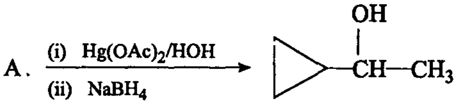


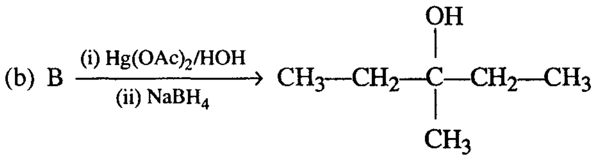
(c)

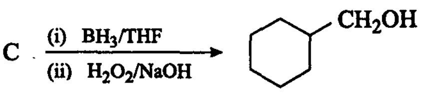


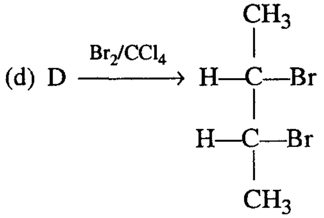
27. Give structure of the substrate in each of the following reactions :

(a)



(b) 
$$B \xrightarrow[\text{(ii) NaBH}_4]{\text{(i) Hg(OAc)}_2\text{/HOH}} CH_3-CH_2-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-CH_3$$

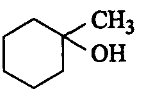
(c) 

(d) 
$$D \xrightarrow{Br_2/CCl_4} \begin{array}{c} CH_3 \\ | \\ H-C-Br \\ | \\ H-C-Br \\ | \\ CH_3 \end{array}$$

28. Draw the structure of

(a) a six carbon alkene that would give the same product from reaction with HBr in the presence or absence of peroxide.

(b) two alkenes that would give the given alcohol by oxymercuration-reduction reaction



(c) two stereoisomeric alkenes that would give 3-hexanol as the major product of hydroboration oxidation reaction.

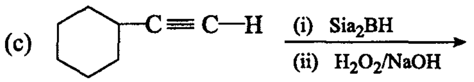
29. Complete the following reactions :

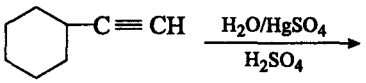
(a) $CH_3-CH_2-CH{=}CH_2 \xrightarrow[\text{(ii) NaBH}_4]{\text{(i) Hg(OAc)}_2\text{/HOH}}$ (b) $CH_3-CH_2-CH{=}CH_2 \xrightarrow[\text{(ii) NaBH}_4]{\text{(i) Hg(OAc)}_2\text{/CH}_3\text{OH}}$

(c) $CH_3-CH_2-CH{=}CH_2 \xrightarrow[\text{(ii) NaBH}_4]{\text{(i) Hg(OAc)}_2\text{/CH}_3\text{COOH}}$

30. Complete the following :

(a) $CH_3-(CH_2)_4-C{\equiv}C-H \xrightarrow[\text{(ii) H}_2\text{O}_2\text{/NaOH}]{\text{(i) Sia}_2\text{BH}}$ (b) $CH_3-(CH_2)_4-C{\equiv}C-H \xrightarrow[H_2SO_4]{H_2O/HgSO_4}$

(c) 

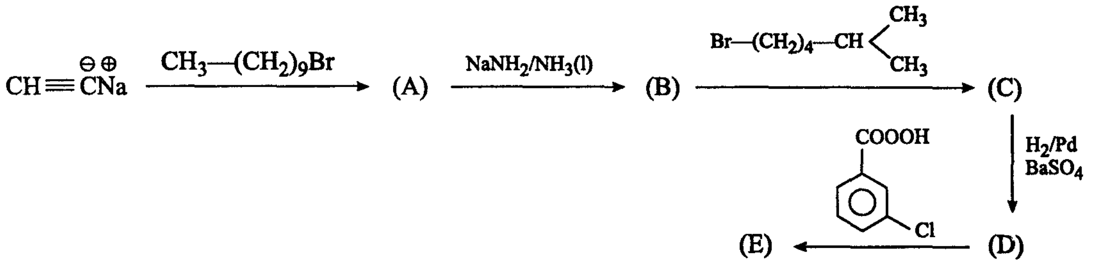
(d) 

31. Complete the following reactions. Indicate stereoisomerism where it is applicable.

(a) $CH_3-CH_2-C{\equiv}C-CH_2-CH_3 \xrightarrow{Na/NH_3(l)} (A) \xrightarrow{D_2/Pd\text{-}C} (B)$

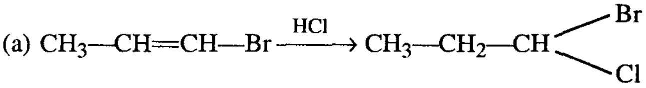
(b) $CH_3-CH_2-C{\equiv}C-CH_2-CH_3 \xrightarrow{H_2/Pd\text{-}BaSO_4-CaCO_3} (C) \xrightarrow{D_2/Pd\text{-}C}$

32. Identify (A) to (E) in the given sequence of reaction :



33. There are two alkenes that react with HBr to give 1-bromomethylcyclopentane.
    (i) Identify the alkenes.
    (ii) Will both alkenes give the same product when they react with HBr/peroxide.
    (iii) With BH_3 followed by $NaOH/H_2O_2$.
    (iv) With DCl.
    (v) With HCl/peroxide.

34. Account for the following reactions :



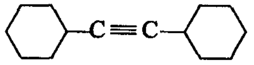
(a) $CH_3-CH=CH-Br \xrightarrow{HCl} CH_3-CH_2-CH{<}^{Br}_{Cl}$

(b) $CH_2=CH-COOH \xrightarrow{HCl} Cl-CH_2-CH_2-COOH$

35. Indicate the ultimate product fromed by reacting the following alkynes with $HgSO_4, H_2O, H_2SO_4$.

(a) $CH_3-CH_2-CH_2-C\equiv CH$

(b)



(c) $CH_3-CH_2-C\equiv C-CH_2-CH_2-CH_3$

(d) $HC\equiv C-(CH_2)_8-C\equiv CH$

36. Compare the final products for the four sequences below :

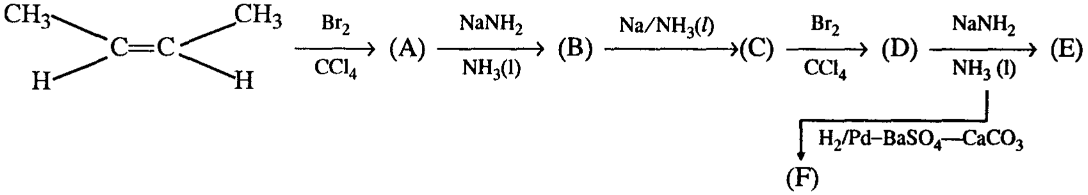
(a) $CH_3-C\equiv CH + HBr \xrightarrow{R-O-O-R} (A) \xrightarrow{HBr} (B)$

(b) $CH_3-C\equiv CH + HBr \longrightarrow (C) \xrightarrow[R-O-O-R]{HBr} (D)$

(c) $CH_3-C\equiv C-H + 2HBr \longrightarrow$

(d) $CH_3-C\equiv C-H + 2HBr \xrightarrow{R-O-O-R}$

37. Identify the lettered unknowns in the following sequences :



38. Predict the major product(s) from free radical addition of one mole of $BrCCl_3$ to the following :

(a) $CH_3-CH_2-CH=CH_2$

(b) $CH_2=CH-CH=CH_2$

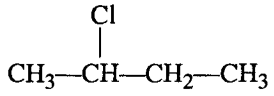
(c) $CH_3-CH=CH-CH=CH_2$

(d) $CH_2=CH-CH_2-CH=CH_2$

39. When 3-iodo-2, 2-dimethylbutane is treated with silver nitrate in ethanol, three elimination products are formed. Give their structures and predict which one will be the major product.

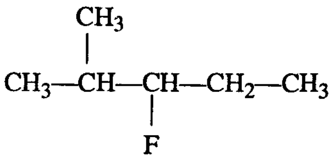
40. Give the major product obtained from an *E2* reaction of each of the following alkyl halides with $\overset{\ominus}{O}H$.

(a)



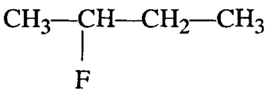
$CH_3-\overset{\overset{Cl}{|}}{C}H-CH_2-CH_3$

(b)



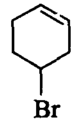
$CH_3-\overset{\overset{CH_3}{|}}{C}H-\underset{\underset{F}{|}}{C}H-CH_2-CH_3$

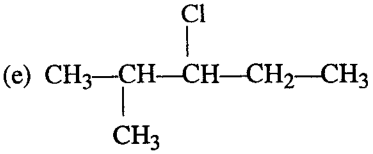
(c)

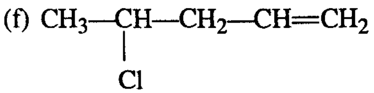


$CH_3-\underset{\underset{F}{|}}{C}H-CH_2-CH_3$

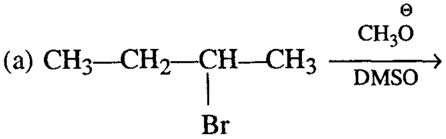
(d)

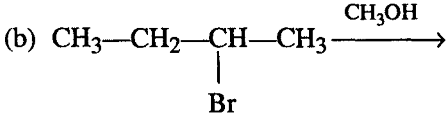


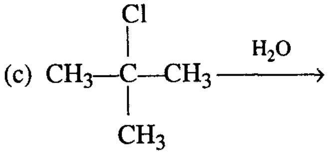
(e) 
$CH_3-\underset{CH_3}{\underset{|}{CH}}-\overset{Cl}{\overset{|}{CH}}-CH_2-CH_3$

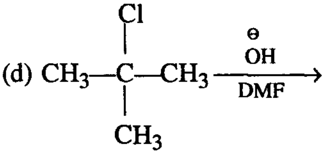
(f) 
$CH_3-\underset{Cl}{\underset{|}{CH}}-CH_2-CH{=}CH_2$

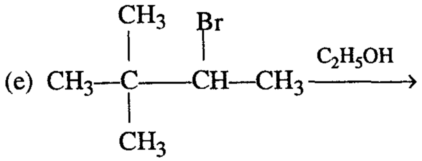
41. Predict whether each of the following reactions is an *E2* or an *E1* reaction. Give the major product of each reaction.

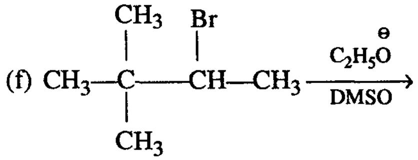
(a) 
$CH_3-CH_2-\underset{Br}{\underset{|}{CH}}-CH_3 \xrightarrow[DMSO]{CH_3\overset{\ominus}{O}}$

(b) 
$CH_3-CH_2-\underset{Br}{\underset{|}{CH}}-CH_3 \xrightarrow{CH_3OH}$

(c) 
$CH_3-\overset{Cl}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3 \xrightarrow{H_2O}$

(d) 
$CH_3-\overset{Cl}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3 \xrightarrow[DMF]{\overset{\ominus}{O}H}$

(e) 
$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-\overset{Br}{\overset{|}{CH}}-CH_3 \xrightarrow{C_2H_5OH}$

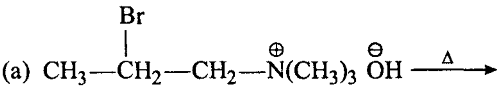
(f) 
$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-\overset{Br}{\overset{|}{CH}}-CH_3 \xrightarrow[DMSO]{C_2H_5\overset{\ominus}{O}}$

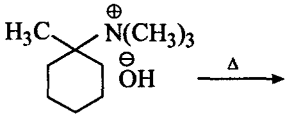
42. Two elimination products are obtained from the following *E2* reaction :

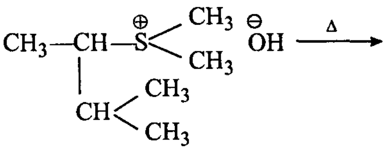
$$CH_3-CH_2-CHD-CH_2Br \xrightarrow{\overset{\ominus}{O}H} (A) + (B)$$

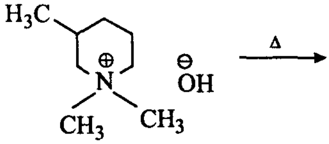
(a) What are the elimination products (A) and (B)?
(b) Which is formed in greater yield? Explain.

43. Give the major products of the following reactions :

(a) 
$CH_3-\overset{Br}{\overset{|}{CH_2}}-CH_2-\overset{\oplus}{N}(CH_3)_3\ \overset{\ominus}{O}H \xrightarrow{\Delta}$

(b) 

(c) 

(d) 

PROBLEMS FOR SELF ASSESSMENT

1. Write structural formulae for the products that are formed when 1-butene and cyclohexene react with each of the following reagents :

(a) HBr
(b) H_2/PtO_2
(c) dil. H_2SO_4, warm
(d) cold conc. H_2SO_4, then H_2O and heat
(e) HBr in the presence of Al_2O_3
(f) Br_2/CCl_4
(g) Br_2/CCl_4 then KI/acetone
(h) Br_2/HOH

(i) HCl in presence of alumina (j) cold dil. $KMnO_4/\overset{\ominus}{OH}$

(k) OsO_4 then $NaHSO_3/H_2O$

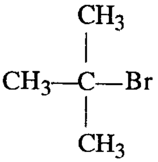
2. Give the structure of the products that you would expect from the reaction of 1-butyne with :

(a) 1 mole of Br_2 (b) 1 molar equivalent of HBr/Al_2O_3

(c) 2 molar equivalent of HBr/Al_2O_3 (d) H_2/P-2 catalyst

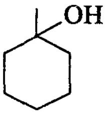
(e) $NaNH_2/NH_3(l)$ then with CH_3I and then with $Na/NH_3(l)$

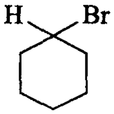
(f) $NaNH_2/NH_3(l)$ then with

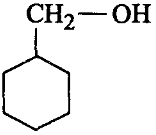


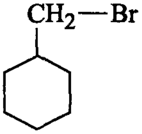
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br$

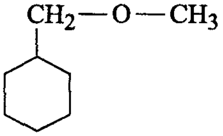
3. Give synthesis of the following compounds starting from methylenecyclohexane.

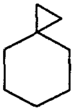
(a)


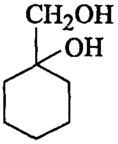
(b)


(c)


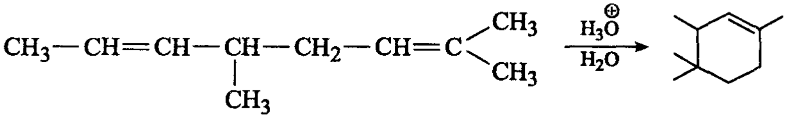
(d)


(e)


(f)


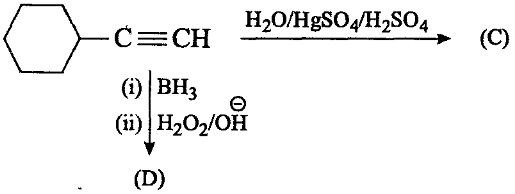
(g)


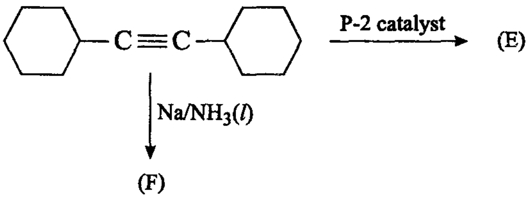
4. Propose a mechanism for the following reaction :



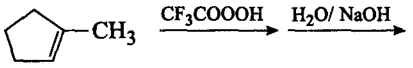
5. Complete the following reactions :

(a)
$$\begin{tikzcd} CH_3-(CH_2)_2-C\equiv C-(CH_2)_2-CH_3 \arrow[r, "H_2", "Pd\text{-}CaCO_3/Pb"'] \arrow[d, "Na/NH_3(l)"] & A \\ (B) \end{tikzcd}$$

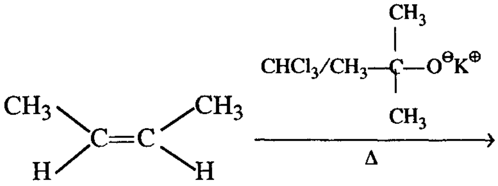
(b)


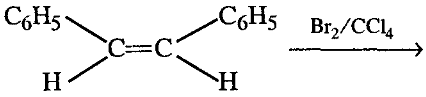
(c)


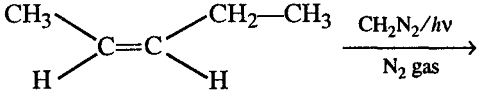
6. Show the final products of the reactions given below. Pay attention to stereochemistry of the product.

(a) 

(b) 

(c) 

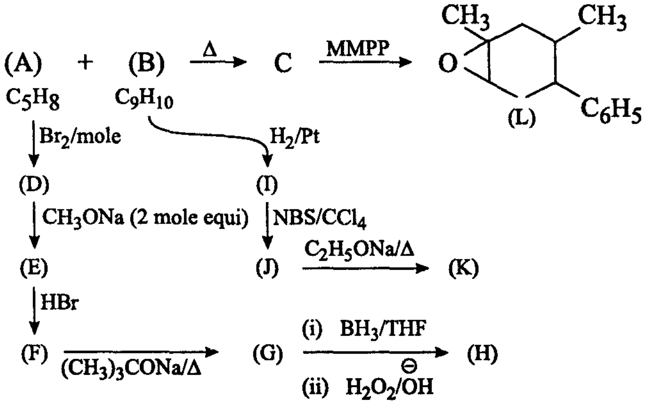
(d) 

(e) 

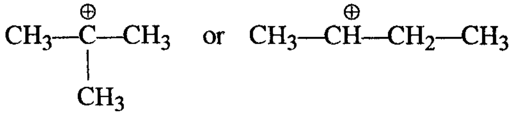
7. There are two dicarboxylic acids (A) and (B) with the general formula HOOC—CH=CH—COOH. (A) is maleic acid and (B) is fumaric acid. Maleic acid on treatment with $KMnO_4/\overset{\ominus}{OH}/HOH$ yields ***meso*** tartaric acid but fumaric acid with the same reagent gives (±) tartaric acid. Show how this information allows you to write configuration of maleic and fumaric acid.

8. Outline a synthesis of 1, 3-butadiene starting from :
   - (a) 1, 4-dibromobutane
   - (b) 1, 4-butanediol
   - (c) 3-buten-1-ol
   - (d) 4-chloro-1-butene
   - (e) 3-chloro-1-butene
   - (f) 3-buten-2-ol
   - (g) 1-buten-3-yne

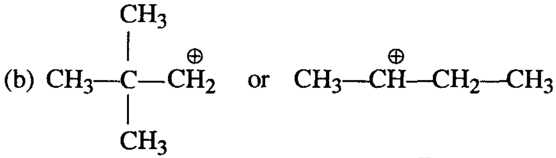
9. What will be the structures of the compounds A to K in the following reaction sequence?



10. Indicate which member of each of the following pairs is more stable.

(a) 

$$\underset{\text{I}}{CH_3—\overset{\oplus}{\underset{CH_3}{\underset{|}{C}}}—CH_3} \quad \text{or} \quad \underset{\text{II}}{CH_3—\overset{\oplus}{C}H—CH_2—CH_3}$$

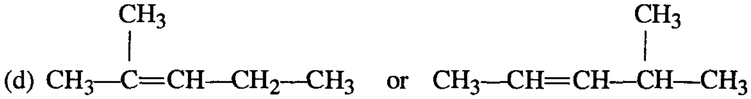


(b) $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{\oplus}{C}H_2$ or $CH_3-\overset{\oplus}{C}H-CH_2-CH_3$

I II

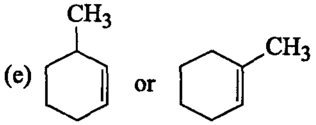
(c) $CH_3-\overset{\oplus}{C}H-CH_3$ or $CH_3-\overset{\oplus}{C}H-CH_2-Br$

I II



(d) $CH_3-\overset{CH_3}{C}=CH-CH_2-CH_3$ or $CH_3-CH=CH-\overset{CH_3}{C}H-CH_3$

I II



(e)

I II

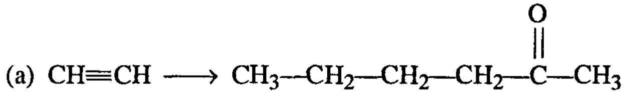
(f) $CH_2=CH-CH=CH_2$ or $CH_3-CH=C=CH_2$

I II

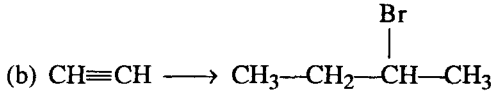
(g) $CH_2=CH-CH_2-CH=CH_2$ or $CH_3-CH=CH-CH=CH_2$

I II

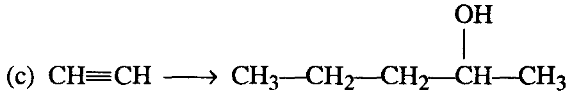
11. Which reagents would be required to carry out the conversion of 1-butyne into :
    (a) *n*-butane (b) 1-bromo-1-butene (c) 2-bromobutane (d) 1-butene
    (e) 2, 2-dibromobutane (f) 2-bromo-1-butene (g) butanone (h) butanol
12. Show how each of the following conversions can be achieved using suitable reagents and solvents.



(a) $CH\equiv CH \longrightarrow CH_3-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

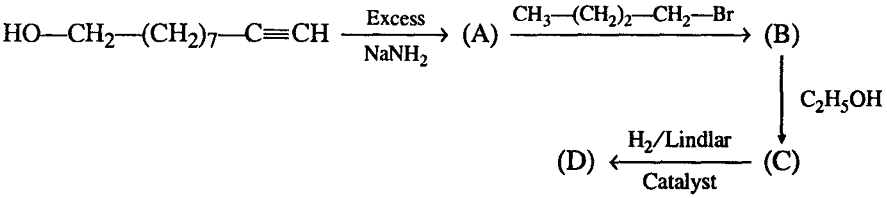


(b) $CH\equiv CH \longrightarrow CH_3-CH_2-\overset{Br}{C}H-CH_3$



(c) $CH\equiv CH \longrightarrow CH_3-CH_2-CH_2-\overset{OH}{C}H-CH_3$

13 . Complete the following :

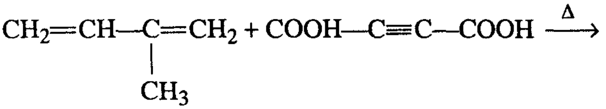


$HO-CH_2-(CH_2)_7-C\equiv CH \xrightarrow[NaNH_2]{Excess} (A) \xrightarrow{CH_3-(CH_2)_2-CH_2-Br} (B) \xrightarrow{C_2H_5OH} (C) \xrightarrow[Catalyst]{H_2/Lindlar} (D)$

14. Give the product of each of the following reactions :

(a) $CH_3-CH=CH-CH=CH_2 + CH\equiv CH \xrightarrow{\Delta}$

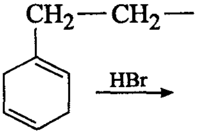
(b) $CH_3-CH=CH-CH=CH-CH_3 + CH\equiv C-CH_3 \xrightarrow{\Delta}$

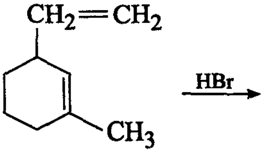
(c) 

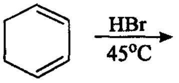
$CH_2{=}CH{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 + COOH{-}C{\equiv}C{-}COOH \xrightarrow{\Delta}$

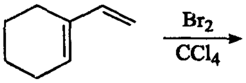
(d) $CH_2{=}CH{-}CH{=}CH_2 + CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{\Delta}$

15. Give major product of each of the following reactions. One equivalent of each reagent is used :

(a) 

(b) 

(c) 

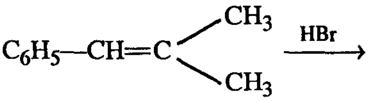
(d) 

16. Define each of the following terms and give an example :

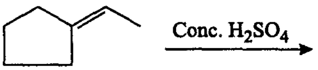
(a) Dimerisation
(b) Polymerisation
(c) Peroxide effect
(d) Hydrogenation
(e) *Syn* addition
(f) *Anti* addition
(g) Electrophilic addition
(h) Nucleophilic addition
(i) Free radical addition
(j) Hydration
(k) Epoxidation
(l) Oxidative cleavage
(m) Hydroboration
(n) Oxymercuration
(o) Carbene addition

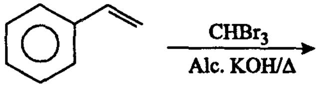
17. Complete the following reactions and propose mechanisms for them :

(a) $C_6H_5{-}CH{=}CH{-}CH_3 \xrightarrow{HBr}$

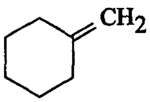
(b) 

$C_6H_5{-}CH{=}C(CH_3)_2 \xrightarrow{HBr}$

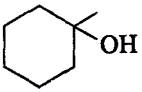
(c) 

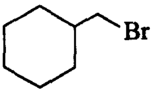
(d) 

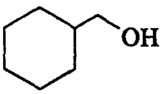
18. Show how would you synthesise each of the following compounds from methylenecyclohexane.

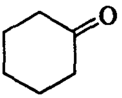


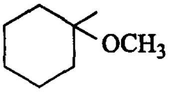
Methylenecyclohexane

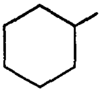
(a) 

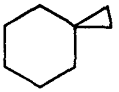
(b) 

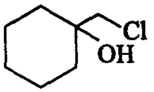
(c) 

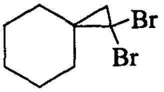
(d) 

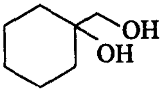
(e) 

(f) 

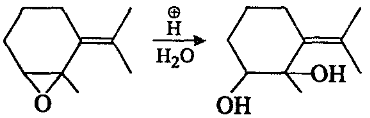
(e) 

(h) 

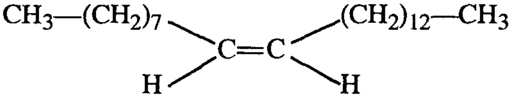
(i) 

(j) 

19. Propose a mechanism for the following reaction :



20. Muscalure, the sex pheromone of common housefly, is *cis*-9-tricosene. Most syntheses of alkenes give mostly the most stable *trans* isomer. Devise a synthesis of muscalure from acetylene and alcohols of your choice. Your synthesis must give entirely the *cis* isomer.



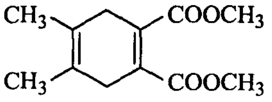
Muscalure

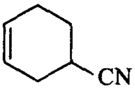
21. Predict the product formed when $CH_3-C\equiv\overset{\ominus}{C}\overset{\oplus}{Na}$ reacts with the following compounds :

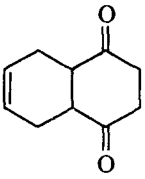
(a) Methyl bromide (b) *t*-butyl chloride (c) Formaldelyde (d) Cyclohexanone
(e) Ethylene oxide (f) Cyclohexanol.

22. When 1, 3-butadiene is allowed to react with hydrogen chloride in acetic acid at room temperature, there is produced a mixture of 22% 1-chloro-2-butene and 78% 3-chloro-1-butene. On treatment with $FeCl_3$ or on prolonged treatment with hydrogen chloride, this mixture is converted to 75% 1-chloro-2-butene and 25% 3-chloro-1-butene. Explain.

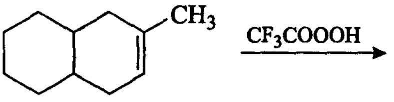
23. What diene and dienophile produce the following Diels-Alder adducts ?

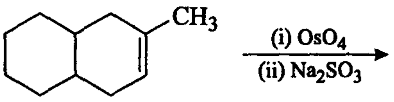
(a)


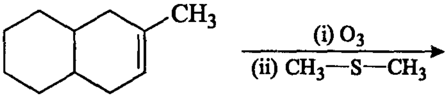
(b)


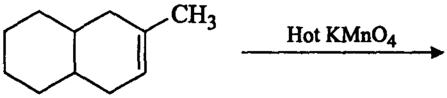
(c)


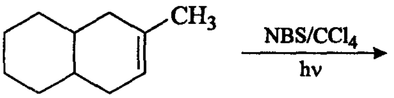
24. Predict the products in the following reactions :

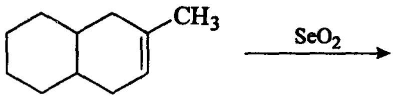
(a)


(b)


(c)


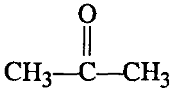
(d)


(e)


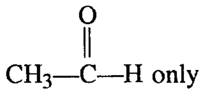
(f)


25. Each of a series of unknown alkenes is treated with (1) O_3 and (2) CH_3-S-CH_3. The following products are obtained. Give the structure (or structures, if there is more than one possibility) of each unknown alkene.

(a) $OHC-CH_2-CH_2-CH_2-CHO$ only (b) CH_3-CH_2-CHO and

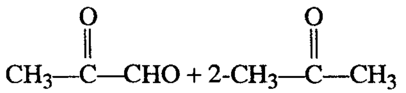


$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

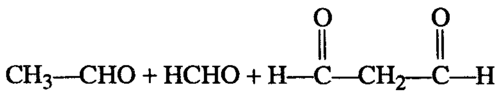


(c) $CH_3-\overset{O}{\overset{\|}{C}}-H$ only

(d) HCHO and cyclohexanone



(e) $CH_3-\overset{O}{\overset{\|}{C}}-CHO + 2\text{-}CH_3-\overset{O}{\overset{\|}{C}}-CH_3$



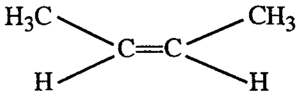
(f) $CH_3-CHO + HCHO + H-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-H$

26. Acid-catalysed dehydration of neopentyl alcohol gives two isomeric alkenes. Predict their structures and outline a suitable pathway for the reaction. Which alkene do you think shall be the major product. Give reasons.

ANSWER TO VERY SHORT ANSWER QUESTIONS

1. *Trans*-2-bromo-2-butene because elimination reaction requires *trans* geometry of the eliminating groups.

2.

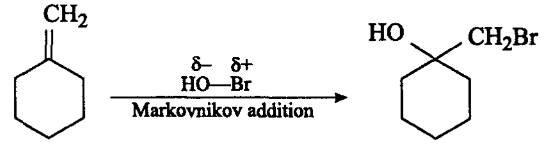


cis-2-butene

3. $CH_3CH_2CH{=}CHCH_2CH_3$

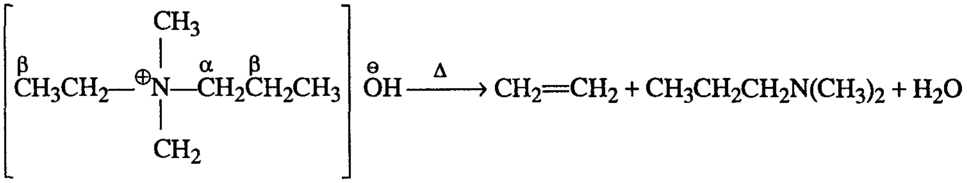
3-Hexene

4.



Methylenecylohexane 1-Bromomethylcyclohexanol

5.



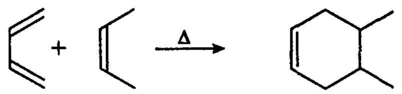
$$\left[\overset{\beta}{C}H_3CH_2-\overset{\oplus}{\underset{CH_2}{\overset{CH_3}{N}}}-\overset{\alpha}{C}H_2\overset{\beta}{C}H_2CH_3\right]\overset{\ominus}{O}H \xrightarrow{\Delta} CH_2{=}CH_2 + CH_3CH_2CH_2N(CH_3)_2 + H_2O$$

β-Hydrogen of ethyl group being more acidic than that of *n*-propyl group is preferentially abstracted to form ethylene.

6. *cis*-1, 2-dideuteriocyclohexane because addition of D_2 is *cis*-addition similar to hydrogenation.

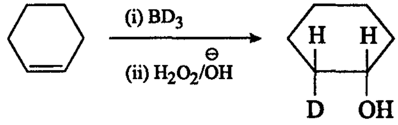
7. Addition of bromine is an *anti*-addition, hence *trans*-1, 2-dibromocyclohexane is produced.

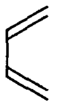
8. From Diels-Alder reaction :

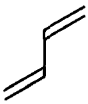


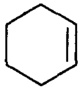
4, 5-Dimethylcyclohexene

9.



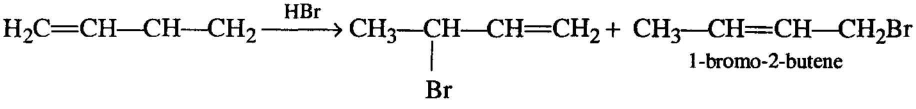
10. 
s-cis conformation
less stable


s-trans conformation
more stable

11. 
cyclohexene

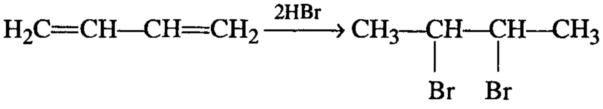
$\xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3}$ $OHCCH_2CH_2CH_2CH_2CHO$
hexanedial

12. (i) With one mole of HBr :

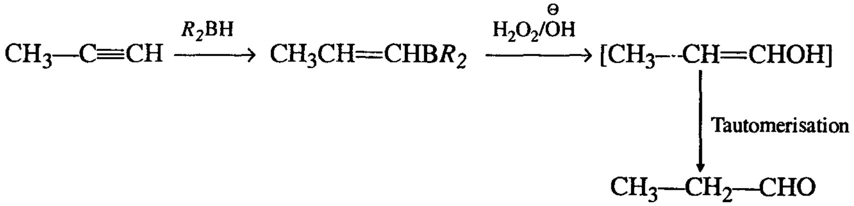


$$H_2C{=}CH{-}CH{-}CH_2 \xrightarrow{HBr} \underset{\text{3-bromo-1-butene}}{CH_3{-}\underset{\displaystyle Br}{CH}{-}CH{=}CH_2} + \underset{\text{1-bromo-2-butene}}{CH_3{-}CH{=}CH{-}CH_2Br}$$

(ii) With two moles of HBr :



$$H_2C{=}CH{-}CH{=}CH_2 \xrightarrow{2HBr} \underset{\text{2, 3-dibromobutane}}{CH_3{-}\underset{\displaystyle Br}{CH}{-}\underset{\displaystyle Br}{CH}{-}CH_3}$$

13. 

$$CH_3{-}C{\equiv}CH \xrightarrow{R_2BH} CH_3CH{=}CHBR_2 \xrightarrow{H_2O_2/\overset{\ominus}{O}H} [CH_3{-}CH{=}CHOH] \xrightarrow{\text{Tautomerisation}} CH_3{-}CH_2{-}CHO$$

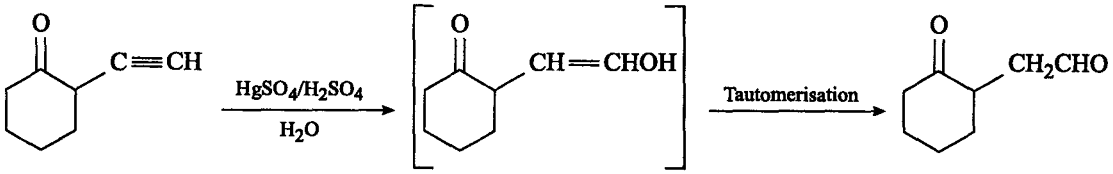
14. $NH_3 < HC{\equiv}CH < CH_3OH < H_2O$

15. Alcohol being more acidic than alkynes reacts first.

$$\underset{\text{Propargyl alcohol}}{HC{\equiv}C{-}CH_2OH} + CH_3MgI \longrightarrow HC{\equiv}C{-}CH_2OMgI + CH_4$$

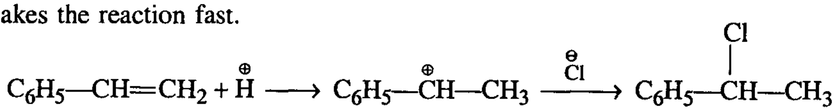
16. 2, 3-Butanedione.

17. *trans*-2-Butene.

18. 

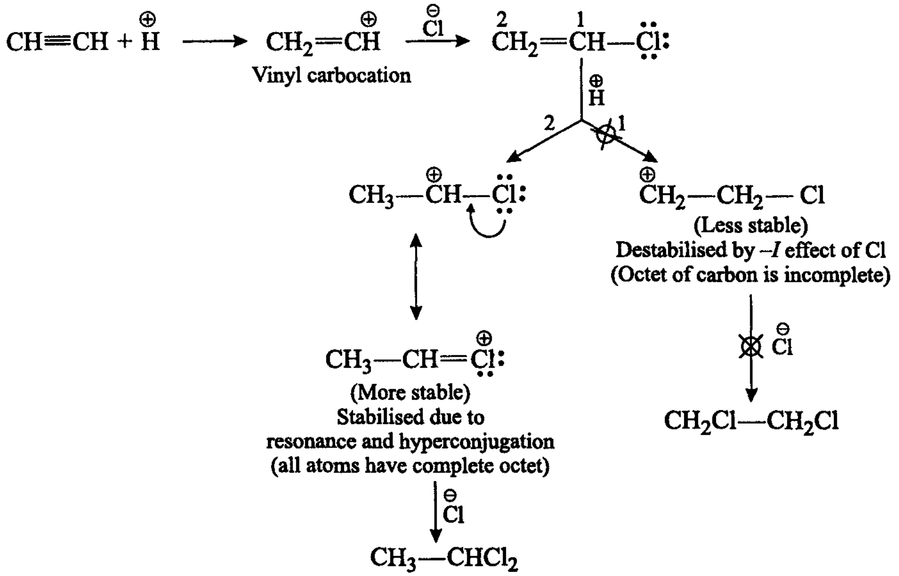
SOLUTIONS OF PROBLEMS

1. Delocalisation of the positive charge of the carbocation intermediate brings stability to the latter which makes the reaction fast.



$$C_6H_5{-}CH{=}CH_2 + \overset{\oplus}{H} \longrightarrow \underset{\substack{\text{Benzylic carbocation,}\\ \text{highly stable}}}{C_6H_5{-}\overset{\oplus}{C}H{-}CH_3} \xrightarrow{\overset{\ominus}{Cl}} C_6H_5{-}\overset{\displaystyle Cl}{CH}{-}CH_3$$

2. This reaction takes place as follows :



1, 1-Dichloroethane will be the product. Here the orientation of the addition of $\overset{\oplus}{H}$ and $\overset{\ominus}{Cl}$ to vinyl chloride is determined by the lone pair π-conjugation. Thus $CH_3—\overset{\oplus}{C}H—Cl$ is more stable than $\overset{\oplus}{C}H_2—CH_2—Cl$. The higher stability of $CH_3—\overset{\oplus}{C}H—Cl$ is also due to the + I effect and hyperconjugative effect of CH_3.

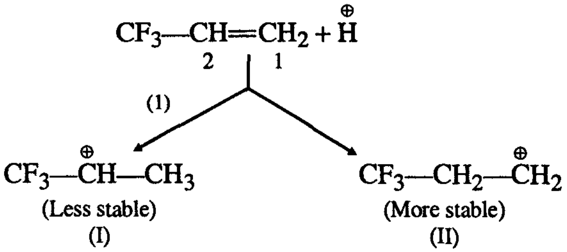
3. Electrophilic addition reaction is a two step reaction and reaction intermediate is carbocation.

$$\underset{\text{Alkene}}{R—CH{=}CH_2} + \overset{\oplus}{H} \longrightarrow \underset{\text{Alkyl carbocation}}{R—\overset{\oplus}{C}H—CH_3}$$

$$\underset{\text{Alkyne}}{R—C{\equiv}CH} + \overset{\oplus}{H} \longrightarrow \underset{\text{Vinyl carbocation}}{R—\overset{\oplus}{C}{=}CH_2}$$

A vinyl carbocation is less stable than an alkyl carbocation hence, alkenes are more reactive than alkynes for electrophilic addition reactions.

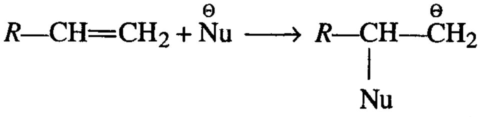
4. As we know intermediate of electrophilic addition reaction is carbocation and product formation takes place by formation of stable carbocation.



Thus product formation will takes place by intermediate (II) which gives anti-Markovnikov's product.

5. First reaction takes place by formation of carbocation as reaction intermediate. Rearrangement is common feature in carbocations. On the other hand, second reaction takes place by formation of four membered cyclic transition state. In cyclic transition state rearrangement does not occur.

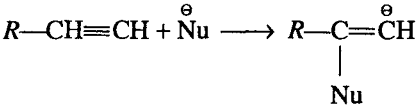
6. Nucleophilic addition reaction is two step and reaction intermediate is carbanion.



$$R\text{—CH=CH}_2 + \overset{\ominus}{\text{Nu}} \longrightarrow R\text{—}\underset{\text{Nu}}{\underset{|}{\text{CH}}}\text{—}\overset{\ominus}{\text{CH}_2}$$

(Alkyl carbanion)

Negative charge is present on sp^3 hybrid carbon which is electropositive in character (less stable).



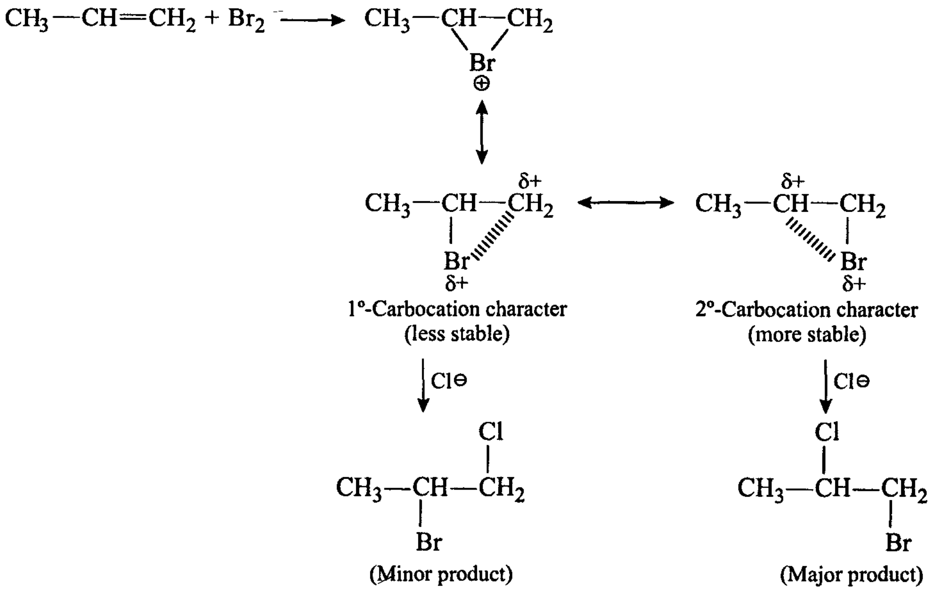
$$R\text{—CH}\equiv\text{CH} + \overset{\ominus}{\text{Nu}} \longrightarrow R\text{—}\underset{\text{Nu}}{\underset{|}{\text{C}}}\text{=}\overset{\ominus}{\text{CH}}$$

(Vinyl carbanion)

Negative charge is present on sp^2 hybrid carbon which is electronegative (more stable).

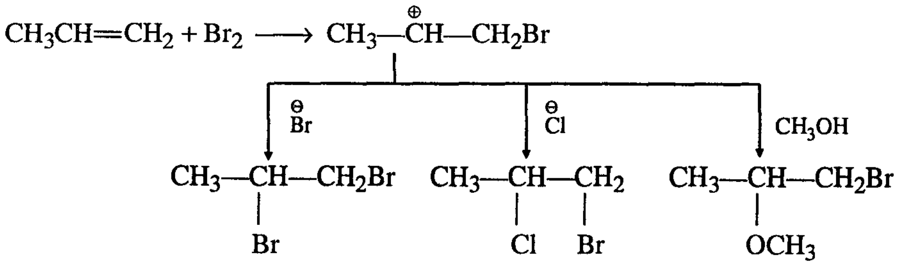
A vinyl carbanion being more stable than an alkyl carbanion. Hence alkyne is more reactive than alkene for nucleophilic addition reactions.

7. In this reaction product formation takes place by bromonium ion. The bromonium ion has also some carbocation character.

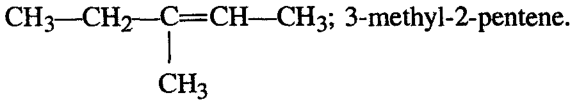


8. Alkenes are adsorbed on the surface of the catalyst only when the plane of the *pi* bond approaches perpendicularly. Because of the cylindrical nature of the *pi* bonds of alkynes, any approach along the axis of the cylinder can be successful. These less constrained transition states cause alkynes to have more positive ΔS^* values. Consequently, in this reaction alkynes react at a faster rate than alkenes.

9.



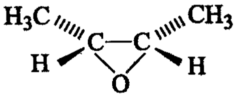
$$CH_3CH\text{=}CH_2 + Br_2 \longrightarrow CH_3\text{—}\overset{\oplus}{CH}\text{—}CH_2Br$$

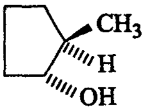
10. 

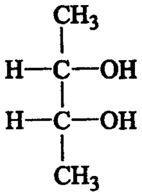
$CH_3-CH_2-\underset{\underset{CH_3}{|}}{C}=CH-CH_3$; 3-methyl-2-pentene.

11. (a) 2-methyl-2-butene (major), 3-methyl-1-butene (minor);
(b) 2-methyl-2-pentene (major), 4-methyl-2-pentene (minor);
(c) 3-methyl-2-pentene (major), 3-methyl-1-pentene (minor);
(d) 3, 3-dimethyl-1-pentene.

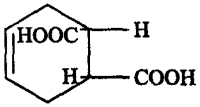
12. (a) *cis*-2-butene

(b) 

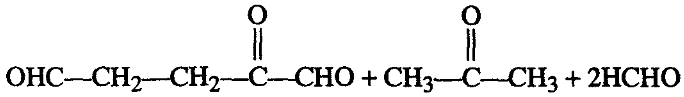
(c) 

(d) 

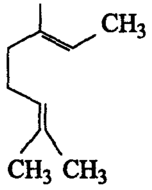
Meso form

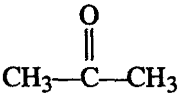
(e) 

trans

13. 

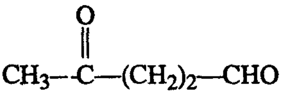
$OHC-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CHO + CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + 2HCHO$

14. (A) 

(B) 

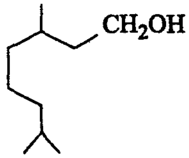
$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

(C) OHC—CHO

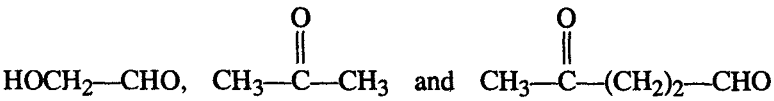
(D) 

$CH_3-\overset{\overset{O}{\|}}{C}-(CH_2)_2-CHO$

15. Reduction product is

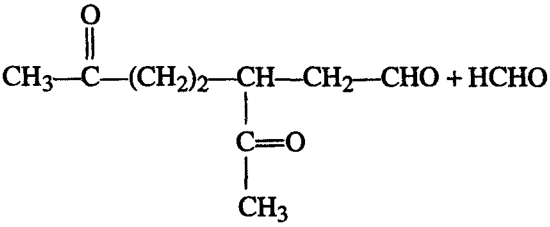


ozonolysis products are :



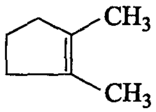
$HOCH_2-CHO$, $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ and $CH_3-\overset{\overset{O}{\|}}{C}-(CH_2)_2-CHO$

16. Two products

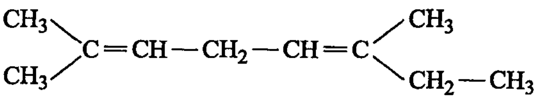


$CH_3-\overset{\overset{O}{\|}}{C}-(CH_2)_2-\underset{\underset{\underset{\underset{CH_3}{|}}{C=O}}{|}}{CH}-CH_2-CHO + HCHO$

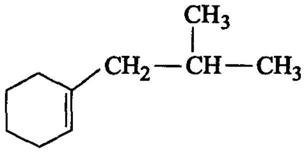
17. (a)



(b)



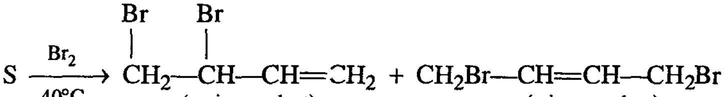
(c)



(d)

18. $CH_2{=}CH{-}CH{=}CH_2 \equiv S$

(a)



$S \xrightarrow[40°C]{Br_2} \underset{\text{(major product)}}{CH_2(Br){-}CH(Br){-}CH{=}CH_2} + \underset{\text{(minor product)}}{CH_2Br{-}CH{=}CH{-}CH_2Br}$

(b) $S \xrightarrow[\text{excess}]{Br_2} CH_2Br{-}CHBr{-}CHBr{-}CH_2Br$

(c) $S \xrightarrow{H_2/Pt} \underset{\text{(major)}}{CH_3{-}CH{=}CH{-}CH_3} + \underset{\text{(minor)}}{CH_3{-}CH_2{-}CH{=}CH_2}$

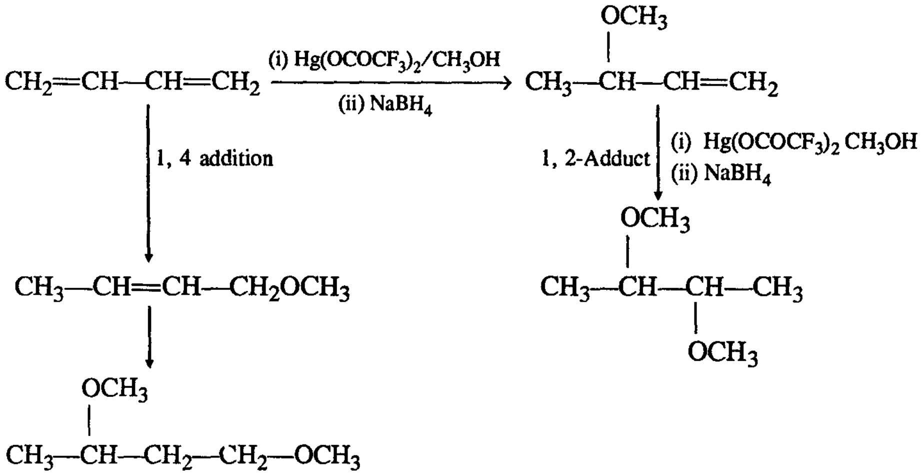
(d) $S \xrightarrow{D_2/Pt} \underset{\text{(minor product)}}{CH_2D{-}CHD{-}CH{=}CH_2} + \underset{\text{(major product)}}{CH_2D{-}CH{=}CH{-}CH_2D}$

(e) $S \xrightarrow[\text{excess}]{H_2/Pt} CH_3{-}CH_2{-}CH_2{-}CH_3$

(f) $S \xrightarrow[40°C]{DCl} \underset{\text{(major product)}}{CH_2DCH_2{-}CH{=}CH_2} + \underset{\text{(minor product)}}{CH_2D{-}CH{=}CH{-}CH_3}$

(g) $S \xrightarrow[DCl]{\text{Excess}} CH_2D{-}CHCl{-}CH{=}CH_2 \xrightarrow{DCl} CH_2D{-}CHCl{-}CHCl{-}CH_2D$

(h)

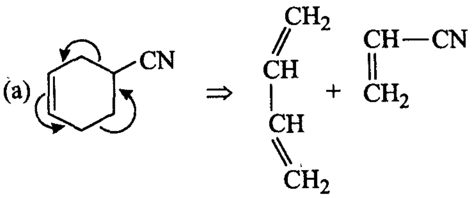


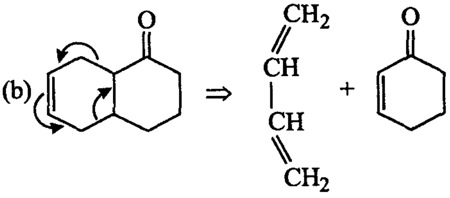
(i) $CH_2{=}CH{-}CH{=}CH_2 \xrightarrow[\text{(ii) Zn/CH}_3\text{COOH}]{\text{(i) O}_3\text{ (excess)}} CH_2O + OHC{-}CHO + CH_2O$

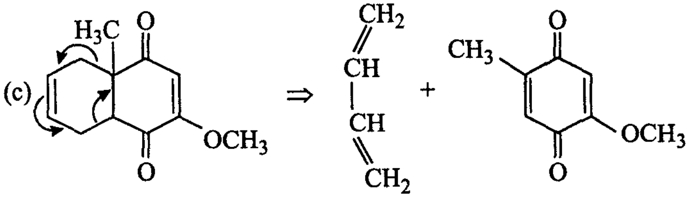
(j)

$$\begin{tikzcd}
CH_2{=}CH{-}CH{=}CH_2 \arrow[r, "(i)\ BH_3", "\begin{array}{c}(ii)\ CH_3{-}CH_2{-}COOD\\(1,2\text{-Additon})\end{array}"'] \arrow[d, "\begin{array}{l}(i)\ BH_3\\(ii)\ CH_3{-}CH_2COOD\\(1,4\text{-Addition})\end{array}"] & CH_2D{-}CH_2{-}CH{=}CH_2 \arrow[d, "\begin{array}{l}(i)\ BH_3\\(ii)\ CH_3{-}CH_2COOD\end{array}"] \\
CH_2D{-}CH{=}CH{-}CH_3 \arrow[d, "\begin{array}{l}(i)\ BH_3\\(ii)\ CH_3{-}CH_2COOD\end{array}"] & CH_2D{-}CH_2{-}CH_2{-}CH_2D \\
\begin{array}{c}CH_2D{-}CH_2{-}CHD{-}CH_3\\+\\CH_2D{-}CHD{-}CH_2{-}CH_3\end{array} &
\end{tikzcd}$$

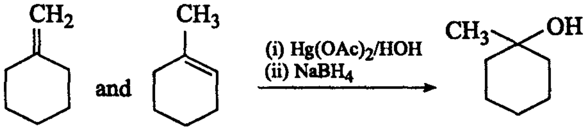
19.







20. Two isomeric alkenes are :



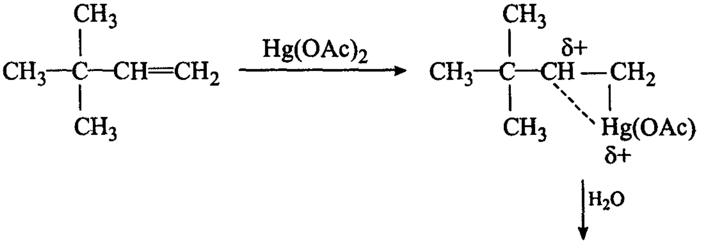
21. (a) $CH_3-CH_2-CH=CH-CH_2-CH_3$

(b) 

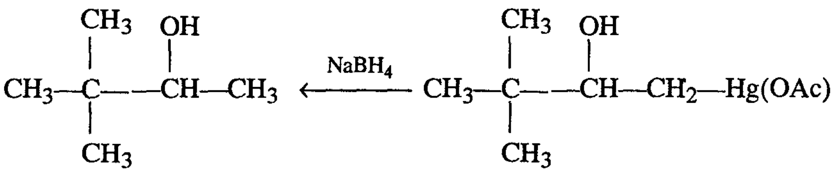
(c) 

(d) $CH_3-CH_2-CH=CH-CH_2-CH_3$ and $CH_3-CH=CH-CH_2-CH_2-CH_3$

22.

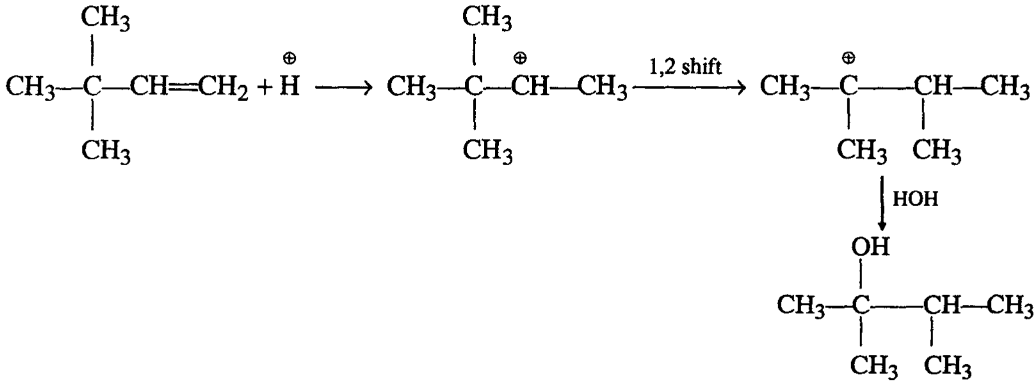


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=CH_2 \xrightarrow{Hg(OAc)_2} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{\delta+}{CH}-\underset{\underset{\delta+}{Hg(OAc)}}{CH_2} \quad \Big\downarrow H_2O$$



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{OH}{CH}-CH_3 \xleftarrow{NaBH_4} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{OH}{CH}-CH_2-Hg(OAc)$$

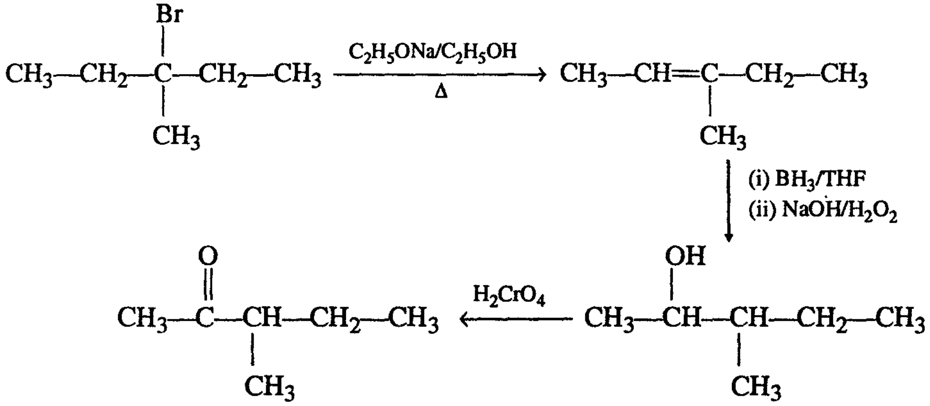
In the above reaction product formation takes place by formation of bridged carbocation as RI. In bridged carbocation there is no rearrangement hence rearranged product formation is not possible.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=CH_2+\overset{\oplus}{H} \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{\oplus}{CH}-CH_3 \xrightarrow{1,2\ \text{shift}} CH_3-\underset{CH_3}{\overset{\oplus}{C}}-\underset{CH_3}{CH}-CH_3 \xrightarrow{HOH} CH_3-\underset{CH_3}{\overset{OH}{C}}-\underset{CH_3}{CH}-CH_3$$

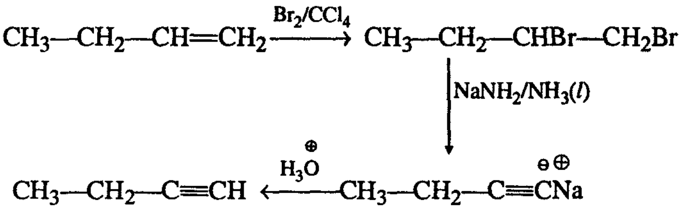
In this case product formation takes place by formation of classical carbocation which undergoes rearrangement. Hence in this case rearranged product will be formed.

23. (a)



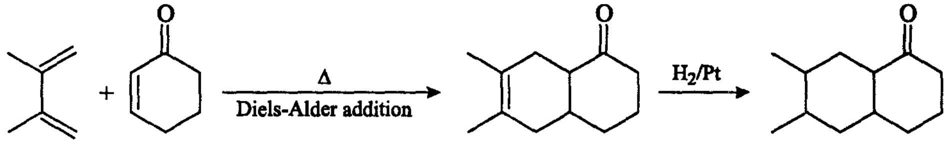
$$CH_3-CH_2-\underset{CH_3}{\overset{Br}{C}}-CH_2-CH_3 \xrightarrow[\Delta]{C_2H_5ONa/C_2H_5OH} CH_3-CH=\underset{CH_3}{C}-CH_2-CH_3 \xrightarrow{\text{(i) }BH_3/THF\ \text{(ii) }NaOH/H_2O_2} CH_3-\overset{OH}{CH}-\underset{CH_3}{CH}-CH_2-CH_3 \xrightarrow{H_2CrO_4} CH_3-\overset{O}{\overset{\parallel}{C}}-\underset{CH_3}{CH}-CH_2-CH_3$$

(b)

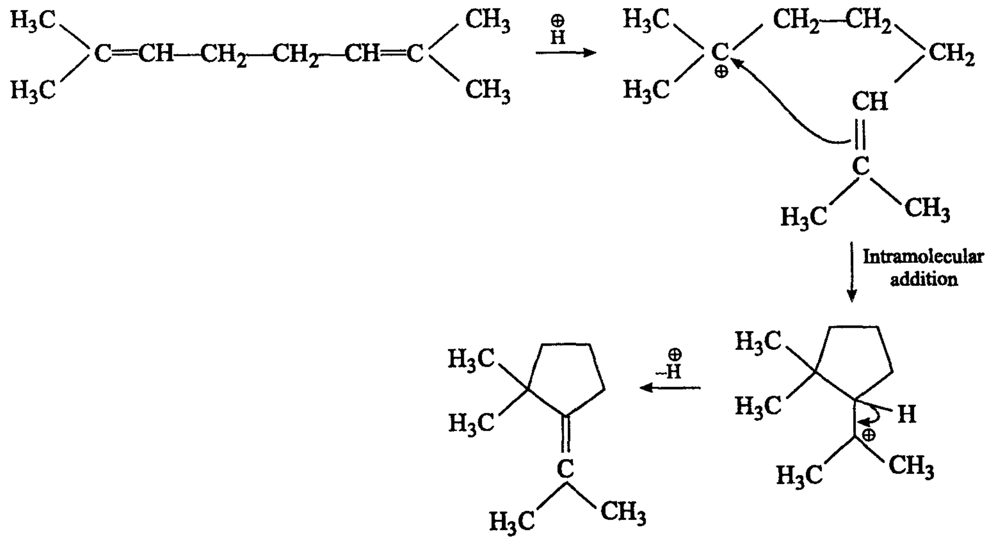


$$CH_3-CH_2-CH=CH_2 \xrightarrow{Br_2/CCl_4} CH_3-CH_2-CHBr-CH_2Br \xrightarrow{NaNH_2/NH_3(l)} CH_3-CH_2-C\equiv C\overset{\ominus\oplus}{Na} \xrightarrow{H_3\overset{\oplus}{O}} CH_3-CH_2-C\equiv CH$$

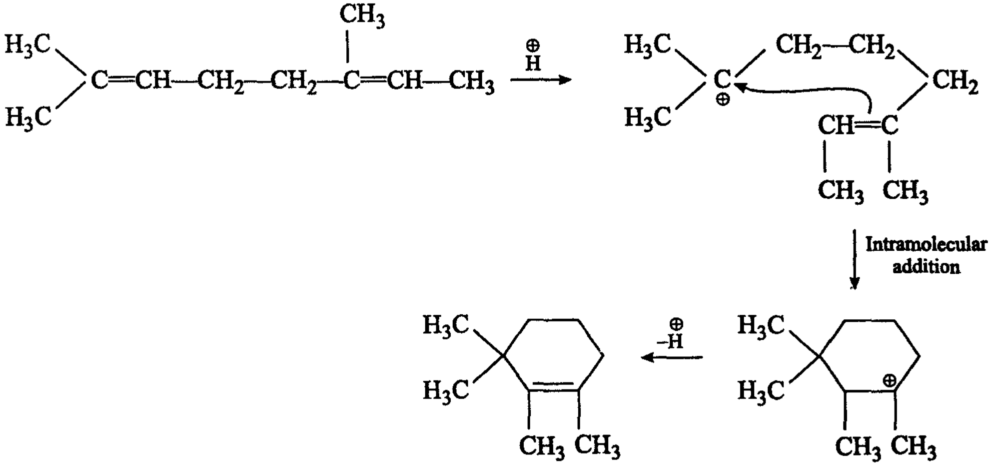
(c)



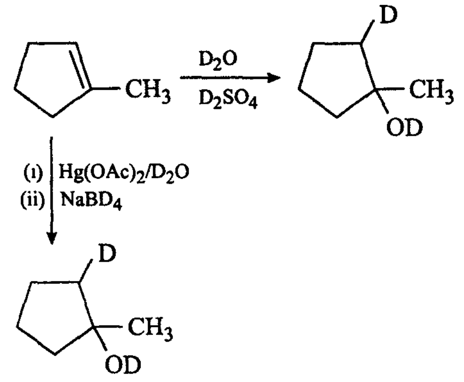
24. (a)


$\overset{\oplus}{H}$
Intramolecular addition
$\overset{\oplus}{-H}$

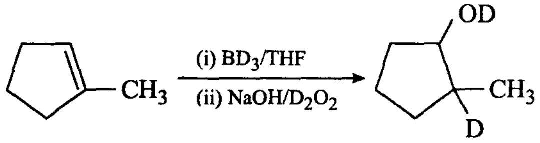
(b)


$\overset{\oplus}{H}$
Intramolecular addition
$\overset{\oplus}{-H}$

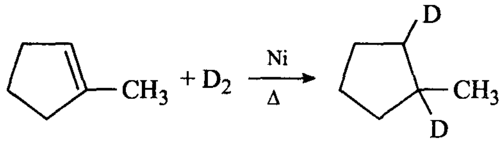
25. (I) (a)


D_2O
D_2SO_4
(i) $Hg(OAc)_2/D_2O$
(ii) $NaBD_4$

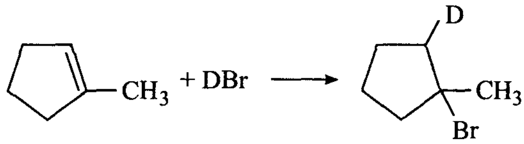
(b)



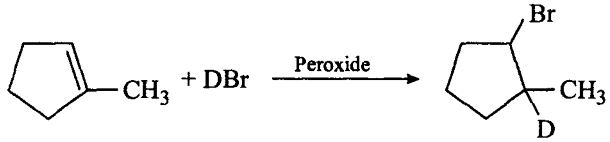
(c)



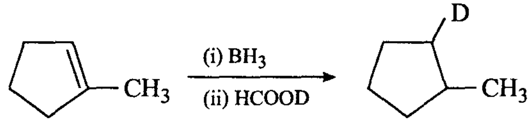
(d)



(e)

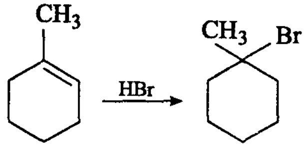


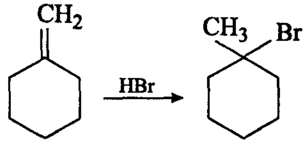
(f)



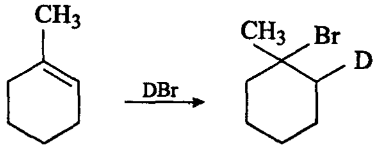
25. (II)

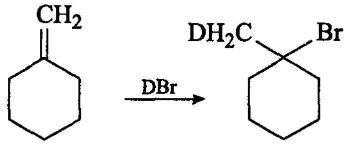
(a) Either of the following two alkenes would react with HBr to give the given alkyl halide :



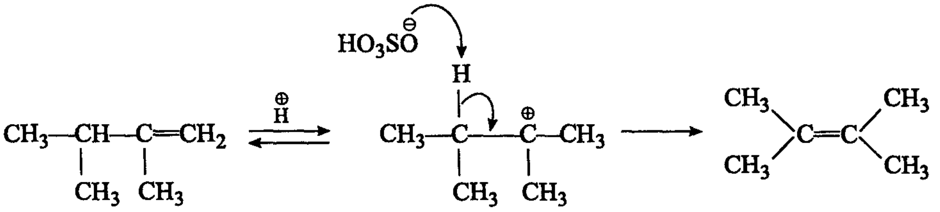


(b) DBr will give different products with these two alkenes :

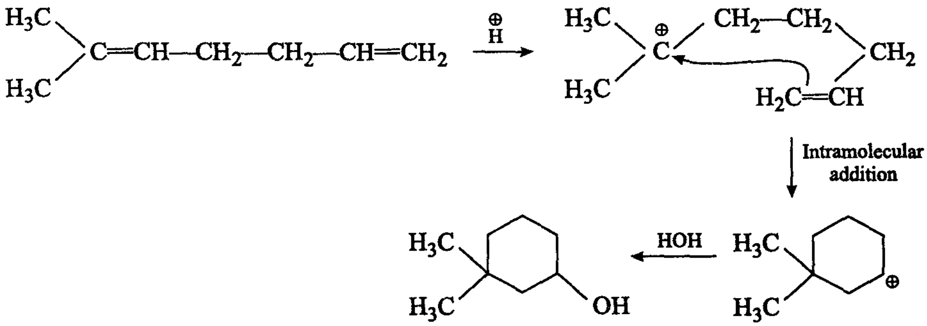




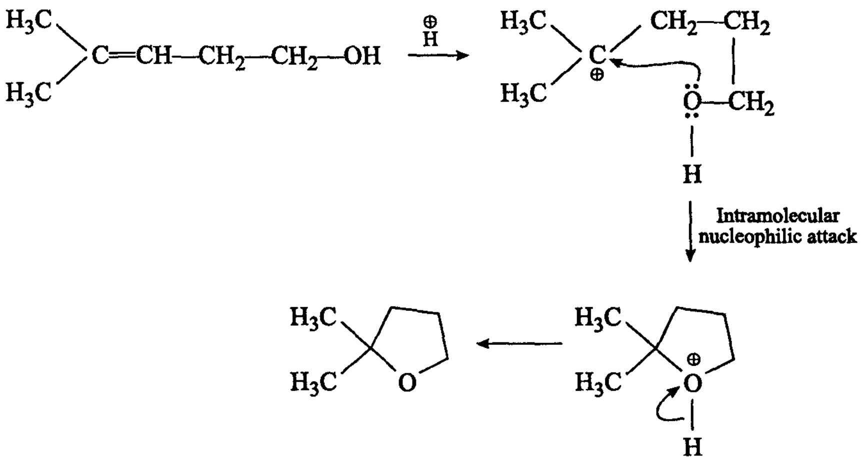
26. (a)



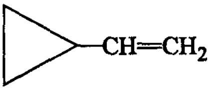
(b)



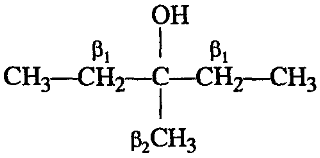
(c)



27. (a) Oxymercuration-demercuration gives Morkovnikov's addition without rearrangement therefore alkene should be

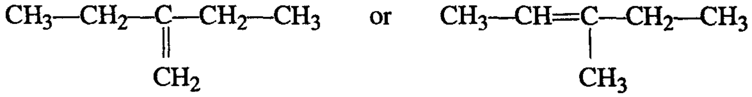


(b) The given product is :



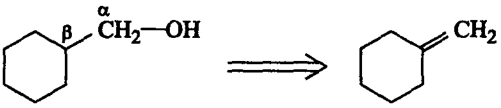
$$CH_3-\overset{\beta_1}{CH_2}-\underset{\beta_2 CH_3}{\overset{OH}{C}}-\overset{\beta_1}{CH_2}-CH_3$$

The alcohol has two type of β-carbons, hence two alkenes are possible :



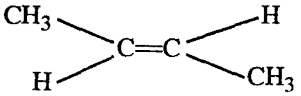
$$CH_3-CH_2-\underset{\overset{\|}{CH_2}}{C}-CH_2-CH_3 \quad \text{or} \quad CH_3-CH=\underset{\overset{|}{CH_3}}{C}-CH_2-CH_3$$

(c) In hydroboration-oxidation reaction, there is no rearrangement thus alkene structure can be obtained by removing —OH from α-carbon and hydrogen from the β-carbon of the product.



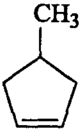
(C)

(d) The product is *meso*-2, 3-dibromobutane, therefore alkene should be *trans*-2-butene



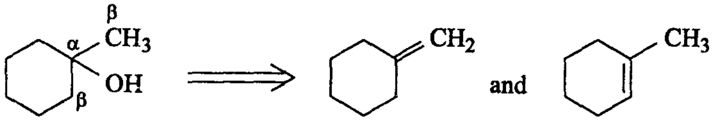
(D)

28. (a) Any symmetrical alkene with six carbons will give the same product with HBr and HBr/peroxide



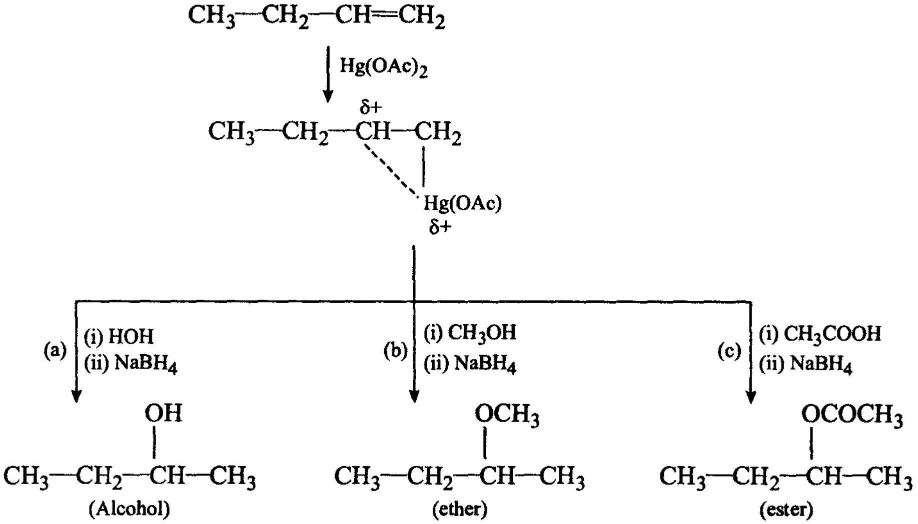
$CH_3—CH_2—CH{=}CH—CH_2—CH_3$

(b)

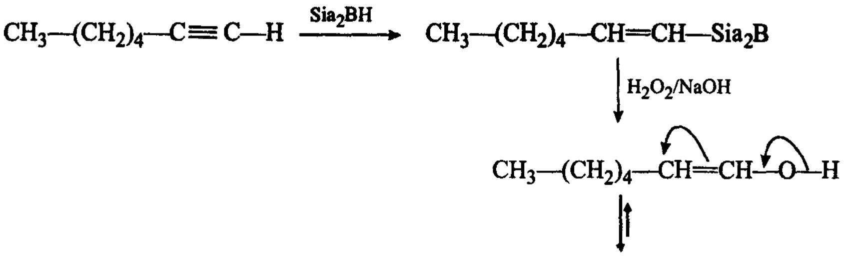


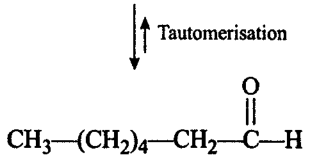
(c) The alkenes should be *cis* and *trans*-3-hexene.

29.



30. (a)

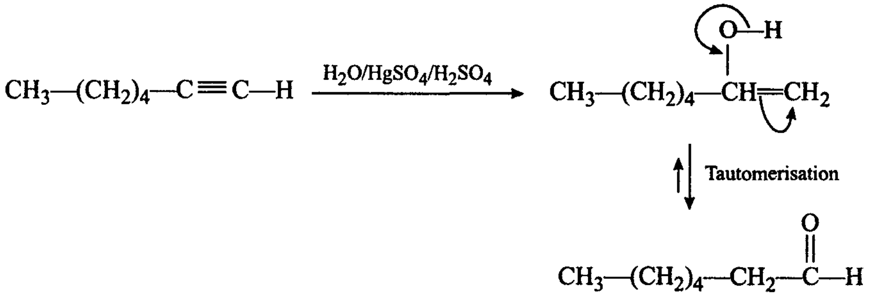




Tautomerisation

$CH_3-(CH_2)_4-CH_2-\overset{\overset{O}{\|}}{C}-H$

(b)

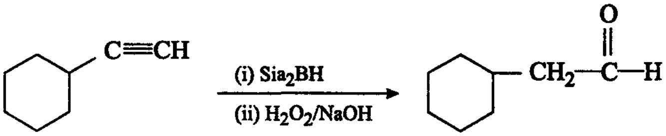


$CH_3-(CH_2)_4-C\equiv C-H \xrightarrow{H_2O/HgSO_4/H_2SO_4} CH_3-(CH_2)_4-\overset{\overset{O-H}{|}}{CH}=CH_2$

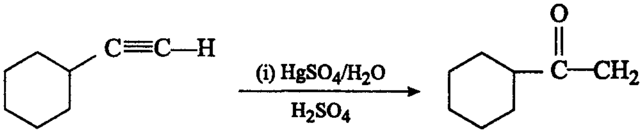
Tautomerisation

$CH_3-(CH_2)_4-CH_2-\overset{\overset{O}{\|}}{C}-H$

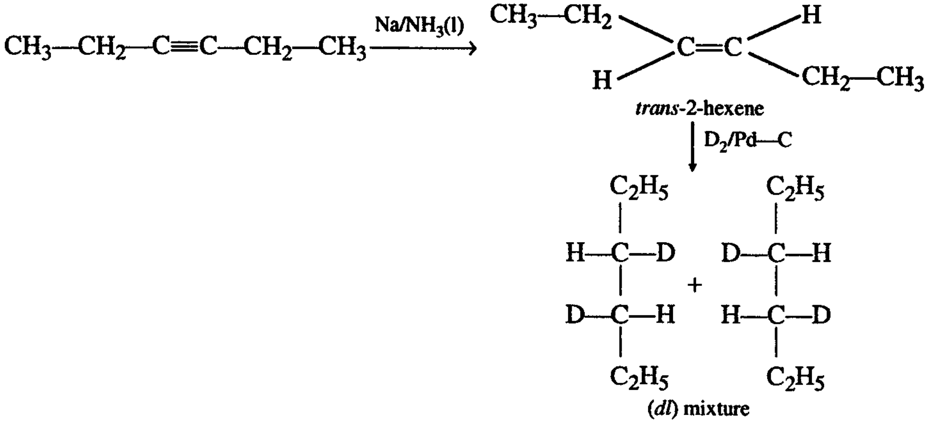
(c)



(d)



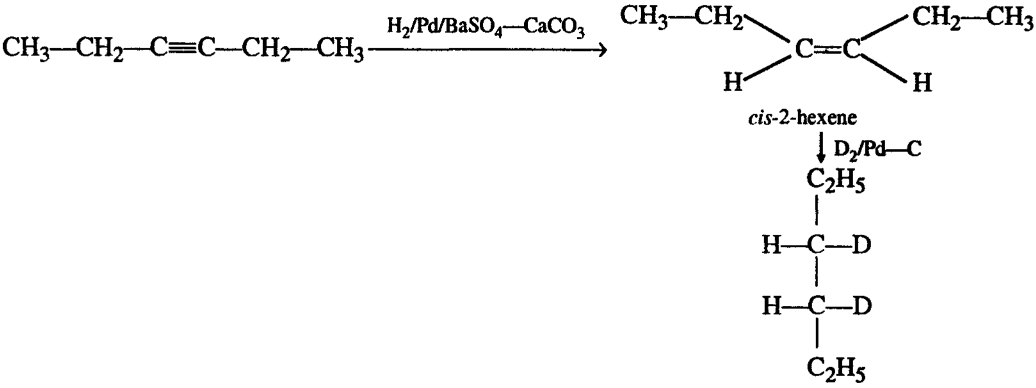
31. (a)



trans-2-hexene

(*dl*) mixture

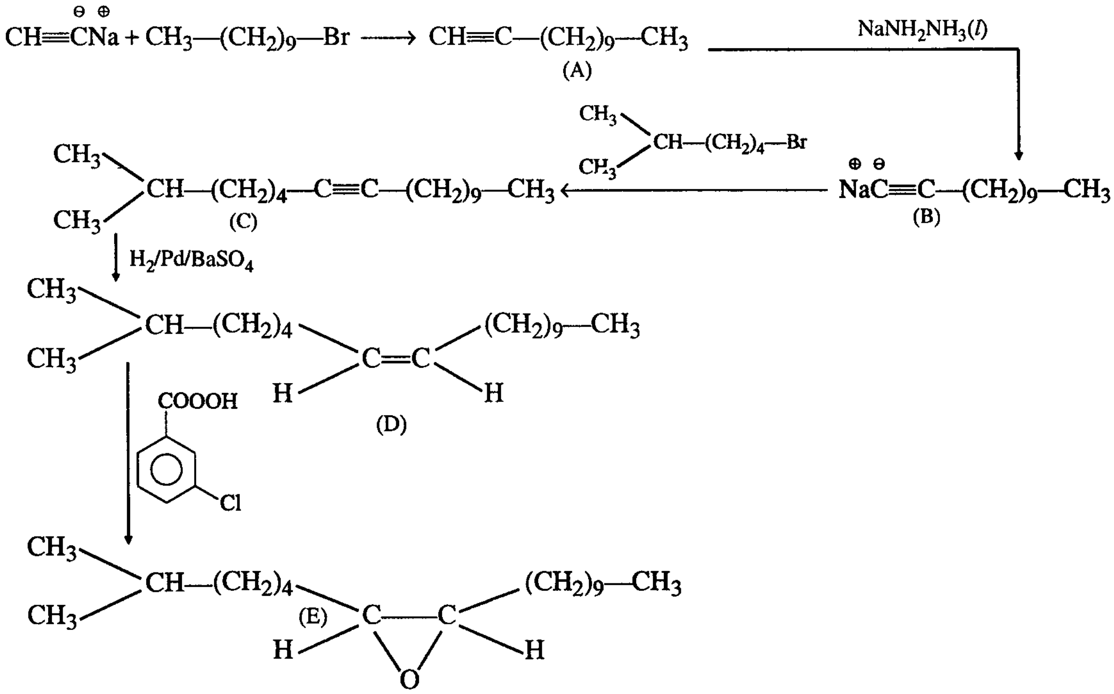
(b)



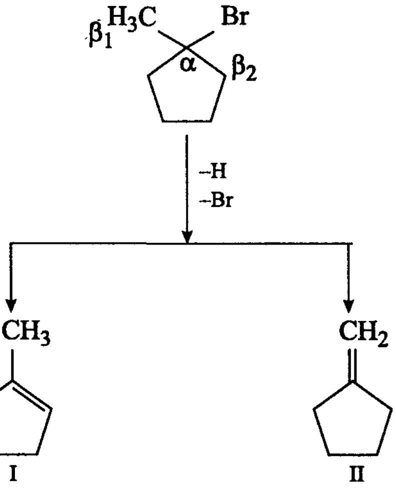
cis-2-hexene

meso form

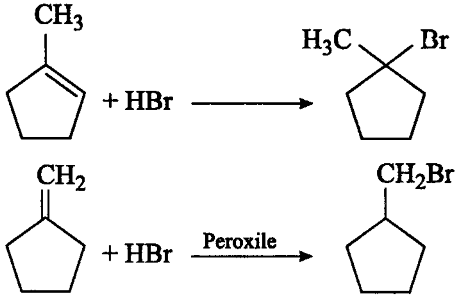
32.



33. (i) Both alkenes can be obtained as follows :

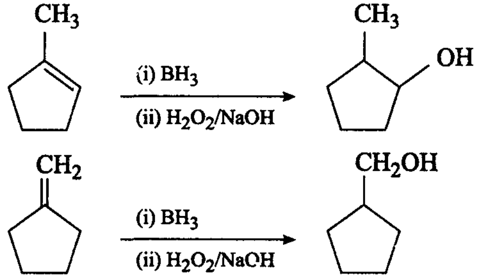


(ii)



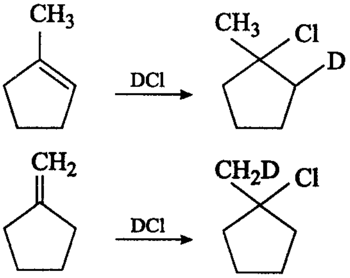
Thus both will give different product.

(iii)



Thus both will give different product.

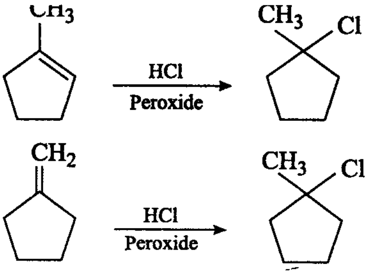
(iv)



Thus both will give different products.

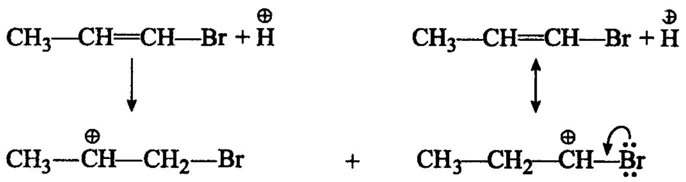
(v) HCl always gives electrophilic addition reaction.

(v)



Thus both will give same products.

34. (a) Consider the mechanism of the reaction :

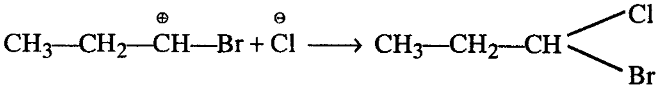


$$CH_3-CH=CH-Br+\overset{\oplus}{H} \quad CH_3-CH=CH-Br+\overset{\oplus}{H}$$

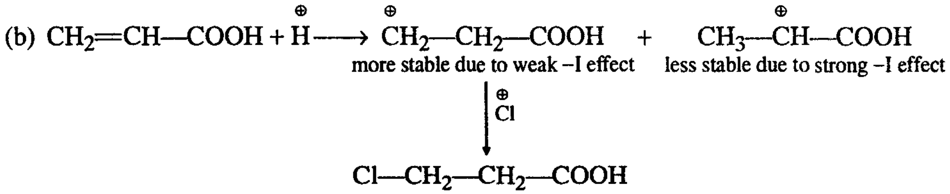
$$CH_3-\overset{\oplus}{C}H-CH_2-Br \quad + \quad CH_3-CH_2-\overset{\oplus}{C}H-\ddot{\underset{\cdot\cdot}{Br}}$$

Sec carbocation destabilesed by -I group (Br) which is present at β-carbon

Sec carbocation stabilised by delocalisation of positive charge by the vacant *d* orbital of Br which is present at α-carbon



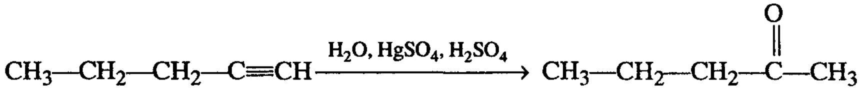
$$CH_3-CH_2-\overset{\oplus}{C}H-Br+\overset{\ominus}{Cl} \longrightarrow CH_3-CH_2-CH\begin{matrix}Cl\\Br\end{matrix}$$



$$\text{(b) } CH_2{=}CH{-}COOH + \overset{\oplus}{H} \longrightarrow \underset{\text{more stable due to weak −I effect}}{\overset{\oplus}{C}H_2{-}CH_2{-}COOH} + \underset{\text{less stable due to strong −I effect}}{CH_3{-}\overset{\oplus}{C}H{-}COOH}$$

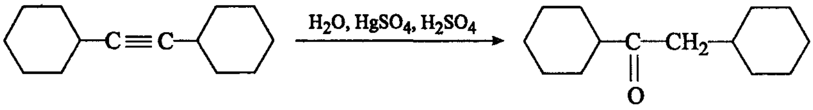
$$\xrightarrow{\overset{\ominus}{Cl}} Cl{-}CH_2{-}CH_2{-}COOH$$

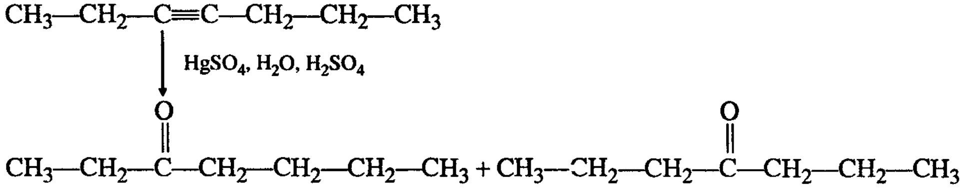
35.



$$\text{(a) } CH_3{-}CH_2{-}CH_2{-}C{\equiv}CH \xrightarrow{H_2O,\ HgSO_4,\ H_2SO_4} CH_3{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$$

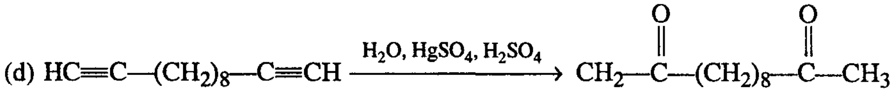
(b)





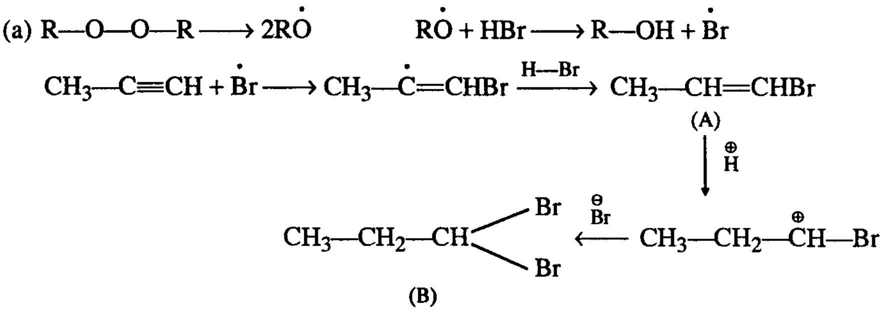
$$\text{(c) } CH_3{-}CH_2{-}C{\equiv}C{-}CH_2{-}CH_2{-}CH_3 \xrightarrow{HgSO_4,\ H_2O,\ H_2SO_4}$$

$$CH_3{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2{-}CH_2{-}CH_2{-}CH_3 + CH_3{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2{-}CH_2{-}CH_3$$



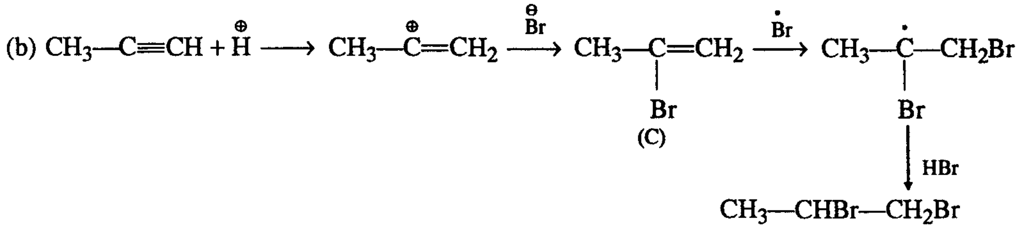
$$\text{(d) } HC{\equiv}C{-}(CH_2)_8{-}C{\equiv}CH \xrightarrow{H_2O,\ HgSO_4,\ H_2SO_4} CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}(CH_2)_8{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$$

36.

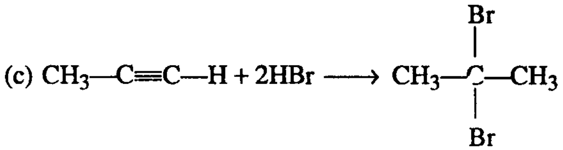


$$\text{(a) } R{-}O{-}O{-}R \longrightarrow 2R\dot{O} \qquad R\dot{O} + HBr \longrightarrow R{-}OH + \dot{B}r$$

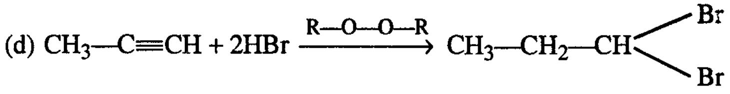
$$CH_3{-}C{\equiv}CH + \dot{B}r \longrightarrow CH_3{-}\dot{C}{=}CHBr \xrightarrow{H{-}Br} \underset{(A)}{CH_3{-}CH{=}CHBr} \xrightarrow{\overset{\oplus}{H}} CH_3{-}CH_2{-}\overset{\oplus}{C}H{-}Br \xrightarrow{\overset{\ominus}{Br}} \underset{(B)}{CH_3{-}CH_2{-}CH\langle{}^{Br}_{Br}}$$



$$\text{(b) } CH_3{-}C{\equiv}CH + \overset{\oplus}{H} \longrightarrow CH_3{-}\overset{\oplus}{C}{=}CH_2 \xrightarrow{\overset{\ominus}{Br}} \underset{(C)}{CH_3{-}\underset{\displaystyle Br}{\underset{|}{C}}{=}CH_2} \xrightarrow{\dot{B}r} CH_3{-}\underset{\displaystyle Br}{\underset{|}{\dot{C}}}{-}CH_2Br \xrightarrow{HBr} \underset{(D)}{CH_3{-}CHBr{-}CH_2Br}$$

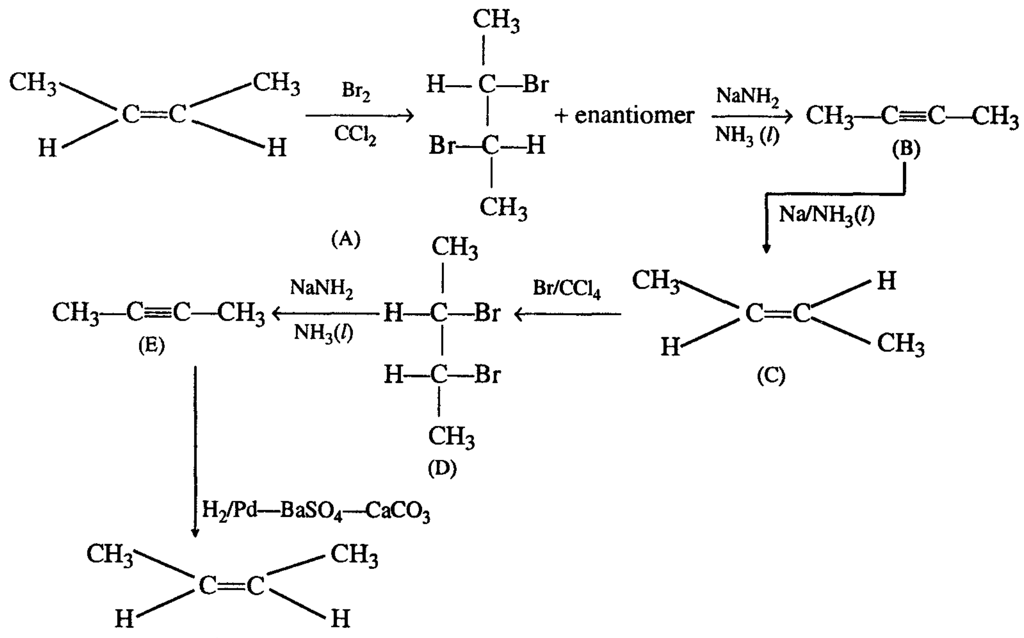


$$\text{(c) } CH_3{-}C{\equiv}C{-}H + 2HBr \longrightarrow CH_3{-}\underset{\displaystyle Br}{\underset{|}{\overset{\displaystyle Br}{\overset{|}{C}}}}{-}CH_3$$

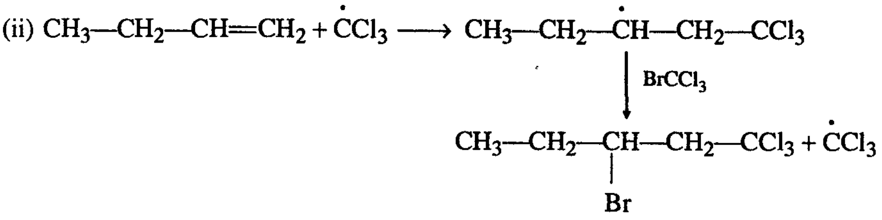


$$\text{(d) } CH_3{-}C{\equiv}CH + 2HBr \xrightarrow{R{-}O{-}O{-}R} CH_3{-}CH_2{-}CH\langle{}^{Br}_{Br}$$

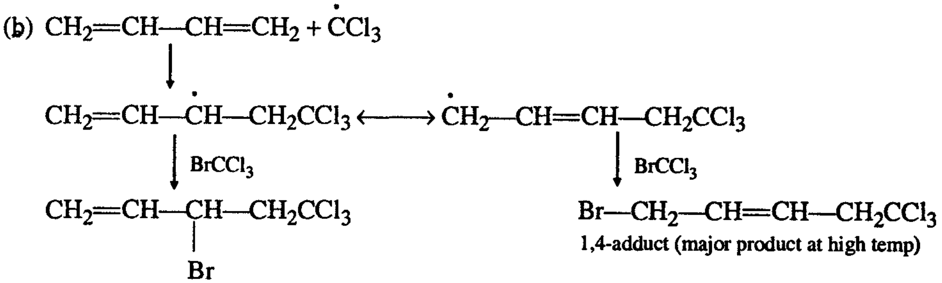
37.



38. (a) (i) $BrCCl_3 \xrightarrow{h\nu} \dot{B}r + \dot{C}Cl_3$



(ii) $$CH_3-CH_2-CH=CH_2+\dot{C}Cl_3 \longrightarrow CH_3-CH_2-\dot{C}H-CH_2-CCl_3 \xrightarrow{BrCCl_3} CH_3-CH_2-\underset{Br}{\underset{|}{C}H}-CH_2-CCl_3+\dot{C}Cl_3$$



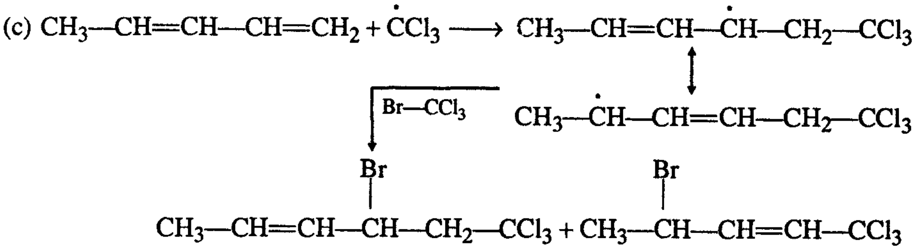
(b) $$CH_2=CH-CH=CH_2+\dot{C}Cl_3 \longrightarrow CH_2=CH-\dot{C}H-CH_2CCl_3 \longleftrightarrow \dot{C}H_2-CH=CH-CH_2CCl_3$$

$$CH_2=CH-\dot{C}H-CH_2CCl_3 \xrightarrow{BrCCl_3} CH_2=CH-\underset{Br}{\underset{|}{C}H}-CH_2CCl_3$$

1, 2-adduct (major product at low temp)

$$\dot{C}H_2-CH=CH-CH_2CCl_3 \xrightarrow{BrCCl_3} Br-CH_2-CH=CH-CH_2CCl_3$$

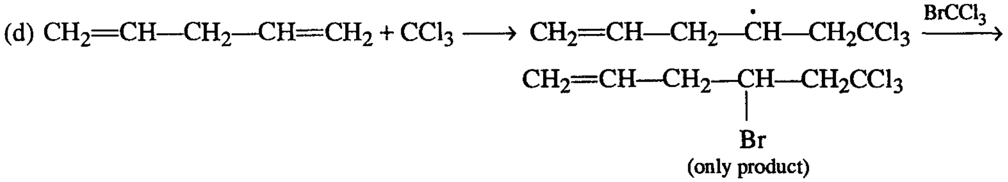
1,4-adduct (major product at high temp)



(c) $$CH_3-CH=CH-CH=CH_2+\dot{C}Cl_3 \longrightarrow CH_3-CH=CH-\dot{C}H-CH_2-CCl_3 \longleftrightarrow CH_3-\dot{C}H-CH=CH-CH_2-CCl_3$$

$$\xrightarrow{Br-CCl_3} CH_3-CH=CH-\overset{Br}{\overset{|}{C}H}-CH_2-CCl_3+CH_3-\overset{Br}{\overset{|}{C}H}-CH=CH-CCl_3$$

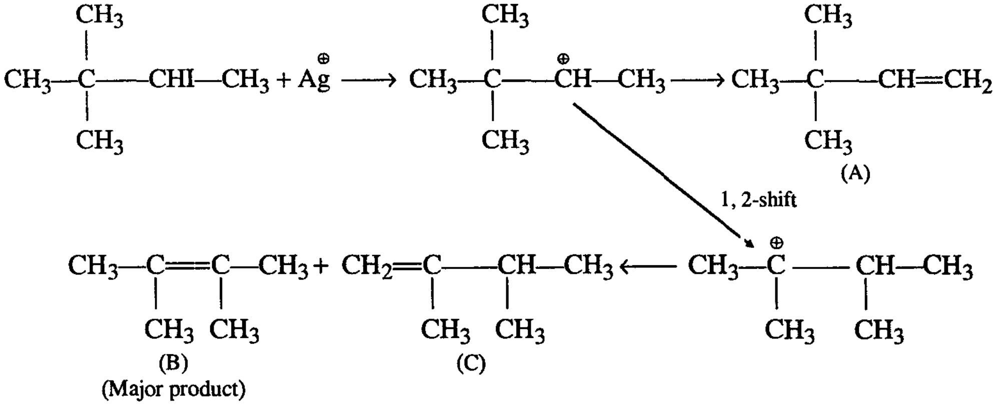
(1 : 1)



$$\text{(d) } CH_2=CH-CH_2-CH=CH_2+CCl_3\longrightarrow CH_2=CH-CH_2-\overset{\bullet}{C}H-CH_2CCl_3\xrightarrow{BrCCl_3}$$

$$\underset{\text{(only product)}}{CH_2=CH-CH_2-\underset{\underset{Br}{|}}{C}H-CH_2CCl_3}$$

39. Silver.nitrate reacts with alkyl iodide to give silver iodide and a cation.

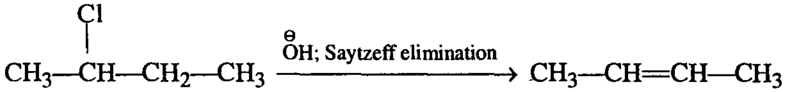


$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CHI-CH_3+\overset{\oplus}{Ag}\longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\oplus}{C}H-CH_3\longrightarrow \underset{\text{(A)}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=CH_2}$$

$$\xrightarrow{1,2\text{-shift}}$$

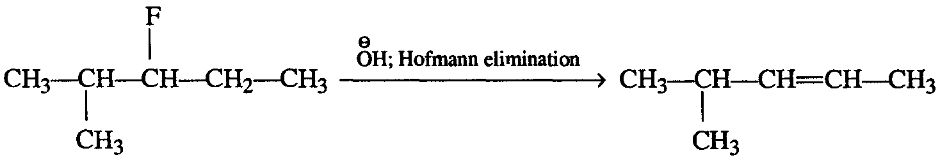
$$\underset{\substack{\text{(B)}\\ \text{(Major product)}}}{CH_3-\underset{\underset{CH_3}{|}}{C}=\underset{\underset{CH_3}{|}}{C}-CH_3}+\underset{\text{(C)}}{CH_2=\underset{\underset{CH_3}{|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_3}\longleftarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\oplus}{C}}-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

40. (a)



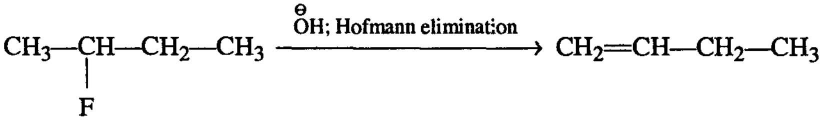
$$CH_3-\overset{\overset{Cl}{|}}{C}H-CH_2-CH_3\xrightarrow{\overset{\ominus}{O}H;\ \text{Saytzeff elimination}}CH_3-CH=CH-CH_3$$

(b)



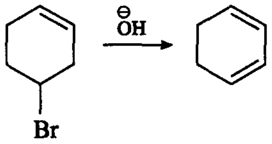
$$CH_3-\underset{\underset{CH_3}{|}}{C}H-\overset{\overset{F}{|}}{C}H-CH_2-CH_3\xrightarrow{\overset{\ominus}{O}H;\ \text{Hofmann elimination}}CH_3-\underset{\underset{CH_3}{|}}{C}H-CH=CH-CH_3$$

(c)

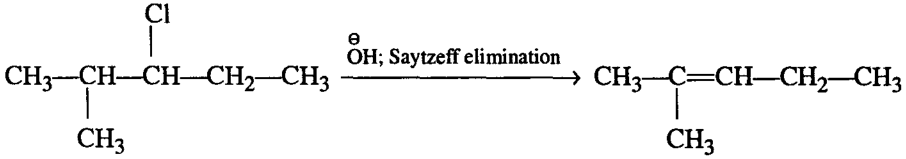


$$CH_3-\underset{\underset{F}{|}}{C}H-CH_2-CH_3\xrightarrow{\overset{\ominus}{O}H;\ \text{Hofmann elimination}}CH_2=CH-CH_2-CH_3$$

(d)

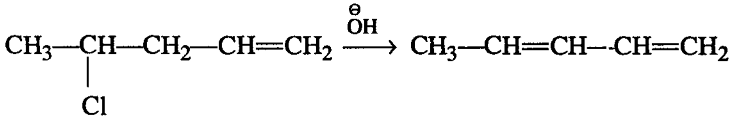


(e)



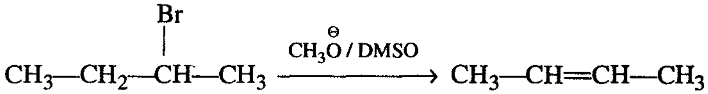
$$CH_3-\underset{\underset{CH_3}{|}}{C}H-\overset{\overset{Cl}{|}}{C}H-CH_2-CH_3\xrightarrow{\overset{\ominus}{O}H;\ \text{Saytzeff elimination}}CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CH_3$$

(f)



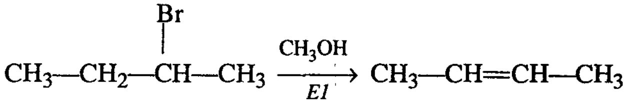
$$CH_3-\underset{\underset{Cl}{|}}{C}H-CH_2-CH=CH_2\xrightarrow{\overset{\ominus}{O}H}CH_3-CH=CH-CH=CH_2$$

41. (a) Elimination is taking place in the presence of strong base and polar aprotic solvent. Therefore, reaction is $E2$ reaction.



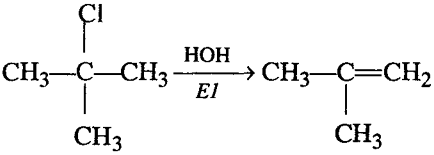
$$CH_3-CH_2-\overset{Br}{\overset{|}{C}H}-CH_3 \xrightarrow{CH_3\overset{\ominus}{O}\,/\,DMSO} CH_3-CH=CH-CH_3$$

(b) Base is weak and solvent is polar protic, therefore, reaction is $E1$.



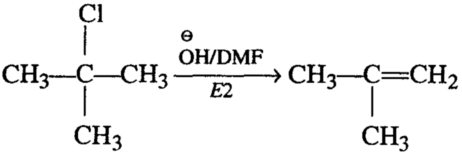
$$CH_3-CH_2-\overset{Br}{\overset{|}{C}H}-CH_3 \xrightarrow[E1]{CH_3OH} CH_3-CH=CH-CH_3$$

(c)



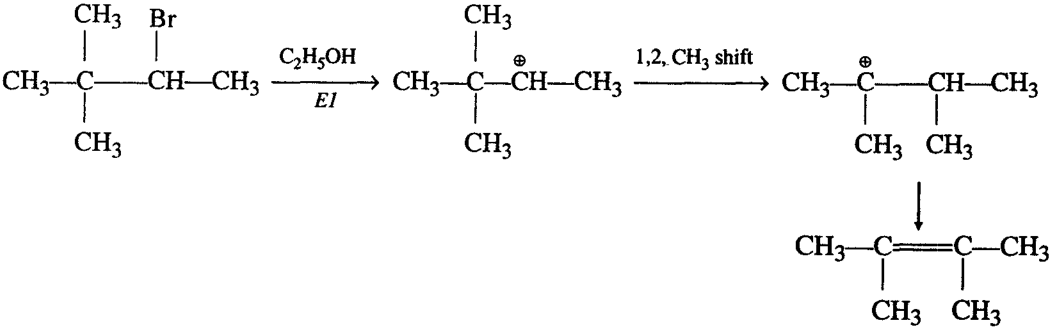
$$CH_3-\underset{CH_3}{\overset{Cl}{C}}-CH_3 \xrightarrow[E1]{HOH} CH_3-\underset{CH_3}{C}=CH_2$$

(d)



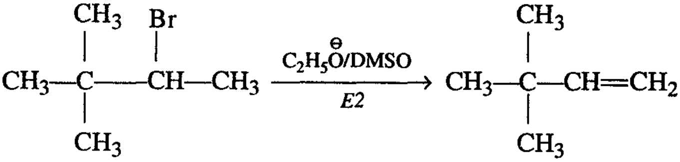
$$CH_3-\underset{CH_3}{\overset{Cl}{C}}-CH_3 \xrightarrow[E2]{\overset{\ominus}{O}H/DMF} CH_3-\underset{CH_3}{C}=CH_2$$

(e)



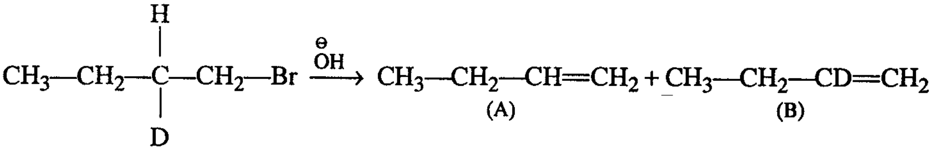
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{Br}{CH}-CH_3 \xrightarrow[E1]{C_2H_5OH} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{\oplus}{C}H-CH_3 \xrightarrow{1,2,\ CH_3\ shift} CH_3-\underset{CH_3}{\overset{\oplus}{C}}-\underset{CH_3}{CH}-CH_3 \longrightarrow CH_3-\underset{CH_3}{C}=\underset{CH_3}{C}-CH_3$$

(f)



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{Br}{CH}-CH_3 \xrightarrow[E2]{C_2H_5\overset{\ominus}{O}/DMSO} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=CH_2$$

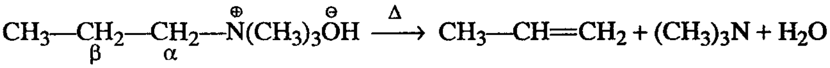
42. (a) In the substrate, β-carbon has hydrogen as well as D, hence one product will be formed due to breaking of C—H bond and other product due to C—D bond.



$$CH_3-CH_2-\underset{D}{\overset{H}{C}}-CH_2-Br \xrightarrow{\overset{\ominus}{O}H} \underset{(A)}{CH_3-CH_2-CH=CH_2} + \underset{(B)}{CH_3-CH_2-CD=CH_2}$$

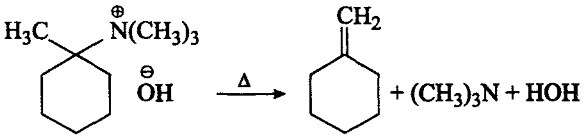
(b) Amount of product (B) will be more than the amount of (A) because (B) is formed due to breaking of C—H bond which is weaker bond whereas (A) is formed due to the breaking of C—D bond which is stronger bond.

43. (a)

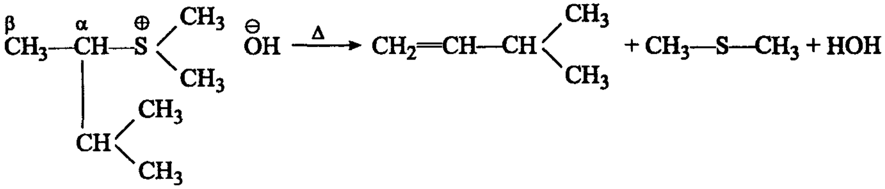


$$\mathrm{CH_3{-}\underset{\beta}{CH_2}{-}\underset{\alpha}{CH_2}{-}\overset{\oplus}{N}(CH_3)_3\overset{\ominus}{O}H \xrightarrow{\Delta} CH_3{-}CH{=}CH_2 + (CH_3)_3N + H_2O}$$

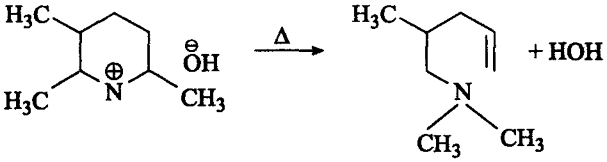
(b)

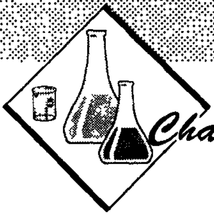


(c)



(d)





Chapter 6

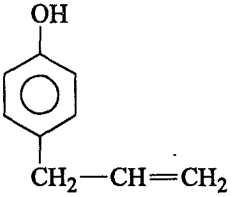
ARENES AND AROMATICITY

6.0 AROMATIC HYDROCARBONS (ARENES)

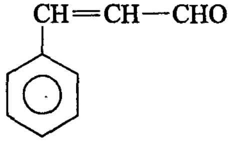
Benzene and compounds resembling benzene in chemical behaviour are known as **aromatic compounds.**

Benzene

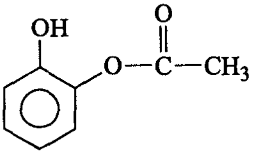
The generic name 'aromatic' was given originally to a structurally diverse collection of compounds which had one common property, a fragrrant odour (sweet smell). The fragrance was an important specificity, since many aromatic compounds smell. In fact, some contain other additional functional groups which are responsible for the characteristic fragrances of cloves, cinnamon, vanilla, wintergreen and roses.



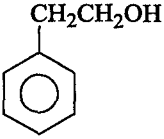
Eugenol (Cloves)



Cinnamaldehyde (Cinnamon)

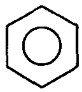


Methylsalicylate (Wintergreen)

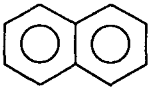


2-phenylethanol (Roses)

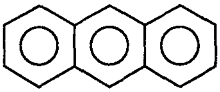
These compounds differ widely from aliphatic hydrocarbons in their chemical behaviour and all of them have been shown to be closely related to the parent cyclic hydrocarbon, benzene. This hydrocarbon (C_6H_6), though expected to be highly unsaturated, shows a high degree of **stability.** Benzene and all the aromatic compounds show a tendency to undergo **substitution** rather than **addition** reactions. In all such reactions the parent structure, called benzene nucleus, is retained. Aromatic compounds which possess benzene nucleus (or nuclei) are termed **benzenoid compounds,** for example :



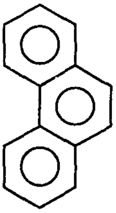
Benzene



Naphthalene



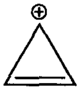
Anthracene



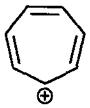
Phenanthrene

The term aromatic, however also includes another class of compounds possessing aromatic character but having structures that differ considerably from that of benzene. Such compounds are called non-benzenoid aromatics.

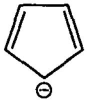
Non-benzenoid aromatic compounds may be cation, anion or neutral species, for example :



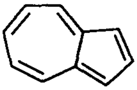
Cyclopropenyl cation



Tropylium ion (cycloheptatrienyl cation)



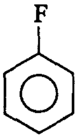
Cyclopentadienyl anion



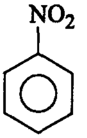
Azulene

6.1 NOMENCLATURE OF BENZENE DERIVATIVES

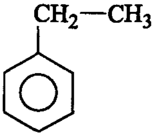
In systematic nomenclature of benzene derivatives all the benzenoid compounds are named as substituted benzenes. Two systems are used in naming monosubstituted benzenes. In certain compounds benzene is the parent name and the substituent is simply indicated by a prefix. For example :



Fluorobenzene

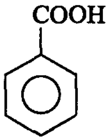


Nitrobenzene

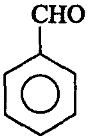


Elthylbenzene

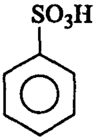
For other compounds, the substituent and the benzene ring taken together may form a new parent name. Methylbenzene is usually called **toluene**, hydroxybenzene is almost always called phenol and aminobenzene is almost always called aniline. The following are the common names of some compounds which are still in use :



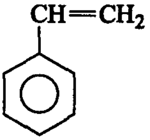
Benzoic acid



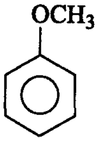
Benzaldehyde



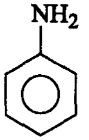
Benzenesulphonic acid



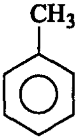
Styrene



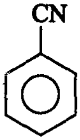
Anisole



Aniline

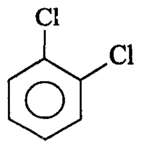


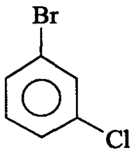
Toluene

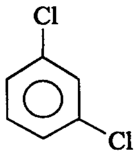


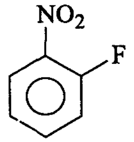
Benzonitrile

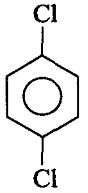
When two substituents are present, three positional isomers are possible. Their relative positions are indicated by the prefixes *ortho*, *meta* and *para* (abbreviated as *o*-, *m*- and *p*-) or by the use of number. For example :

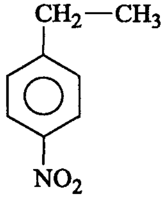

1, 2-Dichlorobenzene
(*o*-Dichlorobenzene)


1-Bromo-3-chlorobenzene
(*m*-Bromochlorobenzene)

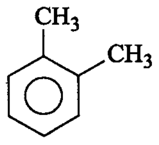

1, 3-Dichlorobenzene
(*m*-Dichlorobenzene)

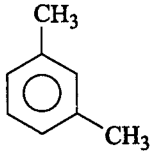

1-Fluoro-2-nitrobenzene
(*o*-Fluoronitrobenzene)

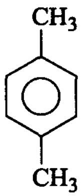

1, 4-Dichlorobenzene
(*p*-Dichlorobenzene)


1-Ethyl-4-nitrobenzene
(*p*-Ethylnitrobenzene)

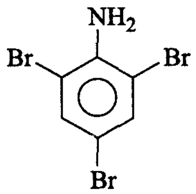
The dimethylbenzenes are often called xylenes

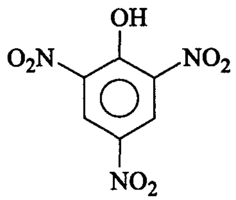

o-Xylene

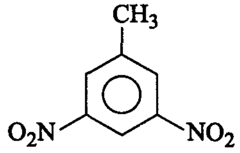

m-Xylene


p-Xylene

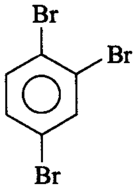
When more than two groups are on a benzene ring, their position must be numbered. *o*-, *m*- or *p*- designation is not acceptable. If one of the groups is associated with the common name, the molecule can be named as a derivative of the monosubstituted compound numbering from the group designated in the common name. For example :

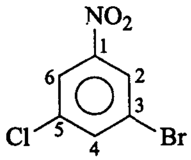

2, 4, 6-Tribromoaniline
(NH_2 group is associated with
the common name aniline)


2, 4, 6-Trinitrophenol
(OH group is associated with
the common name phenol)


3, 5-Dinitrotoluene
(CH_3 group is associated with
the common name toluene)

If all the groups are the same, each is given a number, the sequence being the one that gives the lowest sum of numbers, if the groups are different, then the last-named group (according to the alphabetical order) is understood to be in position 1 and the other groups follow the sequence numbers of the lowest sum, for example :

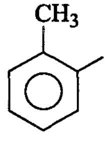

1, 2, 4-Tribromobenzene
(not 1, 3, 4-tribromobenzene)

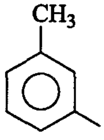

3-Bromo-5-chloronitrobenzene

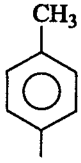
6.2 THE ARYL GROUP

The univalent group obtained by the removal of one hydrogen atom from the benzene nucleus is called phenyl (usually written as Ph—, C_6H_5— or ϕ) group and the univalent group derived from any other aromatic hydrocarbon is known as aryl group (Ar—) some of the common aryl groups are :

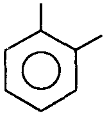
C_6H_5
Phenyl

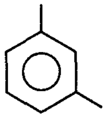

o-Tolyl


m-Tolyl


p-Tolyl

Removal of two hydrogen atoms from the benzene nucleus gives rise to divalent phenylene group. For example :


o-Phenylene


m-Phenylene


p-Phenylene

The groups derived by the removal of hydrogen atom from the side chain are called **arakyl** groups. For example :

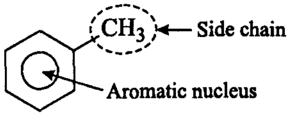
$C_6H_5\text{—}CH_2\text{—}$
Benzyl
(Bz)

$C_6H_5\text{—}CH<$
Benzal

$C_6H_5\text{—}C\leqq$
Benzo

6.3 AROMATIC NUCLEUS AND SIDE CHAIN

The basic carbon skeleton of the benzene ring is called the **aromatic nucleus.** An alkyl group attached to the aromatic ring by the replacement of a hydrogen atom is called **side chain.**



6.4 STRUCTURE OF BENZENE

6.4.1 Molecular Formula and Kekule' Structure

Elemental analysis and molecular weight determination have shown that the molecular formula of benzene is C_6H_6.

Since alkane having six carbon atoms is C_6H_{14}, benzene (C_6H_6) is expected to be a highly unsaturated hydrocarbon which is further indicated by its following reactions :

(i) It adds three molecules of halogen forming benzene hexahalide.

$$C_6H_6 + 3Cl_2 \xrightarrow{h\nu} \underset{\text{Benzene hexachloride (BHC)}}{C_6H_6Cl_6}$$

(ii) It may catalytically be hydrogenated to cyclohexane.

$$C_6H_6 + 3H_2 \xrightarrow[\Delta]{Ni}$$


C_6H_{12}

(iii) It forms a triozonide with ozone.

$$C_6H_6 + 3O_3 \longrightarrow \underset{\text{Benzene triozonide}}{C_6H_6O_9}$$

The above reactions indicate that benzene contains three double bonds.

However, benzene does not give the following characteristic reactions of double bonds :

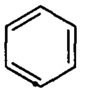
(i) Benzene remains unaffected on treatment with $KMnO_4$ under normal conditions.

(ii) Benzene does not give addition reaction with halogen acids.

(iii) In the absence of sunlight and in the presence of Lewis acid catalyst, it undergoes electrophilic substitution rather than addition reactions.

The above reactions lead to the conclusion that although benzene contains three double bonds, these are remarkably different from the ordinary double bonds. This difference gives rise to aromatic properties (*i.e.*, unusual degree of saturation and stability).

Kekule' (1865) was the first to suggest arbitrarily a ring structure for benzene. He proposed structure (I), which is known as Kekule's structure of benzene and it satisfies the following observations :



(I)

(i) That benzene contains three double bonds.

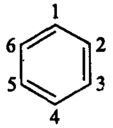
(ii) All the carbons and hydrogen atoms in benzene are equivalent; consequently there is only one possible mono-substituted derivative.

However, structure (I) failed to explain the following characteristic properties of benzene :

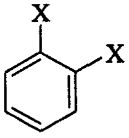
(i) Heat of hydrogenation of benzene (experimental value = – 49·8 kcal/mole) is much lower than expected from Kekule's structure (I) (cyclohexatriene, 85·8 kcal/mole, theoretical value). Benzene is 36 kcal/mole (85·5–49·8) more stable than 1, 3, 5-cyclohexatriene (*i.e.*, Kekule's structure). Thus benzene has extra stability.

(ii) Although benzene contains three double bonds, it is quite stable and behaves like a saturated compound (undergoes substitution instead of addition reactions). Thus benzene has unusual degree of saturation.

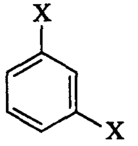
(iii) Benzene forms only three disubstituted derivatives of the formula $C_6H_4X_2$ or C_6H_4XY. The proposed structure should give four disubstituted derivatives instead of three since C_1—C_2 bond is different from C_1—C_6 bond; the former has a single bond character while the latter has a double bond character.



(I)

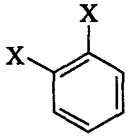


(II)



(III)

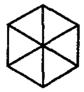
(IV)



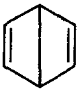
(V)

In other words, structure (I) predicts four (two *ortho*, one *meta* and one *para*) rather than the observed three isomeric disubstituted products (one *ortho*, one *meta* and one *para*) for $C_6H_4X_2$.

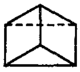
In order to meet the objections against Kekule's structure, a number of alternative formulae were suggested by different scientists from time to time. However, none of them could satisfy all the observed properties of benzene and were consequently rejected.



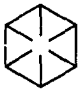
Claus diagonal structure (1867)



Dewar's parallel structure (1867)



Ladenberg's prism structure (1869)



Baeyer's and Armstrong centric structure (1887)

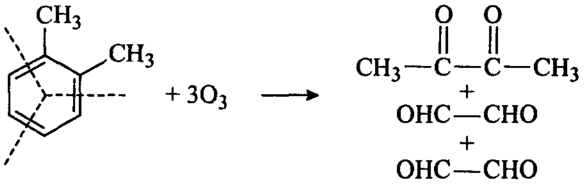
Thiele's partial valeney structure (1899)

In 1872 Kekule' pointed out that carbon atoms in benzene are in a state of continuous vibration owing to which each carbon-carbon bond sometimes behaves as a C—C single bond and sometimes behaves as a C=C double bond. Thus the two structures (**Ia** and **Ib**) are in a state of continuous oscillation and the structure of benzene is neither represented by Ia nor by Ib but it is a combination of the two.

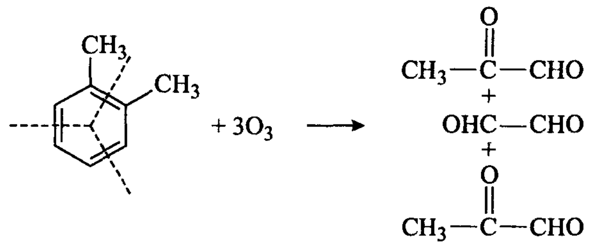
Ia **Ib**

This left no difference between the two *ortho* positions and hence explained the formation of only three disubstituted derivatives. This was referred to as the Kekule's dynamic formula of benzene.

If the modified structure for benzene, as suggested by Kekule', is considered to be correct, then, theoretically one should get three molecules of glyoxal, one molecule of dimethylglyoxal and two molecules of methylglyoxal from the ozonolysis of two molecules of *o*-xylene; in fact at that time two scientists got these from ozonolysis of two molecules of *o*-xylene.



$$+ 3O_3 \longrightarrow CH_3—\overset{\overset{\large O}{\|}}{C}—\overset{\overset{\large O}{\|}}{C}—CH_3 + OHC—CHO + OHC—CHO$$



$$+ 3O_3 \longrightarrow CH_3—\overset{\overset{\large O}{\|}}{C}—CHO + OHC—CHO + CH_3—\overset{\overset{\large O}{\|}}{C}—CHO$$

However, the modified Kekule' structure for benzene also fails to explain the extra stability and C—C bond lengths of benzene.

6.4.2 Present Day Position of the Structure of Benzene

Stability and carbon-carbon bond lengths of benzene : Now-a-days X-ray diffraction and electron—diffraction studies have led scientists to conclude that :

(i) All the carbons and hydrogens in benzene are planar.

(ii) All the six carbon atoms are arranged at the corners of a regular hexagon and the C—C—C bond angles are 120°. All C—C bonds are equal in length (1·39 Å) and this value of bond length lies between the values of C—C single bond (1·54 Å) and C=C double bond (1·34 Å).

Both the valence bond and molecular orbital theories can well explain the modern structure of benzene as well as the peculiar properties of benzene, *i.e.*,

(i) unusual thermal stability (low heat of hydrogenation and low heat of combustion), and

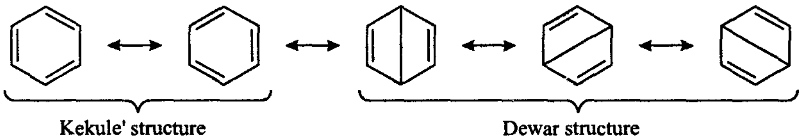
(ii) unusual chemical stability (electrophilic substitution rather than the addition reactions and resistance to oxidation by aqueous $KMnO_4$, HNO_3 and all except vigorous oxidising agents) called aromatic characters.

The following modern structures of benzene explain all the above facts which could not be explained by its Kekule' structure :

(i) Resonance Structure

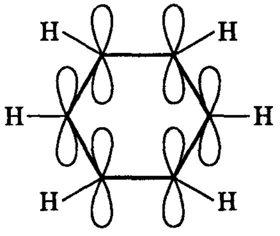
(ii) Molecular Orbital (MO) Picture

(i) Resonance Structure : According to valence bond theory benzene is considered to be a resonance hybrid of two Kekule' and three Dewar structures, the Kekule' structures making major contributions.

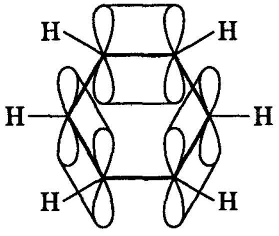


Since a resonance hybrid is always more stable than any of the contributing structures, benzene should be more stable than expected from any of the above structures. This is the case also as shown by its high resonance energy (36 kcal/mole). Further, the resonance structure also explains the equivalence of all C—C bond lengths and the formation of only three disubstituted derivatives.

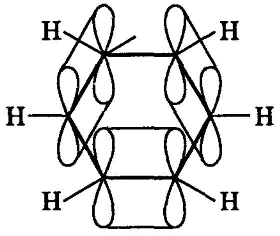
(ii) Molecular Orbital (MO) Picture : All the carbon atoms in benzene are in sp^2 hybrid state. Each carbon has three sp^2 AO's and one p AO. Each AO, p or sp^2, contains one electron. The p AO is perpendicular to the plane of three sp^2 AO's which are oriented in space in a plane trigonally. Each carbon utilises its three sp^2 AO's to form two sp^2-sp^2 σ bonds with two adjacent carbons and one sp^2-s *sigma* bond with a hydrogen atom. Thus the six carbons form a planar ring in which C—H bonds are also co-planar as shown in structure (I). Thus the six p oribitals of the six carbon atoms are parallel to each other and perpendicular to the plane of the molecule (structure I).



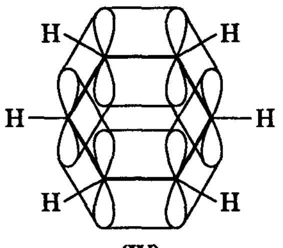
(I)



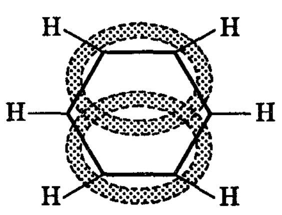
(II)



(III)



(IV)



(V)

The p orbital of each carbon atom can overlap (parallel to axis) with the p orbital of its neighbouring carbon atom on both the sides as shown in structures (II) and (III). The chances of overlap on both the sides are equal, thus all the six p orbitals are considered as overlapped with each other (structure IV). Thus, electron clouds are formed above and below the plane of the benzene ring (structure V).

All the carbon atoms in benzene being in sp^2 hybrid state and each C—C and C—H bond being formed by sp^2-sp^2 and sp^2-s overlap, respectively, the C—C—C and H—C—C bond angles are 120° and the molecule has a planar structure.

Since six p orbital have overlapped (combined), six π molecular orbitals (MO's) are formed three bonding π MO's and three antibonding π molecular orbitals (π^* MO's) as depicted in Fig. 6.1

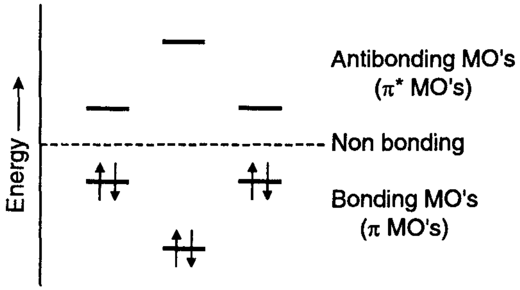
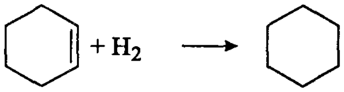


Fig. 6.1

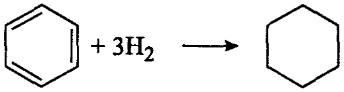
6.5 STABILITY OF BENZENE

The ability of electrons to participate in more than one bond is called delocalisation. A compound with delocalised electrons is more stable than that compound would be if all its electrons were localised. The extra stability a compound gains as a result of having delocalised electrons is called **delocalisation energy** or **resonance energy**. Let us determine how much more stable benzene with three pairs of delocalised *pi* electrons is than a hypothetical "cyclohexatriene" with three pairs of localised *pi* electrons.

The heat of hydrogenation of cyclohexene, a compound with one localised double bond has been experimentally determined to be – 28·6 kcal/mole. We would expect "cyclohexatriene" a hypothetical compound with three localised double bonds to have a heat of hydrogenation three times that of the compound with one double bond. Therefore, we can calculate the heat of hydrogenation of "cyclohexatriene" to be 3 × (– 28·6) = – 85·8 kcal/mole.



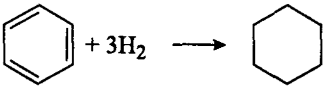
ΔH° = –28.6 kcal/mole
(Experimental)



ΔH° = –85.8 kcal/mole
(Calculated)

Cyclohexatriene
hypothetical

When the heat of hydrogenation of benzene was experimentally determined, it was found to be – 49·8 kcal/mole much smaller than that calculated for the hypothetical "cyclohexatriene" molecule.



ΔH° = – 49.8 kcal/mole
(Experimental)

Benzene

The only way to account for the difference in the heat of hydrogenation is for the reactants to have different stabilities. Since the experimental heat of hydrogenation for benzene is 36 kcal/mole [– 49·8 – (– 85·8)] less than the heat of hydrogenation calculated for cyclohexatriene, benzene must be 36 kcal/mole more stable than cyclohexatriene.

Because benzene and "cyclohexatriene" have different stabilities, they must be different compounds. Benzene has six delocalised *pi* electrons, whereas hypothetical "cyclohexatriene" has six localised *pi* electrons. The difference in energy btween them is the resonance energy of benzene. The resonance energy tells us how much more stable a compound with delocalised electrons is than that it would be if its electrons were localised. Benzene with six delocalised *pi* electrons is 36 kcal/mole more stable than hypothetical "cyclohexatriene" with six localised *pi* electrons.

Notice that the resonance energy is the energy by which benzene is **stabilised;** it is therefore an energy that benzene does not have. The resonance energy of benzene has been estimated in several different ways (heat of hydrogenation, heat of formation and heat of combustion); these estimates range from 30–41 kcal/mole. The important point, however, is not the exact value of this number, but the fact that it is **large**. Thus benzene is very stable compound.

This special stability has come to be known as benzene's **aromatic character** or **aromaticity.**

6.6 AROMATICITY : THE HÜCKEL RULE

It is clear that benzene is an especially stable compound. A number of other compounds have a similar special stability, which is called aromaticity. To be aromatic a compound must conform to *all* of the following criteria :

(i) Aromatic compounds have a cyclic arrangement of *p* orbitals. Thus aromaticity is a property of certain cyclic compounds.

(ii) There is a *p*-orbital on every atom of an aromatic ring.

(iii) Aromatic rings are planar; this planarity allows the *p*-orbitals on every atom to overlap.

(iv) The cyclic arrangement of *p* orbitals in an aromatic compounds, must contain $(4n + 2)\,\pi$ electrons, where n is any integer (0, 1, 2, 3, 4, ...). In other words, aromatic compounds have 2, 6, 10, 18, ..., *pi* electrons.

These criteria for aromatic behaviour were first recognised by Erich Hückel. They are often called collectively the **Hückel $4n + 2$ rule** or simply the **$4n + 2$ rule**.

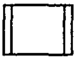
On the other hand, if such system contains $(4n)\,\pi$ electrons it will be **antiaromatic**. Antiaromatic systems are specially unstable. Thus in antiaromatic compounds delocalisation of the *pi* electrons over the ring results in an increase in the electronic energy. Thus in antiaromatic compounds delocalisation decreases stability of the system by increase in energy. Antiaromatic compounds are much less stable even than similar nonaromatic compounds.

Hückel rule can be applied to simple annulenes.

6.6.1 Application of Hückel Rule to Simple Annulenes

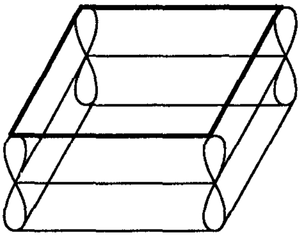
An annulene is monocylic hydrocarbon with alternating single and double bonds. Since carbon atoms occur as doubly bonded pairs, an annulene must have an even number of carbon atoms. Annulenes are named [*x*]annulene where *x* is the number of carbons in the ring. Thus, cyclooctatetraene becomes [8]annulene, cyclodecapentaene becomes [10]annulene and so on. Hückel rule is easily used to determine whether an annulene is aromatic or antiaromatic.

Cyclobutadiene : The simplest annulene is [4]annulene or cyclobutadiene.



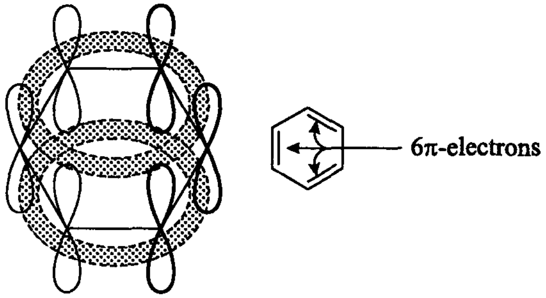
[4]Annulene

Cyclobutadiene has four sp^2 hybrid carbon atoms with the four unhybridised *p* orbitals forming a continuous ring. There are four *pi* electrons (two *pi* bonds in the classical structure), so it is a $4n$ system, with $n = 1$. Thus cyclobutadiene is antiaromatic and its conjugation should make it less stable.



Cyclobutadiene is an antiaromatic system with four *pi* electrons.

Benzene : Benzene is [6]annulene. It is a cyclic compound with the ring composed of sp^2 hybrid carbon atoms. The molecule can easily achieve a planar structure with a continuous ring of overlapping *p* orbitals. There are six *pi* electrons in benzene, so it is a $(4n + 2)\ \pi$ system with $n = 1$. Thus benzene is aromatic.

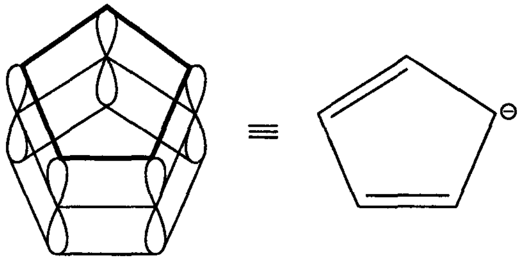


Overlapping *p*-orbitals in *benzene*
Benzene is an aromatic system with six π electrons

6.6.2 Aromatic Ions

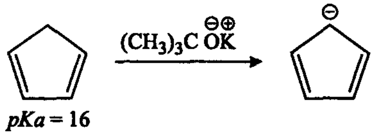
Up to this point we have discussed aromaticity using the annulenes as examples. Annulenes are uncharged molecules having even number of carbon atoms. Hückel rule also applies to the systems having odd number of carbon atoms and bearing positive or negative charges.

The Cyclopentadienyl Ions : Cyclopentadienyl anion with six *pi* electrons is aromatic.

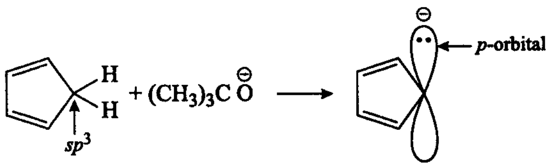


Cyclopentadienyl anion

It is prepared from cyclopentadiene. Cyclopentadiene is 10^8 times more acidic than a terminal alkyne. In fact, cyclopentadiene is nearly as acidic as water and more acidic than any alcohol. It can be deprotonated by potassium *tert*-butoxide.

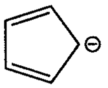


Hückel rule predicts that the cyclopentadienyl anion is aromatic, and this explains why cyclopentadiene is much more acidic than other hydrocarbons. Cyclopentadiene is neither aromatic nor antiaromatic because its ring contains an sp^3 hybrid (—CH_2—) carbon atom. This carbon has no unhybridised *p* orbital, so there can be no continuous ring of *p* orbitals. Deprotonation of the —CH_2— group leaves an orbital occupied by a pair of electrons. This orbital can rehybridise to a *p* orbital, completing a ring of *p* orbitals containing six *pi* electrons; the two electrons on the deprotonated carbon, plus the four electrons in the original double bonds. Thus, the cyclopentadienyl anion is aromatic.

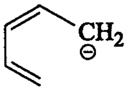


Cyclopentadienyl anion

When we say that the cyclopentadienyl anion is aromatic, this does not imply that it is as stable as benzene. The fact that this ion is aromatic implies that it is more stable than the corresponding open chain ion.

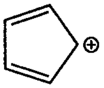


More stable
(aromatic)



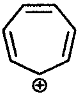
Less stable
(non-aromatic)

Cyclopentadienyl cation

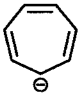


Cyclopentadienyl cation,
4 π-electrons antiaromatic;
highly unstable.

The cycloheptatrienyl ions

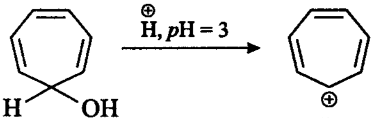


Cycloheptatrienyl
cation, (tropylium ion);
6 π-electrons, aromatic.



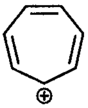
Cycloheptatrienyl
anion; 8 π-electrons,
antiaromatic if planar.

Cycloheptatrienyl cation is prepared from cycloheptatrienol. When this compound is treated with sulphuric acid, the formation of cycloheptatrienyl cation takes place very readily. This is the first cation that is stable in an aqueous solution.

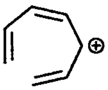


Tropylium ion

Some tropylium salts can be isolated and stored for months without decomposition. Aromatic tropylium ion is not necessarily as stable as benzene. The tropylium ion's aromaticity implies that the cyclic ion is more stable than the corresponding open-chain ion.



Aromatic
(more stable)

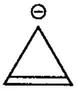


Non-aromatic
(less stable)

In contrast to the easy formation of the tropylium cation, the corresponding anion is difficult to prepare because it is antiaromatic, hence highly unstable. Cycloheptatriene is about as acidic as propene ($pKa = 53$).

The Cyclopropenyl ions

Cyclopropenyl cation, 2π-electrons aromatic



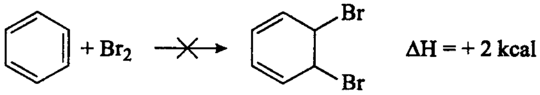
Cyclopropenyl anion, 4π-electrons antiaromatic

Cyclopropenyl cation is prepared from cyclopropenyl bromide. When this compound is treated with water, it ionises and gives cyclopropenyl cation.

6.7 CHEMICAL REACTIONS OF BENZENE

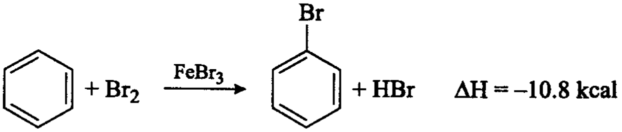
Benzene ring is present in all arenes and their derivatives. Therefore, our study of aromatic compounds must begin with that of benzene.

The characteristic reaction of aromatic compounds is substitution. One might predict addition because of the high degree of unsaturation in benzene and other aromatic compounds. However, addition would destroy one or more of the double bonds and thus the aromaticity. After addition no longer would there be a *p* orbital on every carbon of the ring allowing continuous overlap of the six *pi* electrons. With substitution, however, the integrity of the benzene ring is preserved thus there is no loss of aromaticity.



Addition of bromine to benzene is endothermic because it requires the loss of aromatic stability. The addition is not seen under normal conditions.

The substitution gives an aromatic product. The substitution is exothermic and it occurs readily in the presence of Lewis acid as catalyst.

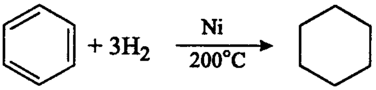


6.7.1 Addition Reactions

As discussed above, benzene resists addition under normal conditions, however, under special conditions, it undergoes addition reactions which show the presence of three double bonds. The following are important addition reactions of benzene :

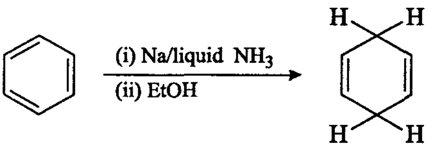
(a) Reduction :

(i) *Catalytic hydrogenation*



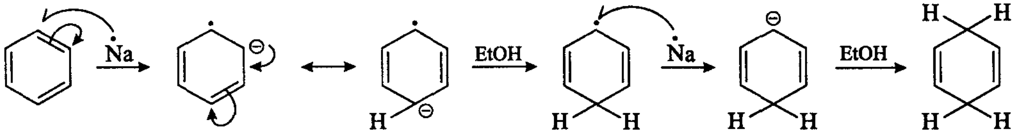
Cyclohexane

(ii) *Birch reduction* : Benzene can also be reduced to 1, 4-cyclohexadiene on treatment with lithium or sodium metal in liquid ammonia and a proton source such as ethanol.



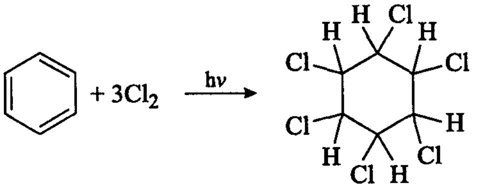
1, 4-cyclohexadiene

Mechanism :



All aromatic hydrocarbons having at least one benzene ring give this reduction.

(b) Addition of halogens : Benzene on treatment with halogens in sunlight or in the presence of a free radical initiator undergoes free radical addition to give benzene hexahalides.

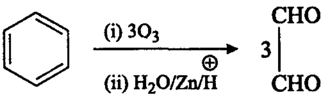


Benzene hexachloride
(BHC or 666)

Eight stereoisomers are possible for benzene hexachloride, five of them have actually been isolated from the reaction mixture. They are called $\alpha, \beta, \gamma, \delta$ and ε forms. This mixture of stereoisomers of benzene hexachloride is a valuable insecticide commonly known as BHC or 666. The insecticidal properties are due to the γ-isomer called *Gammexane* or *Lindane.*

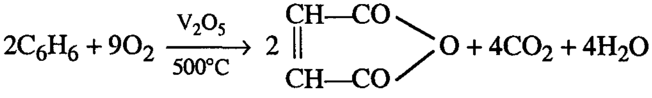
6.7.2 Oxidation Reactions

(a) *Ozonolysis* : Benzene forms triozonide with ozone. The ozonide on decomposition with water gives three molecules of glyoxal.



(b) *Oxidation under drastic conditions*

Under drastic conditions and in the presence of suitable catalysts the ring may rupture to give CO_2 and water through some intermediate aliphatic compounds which can be isolated. For example :



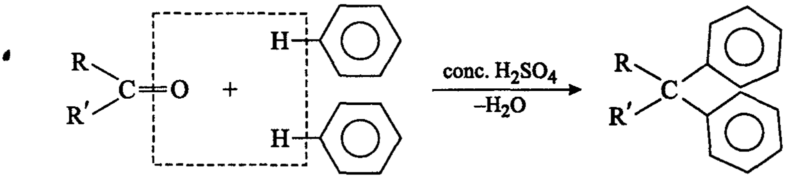
Maleic anhydride

$$2C_6H_6 + O_2 \xrightarrow[300^\circ C]{V_2O_5} 2C_6H_5\text{—}OH$$

Phenol

6.7.3 Condensation with Carbonyl Compounds

Carbonyl compounds react with benzene in the presence of conc. H_2SO_4 to give *gem*-diphenylalkane.



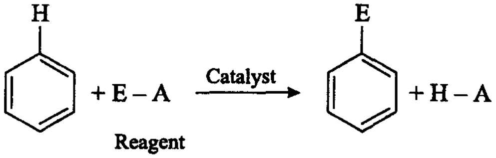
gem-diphenylalkane

6.7.4 Substitution Reactions

Substitution reactions are characteristic of benzene and many other aromatic compounds. In these reactions a hydrogen on the ring is replaced by an electrophile formed in the presence of a suitable catalyst (usually, a Lewis acid). These reactions are grouped as *aromatic electrophilic substitutions* (*e.g.*, halogenation, nitration, sulphonation and Friedel-Crafts reactions), as all of them are initiated by electrophiles. Aromatic electrophilic substitution reactions have been discussed in detail in the next section (Section 6.8).

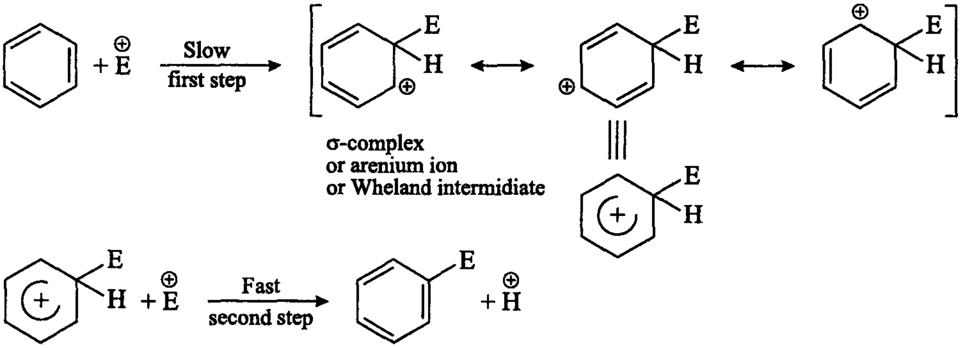
6.8 AROMATIC ELECTROPHILIC SUBSTITUTION REACTIONS

Substitution reactions on benzene nucleus are very simple—a hydrogen on the ring is replaced by an electrophile in the presence of a Lewis acid as catalyst. The catalyst acts to form the electrophile $\overset{\oplus}{E}$ from the reagent *E*—*A*. The electrophile replaces hydrogen in the form of $\overset{\oplus}{\mathrm{H}}$ which forms a by-product with the anion $\overset{\ominus}{\mathrm{A}}$.



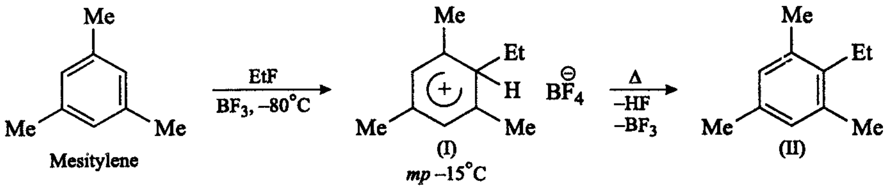
6.8.1 General Pattern of the Mechanism

According to the most accepted theory of aromatic electrophilic substitution, it proceeds by a bimolecular mechanism via the formation of an intermediate and that the formation of this intermediate is the rate-determining step. In this mechanism, which is called the **arenium ion mechanism**, the electrophile attacks in the first step giving rise to a **carbocation intermediate [known as arenium (benzenium) ion or Wheland intermediate or σ complex]** and the leaving group ($\overset{\oplus}{\mathrm{H}}$) departs in the second step. The second step is (nearly always) faster than the first step. The attacking electrophile may be a positive ion or a positive end of a dipole or induced dipole. The σ complex is stabilised by resonance. The resonance energy of the arenium ion intermediate will be much less than that of benzene, but by expulsion of a proton the molecule can revert to the more stable benzenoid (aromatic) state. Sometimes this mchanism is called SE2 mechanism, as it is bimolecular.



Evidence in support of the arenium ion mechanism

(1) Isolation of arenium ion intermediates : The intermediate arenium ions have not only been detected but also have been isolated in many cases. This gives a very strong evidence for the arenium ion mechanism. For example, the arenium ion **I** has been isolated and when it was heated the normal substituted product **II** was obtained.



(2) Isotope effect : In the arenium ion mechanism the C—H bond is not broken in the rate-determining step, hence no isotope effect should be observed. This is the case also because in general, aromatic electrophilic substitutions do not exhibit isotope effect. For example, the rates of nitration of deuterio- and tritiobenzenes are the same as the rate for benzene. Thus, the removal of proton is not the rate-determining step of the reaction therefore, an aromatic electrophilic substitution is not a single step process.

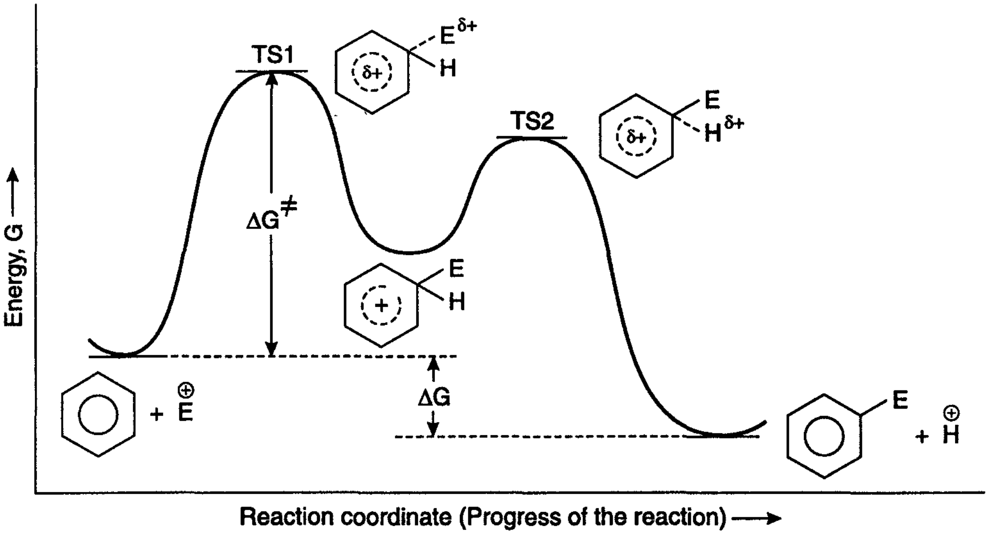


Fig. 6.2. Energy profile for a typical aromatic electrophilic substitution reaction.

A more detailed picture of the arenium ion mechanism may be presented by its energy profile (Fig. 6.2). Similar energy profiles can be constructed for substituted benzenes also.

6.8.2 Role of σ and π Complexes in Aromatic Electrophilic Substitution

The intermediates in aromatic electrophilic substitutions are commonly called σ complexes. In σ complexes there is a covalent bond between the electrophile to a ring carbon. Experimental evidence suggests that the formation of a σ complex takes place after the initial formation of a π complex. A π complex does not involve actual bonding but the electrophile is held near the π electron cloud of the aromatic ring, *i.e.*, the electrophile is strongly attracted to the electron rich π electron cloud of the aromatic ring and π complex is formed (Fig. 6.3).

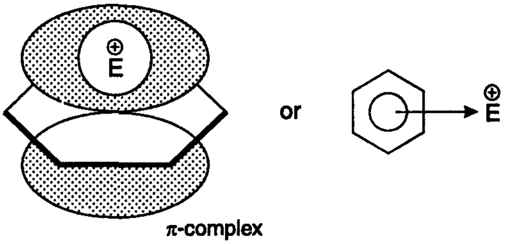


Fig. 6.3. Attraction of electrophile to *pi* electron cloud of benzene to form π complex.

As the electrophile penetrates the *pi* electron cloud and approaches bonding distance, it acquires two electrons from the *pi* system and bonds to benzene ring. In other words, π complex is converted into σ complex.

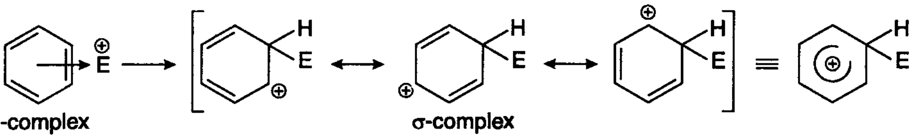
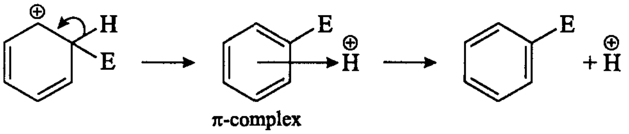
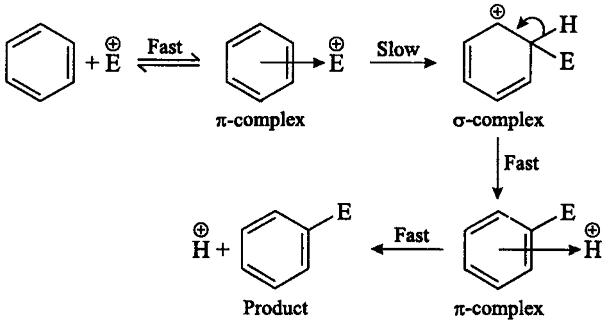


Fig. 6.4. σ **complex (carbocation) stabilised by resonance.**

This σ complex loses a proton which before departing from the σ complex again forms a *pi* complex. This *pi* complex then converts into the product.



Thus the overall mechanism can be written as shown in Scheme 6.1.



Available data suggest that in most of the aromatic sustitutions the first step is the rapid reversible formation of the *pi* complex and a high energy transition state is reached during the conversion of the *pi* complex to the *sigma* complex. This conversion is rate determing step (Scheme 6.1). The energy profile of the substitution is shown in Fig. 6.5.

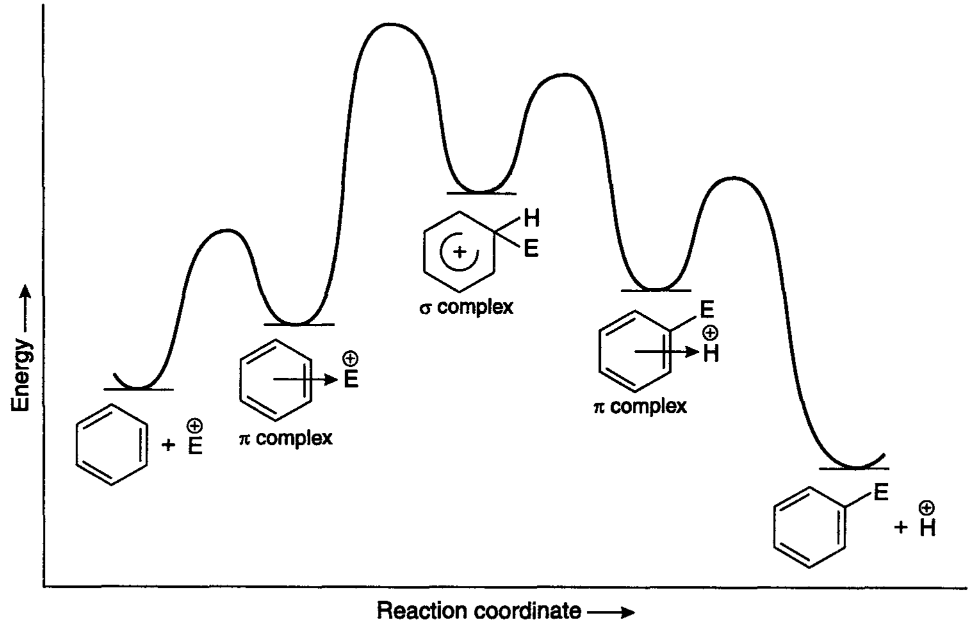
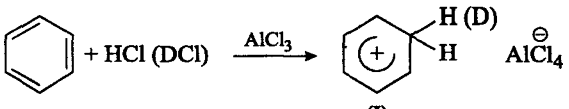


Fig. 6.5. Energy profile showing π **and** σ **complex formation in aromatic electrophilic substitutions where the** σ **complex formation is the rate-determining step.**

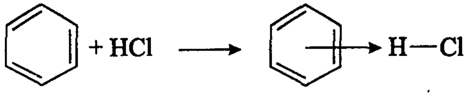
6.8.3 Evidence for the formation of σ and π complexes

In the presence of $AlCl_3$, benzene forms a complex with HCl. The complex is coloured and its solution conducts electricity showing its ionic character. Moreover, when DCl is used in place of HCl, the deuterium exchanges with the benzene protons. This can only be explained if there is the formation of a σ complex **I** as shown below :



(I)

In the absence of $AlCl_3$, benzene still forms a 1 : 1 complex with HCl, but in contrast to the σ complex, the solution of this complex is colourless and does not conduct electricity. In this case when DCl is used in place of HCl, the recovered benzene is not found to contain any deuterium. This type of complex is called a π complex.



(II)

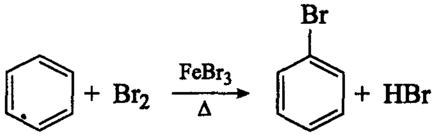
It is formed by the loose association of a proton (or any other electrophile) with the π electron cloud of the benzene ring (**II**). There is no actual bonding in this case, hence deuterium exchange does not occur.

6.9 MECHANISM OF SOME IMPORTANT ELECTROPHILIC AROMATIC SUBSTITUTION REACTIONS

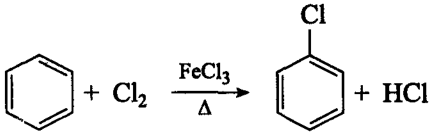
6.9.1 Halogenation of Benzene

Benzene does not react with chlorine or bromine unless a Lewis acid is used as catalyst. In the presence of Lewis acid, benzene reacts readily with bromine or chlorine to give bromobenzene and chlorobenzene, respectively in good yield.

The most common catalyst for the halogenation reaction is anhydrous FeX_3 and anhydrous AlX_3.



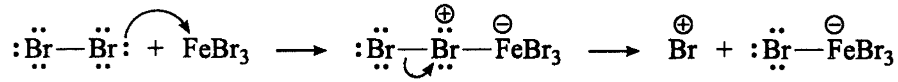
75% yield



90% yield

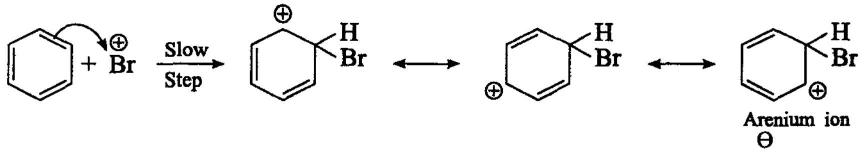
Mechanism of Bromination :

Step I : In the first step of the reaction bromine donates a lone pair of electrons to the Lewis acid to form a complex. This complex on dissociation gives $\overset{\oplus}{Br}$ and $\overset{\ominus}{FeBr_4}$.

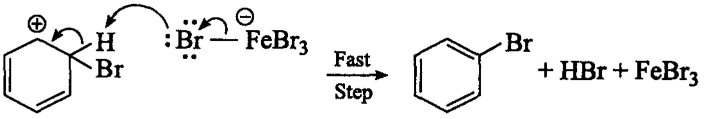


$$:\ddot{\underset{..}{Br}}-\ddot{\underset{..}{Br}}: + FeBr_3 \longrightarrow :\ddot{\underset{..}{Br}}-\overset{\oplus}{\ddot{\underset{..}{Br}}}-\overset{\ominus}{FeBr_3} \longrightarrow \overset{\oplus}{Br} + :\ddot{\underset{..}{Br}}-\overset{\ominus}{FeBr_3}$$

Step II : The positive end of the halogen-Lewis acid complex (halogen dipole) or $\overset{\oplus}{Br}$ attacks benzene to form σ complex (arenium ion).



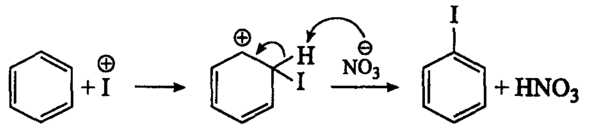
Step III : In this step a proton is removed from the arenium ion by $\overset{\ominus}{FeBr_4}$. This results in the formation of bromobenzene and hydrogen bromide. At the same time catalyst $FeBr_3$ regenerates in this step.



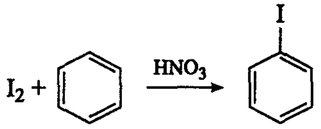
Note :

1. Fluorine is highly reactive. It reacts so rapidly with benzene that aromatic fluorination requires special conditions and special types of apparatus.
2. The mechanism of the chlorination of benzene in the presence of $FeCl_3$ is analogous to the one for bromination.
3. Iodine is so unreactive that a special technique has to be used to effect direct iodination. The iodination is carried out in the presence of an **oxidising agent such as HNO_3.**

$$I_2 \xrightarrow{\text{Conc. } HNO_3} 2I^+ + 2e^-$$



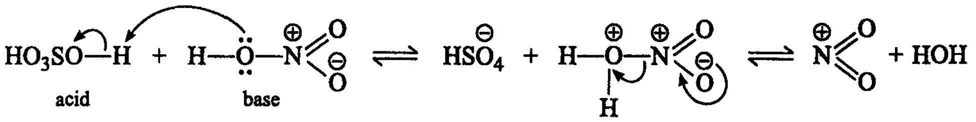
Thus the overall reaction is



6.9.2 Nitration of Benzene

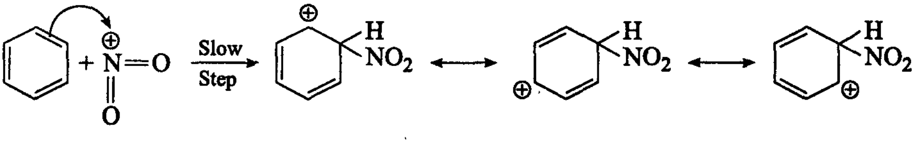
Nitration of benzene requires sulphuric acid as a catalyst. Sulphuric acid protonates nitric acid. Loss of water from the protonated nitric acid forms a nitronium ion, the electrophile required for nitration.

Step I :

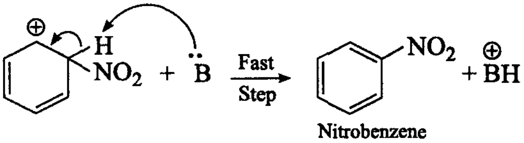


Here nitric acid acts as a base$_{\oplus}$

Step II : The electrophile, NO_2, attacks benzene ring to form σ complex or arenium ion. Arenium ion is stablilised by resonance.



Step III : In the third step the arenium ion loses a proton to a Lewis base (HOH or $\overset{\ominus}{NO_3}$ or $\overset{\ominus}{HSO_4}$) and gives nitrobenzene



Besides mixed acids ($HNO_3 + H_2SO_4$), nitration can also be performed with conc. HNO_3 alone which also occurs *via* nitronium ion. Here HNO_3 acts as both as an acid and a base.

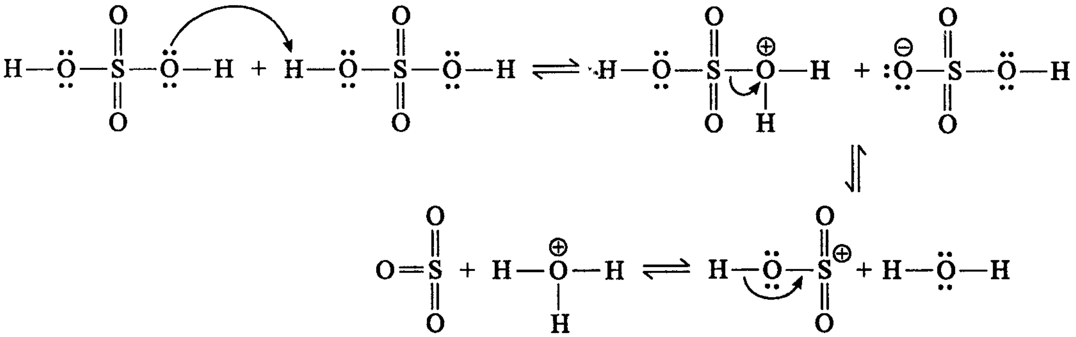
Salts of nitronium ion, *e.g.*, $\overset{\oplus}{NO_2}\overset{\ominus}{ClO_4}$ and $\overset{\oplus}{NO_2}\overset{\ominus}{BF_4}$ have been isolated and used as nitrating agents. This is a very strong evidence for the existence of nitronium ion.

6.9.3 Sulphonation of Benzene

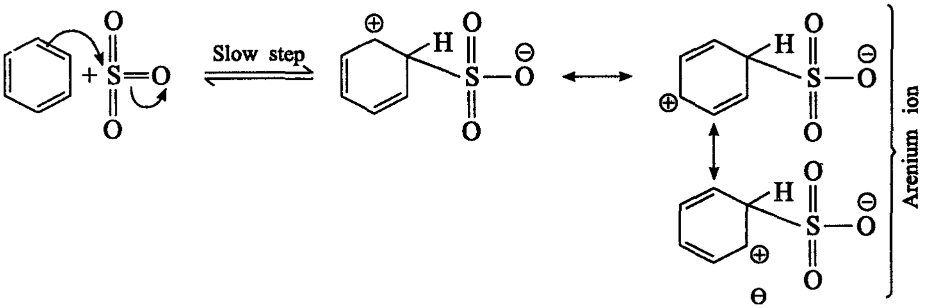
Fuming sulphuric acid or concentrated sulphuric acid is used to sulphonate benzene. Fuming sulphuric acid is sulphuric acid that contains added sulphur trioxide (SO_3).

In either reaction the electrophile appears to be sulphur trioxide. In concentrated sulphuric acid, sulphur trioxide is produced in an equilibrium in which H_2SO_4 acts as both an acid and a base.

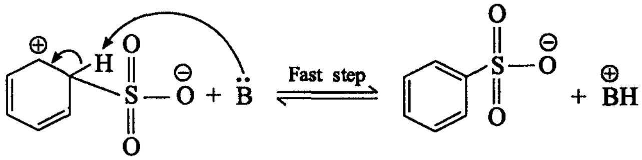
Step I :



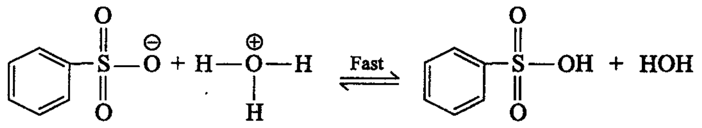
Step II : Sulphur trioxide is the actual electrophile that reacts with benzene to form an arenium ion which is stabilised by resonance.



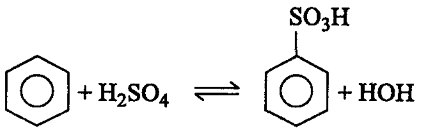
Step III : In the third step a proton is removed by base (HOH or $\overset{\ominus}{HSO_4}$) from the arenium ion to form the benzenesulphonate anion.



Step IV : The benzenesulphonate anion accepts a proton to become benzenesulphonic acid



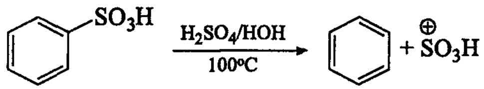
All the steps (Step I to Step IV) are reversible steps. Therefore, sulphonation of benzene is a reversible reaction.



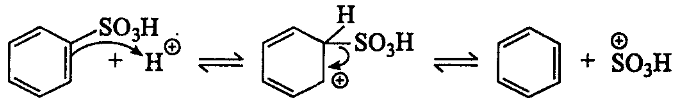
Because all of the steps are reversible, the position of equilibrium can be influenced by the conditions we employ. For example :

(i) If we want to sulphonate benzene we use concentrated sulphuric acid or better fuming sulphuric acid under these conditions the position of equilibrium lies appreciably to the right and we obtain benzenesulphonic acid in good yield.

(ii) On the other hand, we may want to remove a sulphonic acid group from the benzene ring. To do this we employ dilute sulphuric acid and usually pass steam through the mixture. Under these conditions with a high concentration of water the equilibrium lies appreciably to the left and desulphonation occurs.



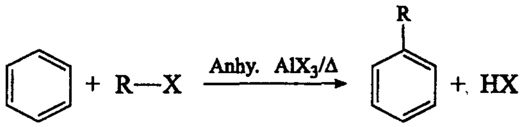
Desulphonation takes place as follows :



6.9.4 Friedel-Crafts Alkylation

Alkylation of aromatic compounds with aliphatic compounds like halides, alcohols, esters, ethers, alkenes, aldehydes and ketones in the presence of Lewis acid or proton acid as catalyst is known as Friedel-Crafts alkylation. This reaction is an example of aromatic electrophilic substitution reaction. If alkylating agent is halide, alcohol, ester or ether then catalyst is Lewis acid, but when alkylating agent is alkene, aldehyde and ketone, catalyst is proton acid.

Halides are the reagents of most frequent choice in alkylation and aluminium halides are usually employed as the catalyst.

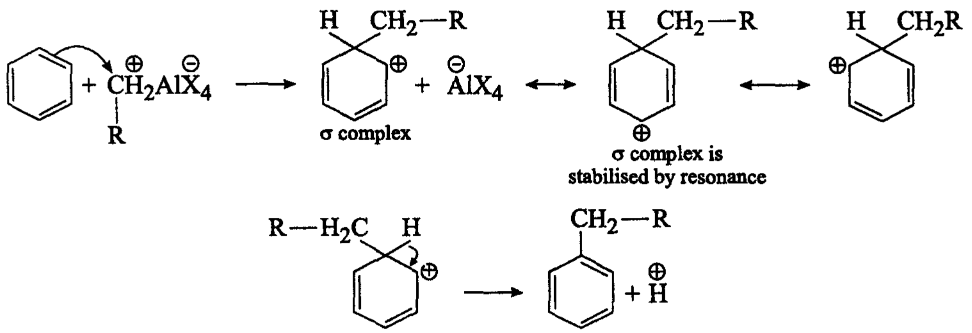


Mechanism :

$$\text{R—CH}_2\text{—X} + \text{AlX}_3 \longrightarrow \text{R—}\overset{\delta+}{\text{CH}_2}\text{---}\overset{\delta-}{\text{X}}\text{AlX}_3 \rightleftharpoons [\text{R—}\overset{\oplus}{\text{CH}_2}\overset{\ominus}{\text{Al}}\text{X}_4]$$

Alkyl halide-Lewis acid complex

Ion pair

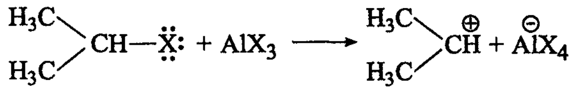


$\overset{\ominus}{AlX_4} + \overset{\oplus}{H} \longrightarrow HX + AlX_3$

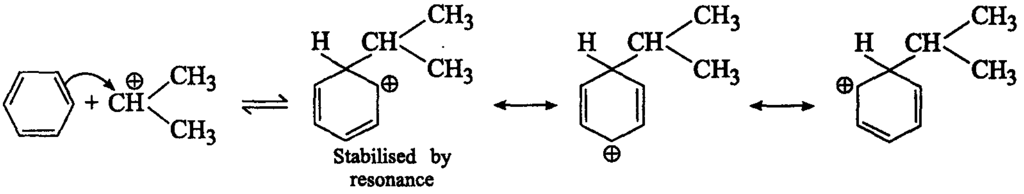
If alkyl halide is tertiary, then reaction starts with the formation of carbocation and this carbocation acts as the electrophile. With primary alkyl halide the electrophile is an alkyl halide-Lewis acid complex with a positively polarised carbon.

Mechanism :

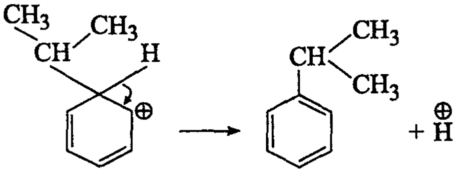
Step I.



Step II.

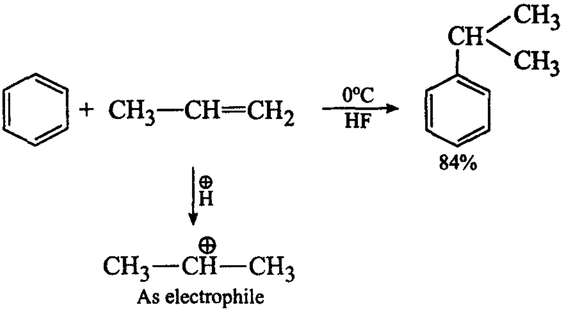


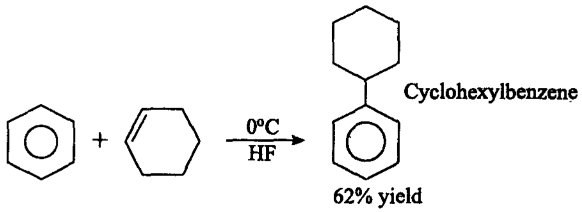
Step III.

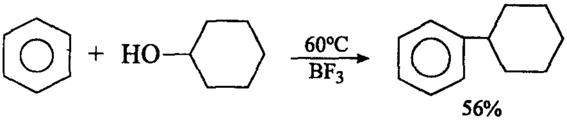


$\overset{\oplus}{H} + \overset{\ominus}{AlX_4} \longrightarrow HX + AlX_3$

Some examples :







Benzyl halides are very reactive for this reaction but vinyl halides and aryl halides do not give this reaction. The use of dihalides and polyhalides leads to successive alkylations. For example :

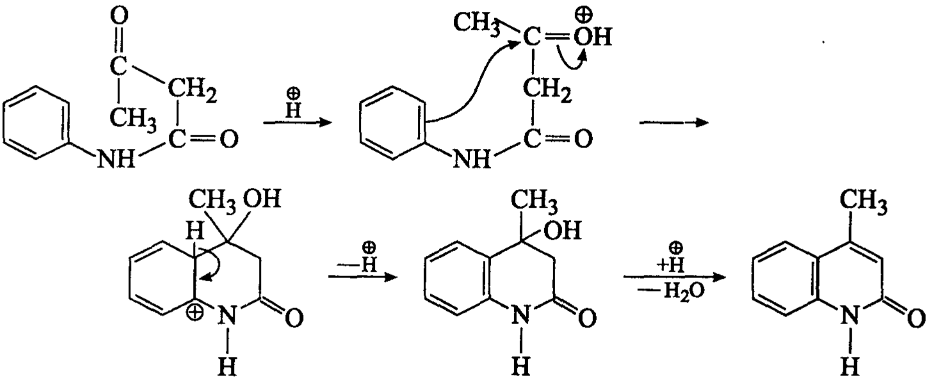
(i) $C_6H_5{-}H + CH_2Cl_2 \xrightarrow{\text{Anhy. AlCl}_3/\Delta} C_6H_5{-}CH_2{-}Cl \xrightarrow[\text{Anhy. AlCl}_3]{C_6H_5{-}H} C_6H_5{-}CH_2{-}C_6H_5$

(ii) $2C_6H_5{-}H + Br{-}CH_2{-}CH_2{-}Br \xrightarrow{\text{Anhy. AlBr}_3/\Delta} C_6H_5{-}CH_2{-}CH_2{-}C_6H_5$

(iii) $3C_6H_5{-}H + CCl_4 \xrightarrow{\text{Anhy. AlCl}_3/\Delta} \underset{\text{(I)}}{(C_6H_5)_3CCl}$

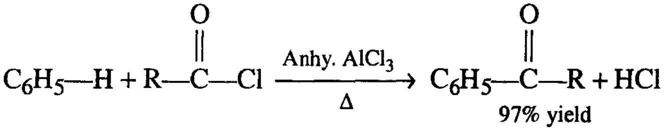
The product (I) does not undergo further reaction due to the steric hindrance. If it would undergo reaction, then product will be $(C_6H_5)_4C$ which is highly unstable.

Aldehyde, ketone and ester mainly give intramolecular Friedel-Crafts alkylation in the presence of proton acid.



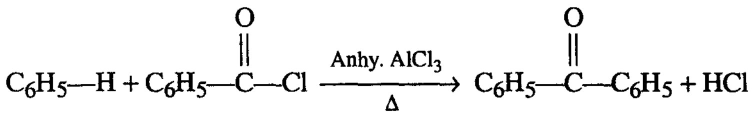
6.9.5 Friedel-Crafts Acylation

The $R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}$ group is called an acyl group and a reaction whereby an acyl group is introduced into a compound is called acylation reaction. Acylation of aromatic compounds takes place in the presence of excess amount of Lewis acid because the product of the reaction is ketone which forms complexes with Lewis acid.



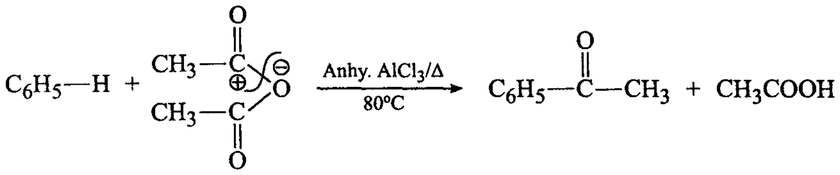
$$C_6H_5{-}H + R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Cl \xrightarrow[\Delta]{\text{Anhy. AlCl}_3} C_6H_5{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R + HCl$$

97% yield
if R=CH_3

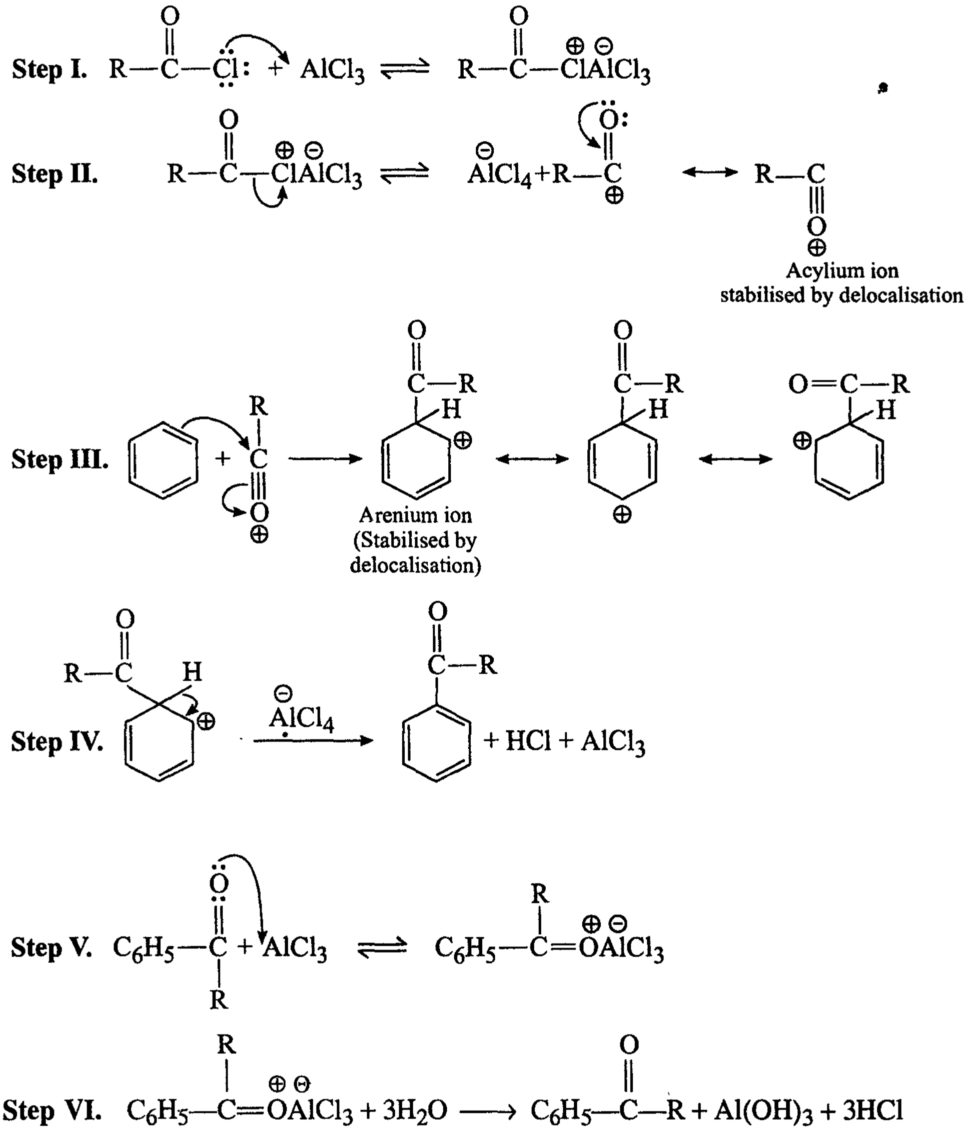


$$C_6H_5{-}H + C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}Cl \xrightarrow[\Delta]{\text{Anhy. AlCl}_3} C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}C_6H_5 + HCl$$

Friedel-Crafts acylation also takes place with acid anhydride.



Mechanism :



Step I. $R{-}\overset{\overset{O}{\|}}{C}{-}\ddot{\underset{..}{Cl}}: + AlCl_3 \rightleftharpoons R{-}\overset{\overset{O}{\|}}{C}{-}\overset{\oplus}{Cl}\overset{\ominus}{Al}Cl_3$

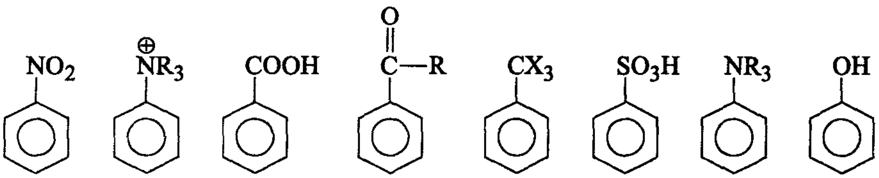
Step II. $R{-}\overset{\overset{O}{\|}}{C}{-}\overset{\oplus}{Cl}\overset{\ominus}{Al}Cl_3 \rightleftharpoons \overset{\ominus}{AlCl_4} + R{-}\underset{\oplus}{\overset{\overset{\ddot{O}:}{\|}}{C}} \longleftrightarrow R{-}C{\equiv}\overset{\oplus}{O}$

Step V. $C_6H_5{-}\underset{R}{\overset{\overset{\ddot{O}}{\|}}{C}} + AlCl_3 \rightleftharpoons C_6H_5{-}\overset{R}{\overset{|}{C}}{=}\overset{\oplus}{O}\overset{\ominus}{Al}Cl_3$

Step VI. $C_6H_5{-}\overset{R}{\overset{|}{C}}{=}\overset{\oplus}{O}\overset{\ominus}{Al}Cl_3 + 3H_2O \longrightarrow C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}R + Al(OH)_3 + 3HCl$

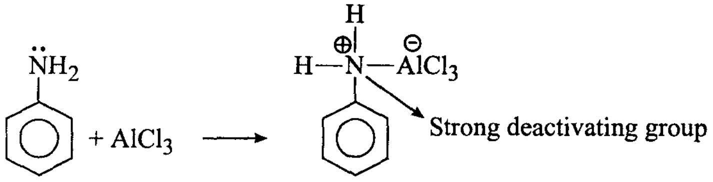
Limitations of Friedel-Crafts Reaction

(i) Reactivity of aromatic compounds : Aromatic compounds whose reactivity is comparable with or greater than that of benzene give this reaction. Compounds having strong deactivating group do not give this reaction. Compounds having —NH_2, —NHR, —$\ddot{N}R_2$ and —OH groups also do not give this reaction.



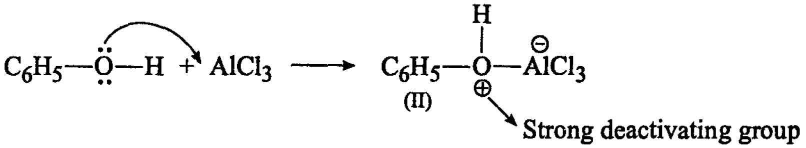
These compounds either do not give Friedel-Crafts reaction or the yield is very-very poor.

Although $\ddot{N}H_2$, $\ddot{N}HR$ and $\ddot{N}R_2$ are activating groups, these groups react with $AlCl_3$ to form complex which has a strong deactivating group.



(I)

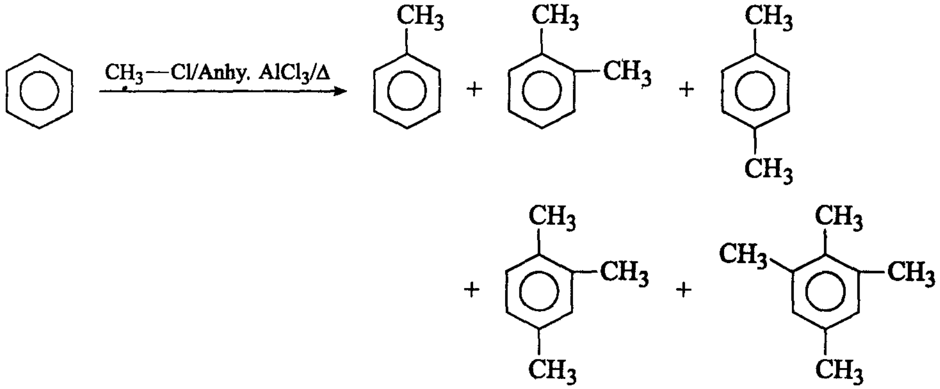
Similary, phenol also has strong activating group but it also reacts with Lewis acid to form a complex which has a strong deactivating group.



$$C_6H_5—\ddot{\underset{\cdot\cdot}{O}}—H + AlCl_3 \longrightarrow C_6H_5—\overset{H}{\overset{|}{\overset{\oplus}{O}}}—\overset{\ominus}{AlCl_3}$$

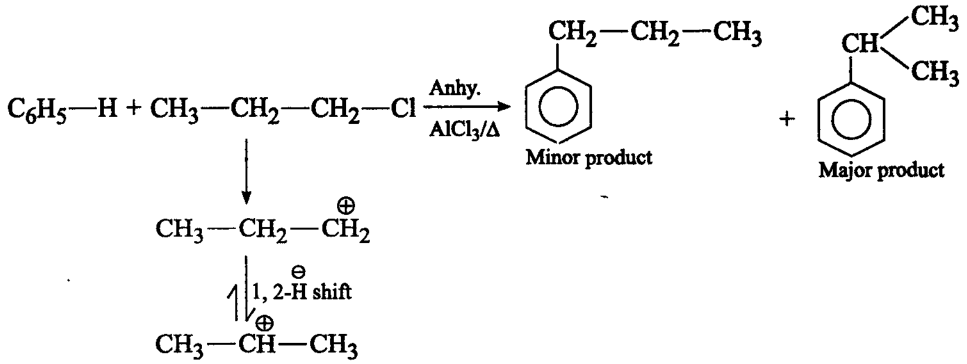
Complex (I) and (II) are sparingly soluble in the reaction medium so that they react slowly.

(ii) Since alkyl groups are activating groups for aromatic electrophilic substitution (ArSE) reaction, the product of alkylation is more reactive than the starting material and further alkylation invariably occurs.

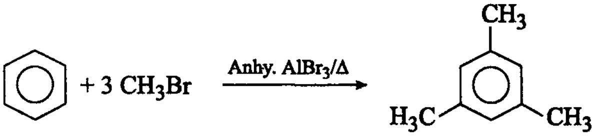


Polyacylation in Friedel-Crafts reaction is not possible because acyl group is a deactivating group and only monosubstituted product is formed.

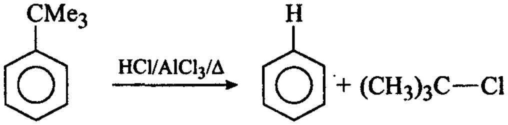
(iii) The carbocation formed from alkyl halide, alkene or alcohol can rearrange to a more stable carbocation, it usually does so, and the major product is obtained from the most stable carbocation.



(iv) Alkylation reaction is a reversible reaction, so this reaction is thermodynamically controlled. Thermodynamically controlled reaction is carried out at high temp. *Meta* alkylated derivatives are thermodynamically most stable; hence at higher temp. *m*-derivatives are formed.

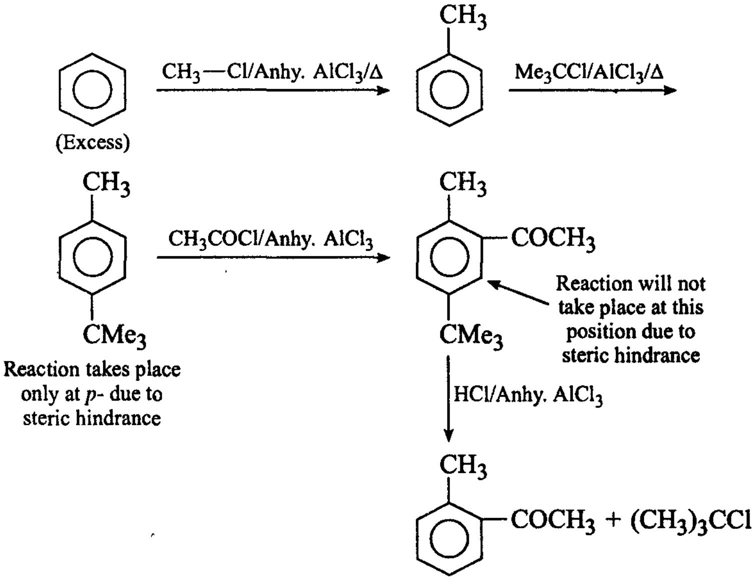


Tertiary alkyl groups are most readily introduced during alkylation; so they are most readily removed because the reaction is a reversible reaction.



Application of this particular case is very important.

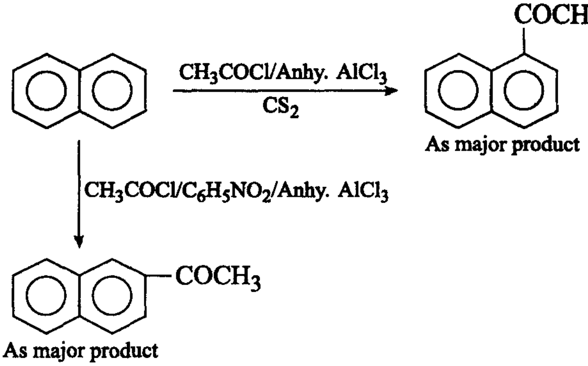
Suppose we want to convert benzene into *o*-methylacetophenone. This conversion can be carried out as follows :



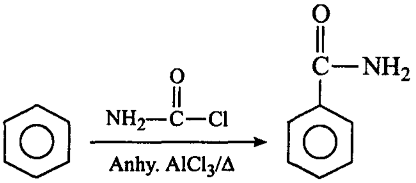
Reaction takes place only at *p*- due to steric hindrance

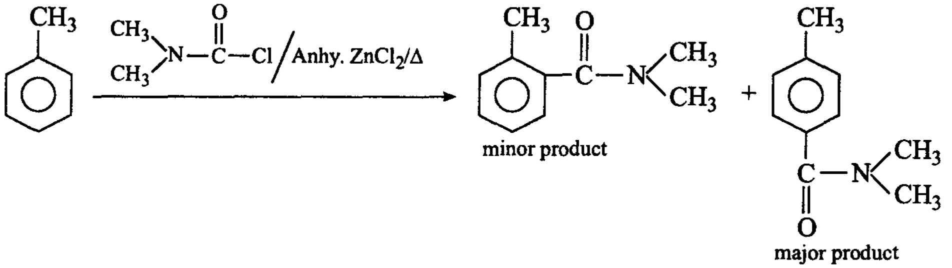
Reaction will not take place at this position due to steric hindrance

(v) **Effect of Solvent :** Nature of product in some cases depends on the solvent used.



Extension of Friedel-Crafts acylation : Benzene, alkylbenzene and anthracene give electrophilic aromatic substitution reaction with carbamoyl chloride ($NH_2-CO-Cl$) and *N,N*—dialkylcarbamoyl chloride $\left(\begin{array}{l}R\diagdown\\R\diagup\end{array}N-CO-Cl\right)$ in the presence of only $AlCl_3$ or $ZnCl_2$. This reaction is known as **Gattermann-Amide synthesis.**



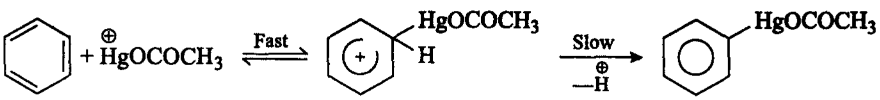


Nitrobenzene is a very common solvent for Friedel-Crafts reactions because it dissolves the reactants and the catalyst ($AlCl_3$) to produce a homogeneous reaction mixture, and it does not undergo Friedel-Crafts reaction due to the deactivation of the ring by the nitro group.

6.9.6 Mercuration

This reaction is carried out by heating benzene with mercuric acetate. The product is phenylmercuric acetate.

Mechanism :

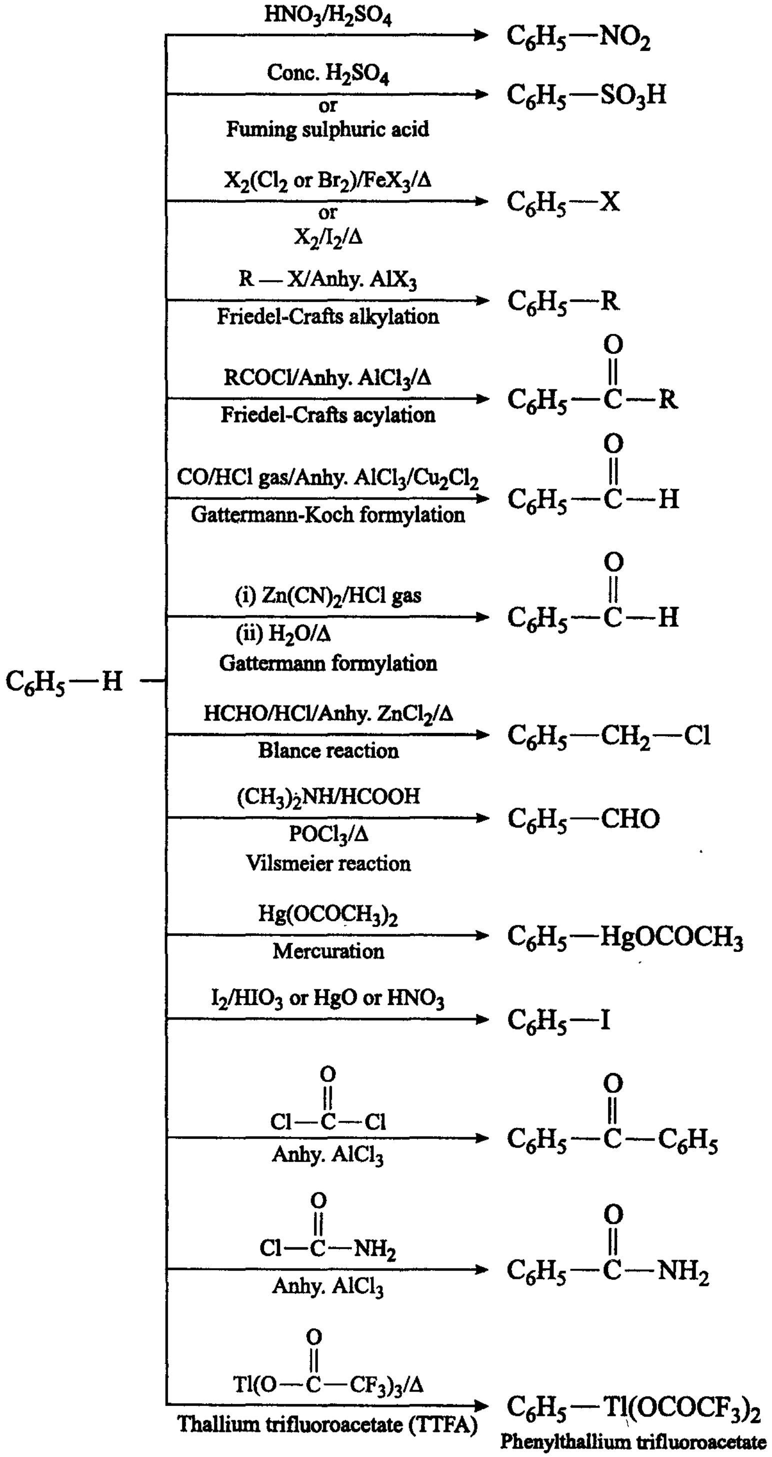


This reaction exhibits a positive isotope effect. It has been observed that benzene reacts six times faster than perdeuteriobenzene under similar conditions. This shows that the removal of proton is the rate-determining step. Similar is the case, at least in some solvent, with sulphonation.

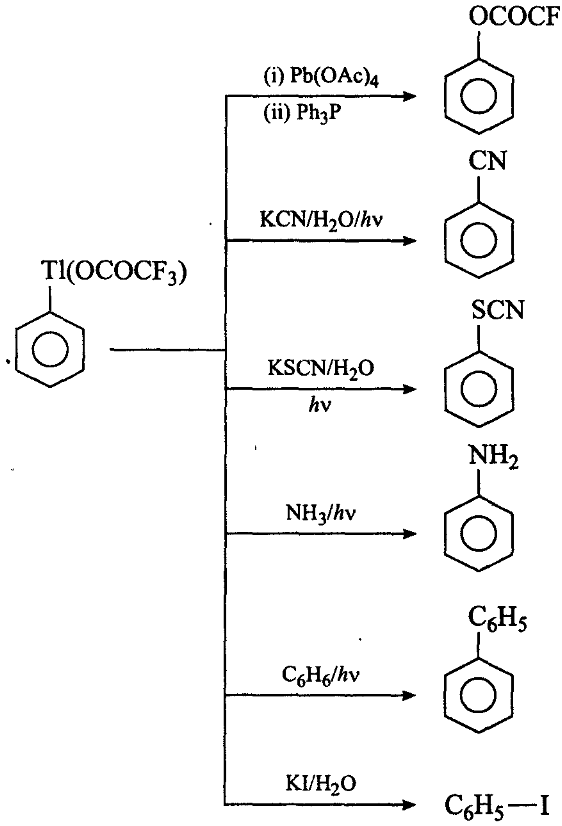
Some Common Electrophilic Substitution Reactions Given by Benzene

S.No.	Substrate	Reagent/Catalyst/Δ	Reacting species ($E^{\oplus}$ or E)	Product	Name of reaction
1.	$C_6H_5—H$	conc. HNO_3, or conc. HNO_3/conc. H_2SO_4 or $\overset{\oplus}{NO_2}\overset{\ominus}{BF_4}$	$\overset{\oplus}{NO_2}$	$C_6H_5—NO_2$	Nitration
2.	$C_6H_5—H$	conc. H_2SO_4/Δ or fuming sulphuric acid	$\overset{\oplus}{S}O_3H$, SO_3	$C_6H_5—SO_3H$	Sulphonation
3.	$C_6H_5—H$	$X_2(Cl_2$ or $Br_2)$/Anhy. AlX_3/Δ or I_2/Δ, Fe/Δ	$X^{\oplus}$	$C_6H_5—X$	Halogenation
4.	$C_6H_5—H$	R—X/Anhy. AlX_3/Δ	$R^{\oplus}$	$C_6H_5—R$	Alkylation, Friedel-Crafts alkylation
5.	$C_6H_5—H$	$R—\overset{O}{\overset{\parallel}{C}}—Cl$/Anhy. $AlCl_3/\Delta$	$R—\underset{\oplus}{\overset{O}{\overset{\parallel}{C}}}$	$C_6H_5—\overset{O}{\overset{\parallel}{C}}—R$	Friedel-Crafts acylation
6.	$C_6H_5—H$	CO + HCl/Anhy. $AlCl_3/Cu_2Cl_2$	$H—\underset{\oplus}{\overset{O}{\overset{\parallel}{C}}}$	$C_6H_5—\overset{O}{\overset{\parallel}{C}}—H$	Gattermann-Koch formylation
7.	$C_6H_5—H$	CH_2O + HCl/Anhy. $ZnCl_2/\Delta$	$\overset{\oplus}{C}H_2OH$	$C_6H_5—CH_2Cl$	Chloromethylation (Blance reaction)
8.	$C_6H_5—H$	(i) HCN/Anhy. $ZnCl_2$ or Anhy. $Zn(CN)_2$/HCl (ii) H_2O/Δ	$H—\overset{\oplus}{C}=NH$	$C_6H_5—CHO$	Gattermann formylation

6.10 SUMMARY OF DIFFERENT ELECTROPHILIC SUBSTITUTION REACTIONS OF BENZENE IS GIVEN BELOW

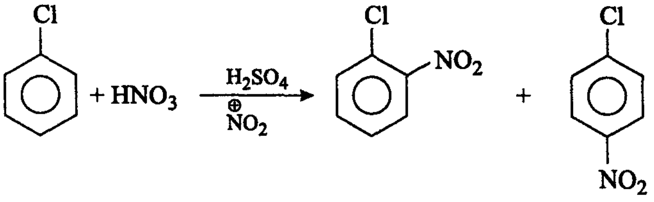


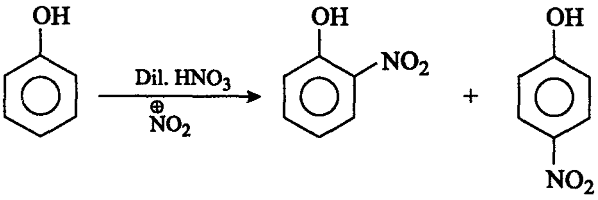
Note : Phenylthallium trifluoroacetate is very good synthetic reagent because thallium trifluoro acetate group can be replaced by different groups.

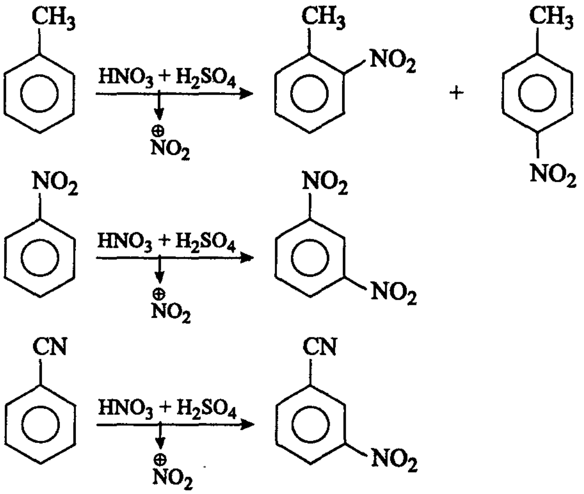


6.11 ORIENTATION OF SUBSTITUTION

Since benzene is a symmetrical molecule, electrophilic substitution of benzene gives only one monosubstitution product. Monosubstituted benzene derivatives, however, are not symmetrical and more than one substitution isomer is usually possible. For example :







Above examples show that a group already present on the benzene ring either directs the incoming group (in the form of electrophile) to the *ortho* and *para* position or to the *meta* position. This is called the **directive** or **orientation** effect. Thus the atom or group already present on the benzene ring (*i.e.*, key atom of the ring) directs the orientation of the substitution of the incoming electrophile. Table 6.1 lists *ortho–para* directors and *meta* directors.

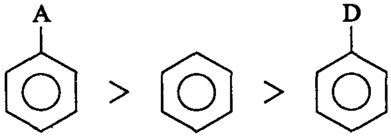
Table 6.1 ***Ortho, para* directors and *meta* directors**

Ortho, para directors	*Meta* directors	*Ortho, para* directors	*Meta* directors
$-\overset{\ominus}{O}$; phenoxide ion	$-\overset{\oplus}{N}R_3$; quaternary ammonium ion	$-\underset{\bullet\bullet}{\overset{\bullet\bullet}{O}}R$; alkoxy	$-\overset{O}{\overset{\Vert}{C}}-R$; keto
$-\overset{\bullet\bullet}{N}H_2$; amino	$-\overset{\oplus}{N}(=O)-\overset{\ominus}{O}$; nitro	$-\overset{\bullet\bullet}{N}HCOCH_3$; N-acetyl	$-\overset{O}{\overset{\Vert}{C}}-OH$; carboxylic
$-\overset{\bullet\bullet}{N}R_2$; dialkylamino		$-R$; alkyl	$-\overset{O}{\overset{\Vert}{C}}-NH_2$; amide
$-\overset{\bullet\bullet}{N}HR$; alkylamino	$-C\equiv N$; cyano	$-\underset{\bullet\bullet}{\overset{\bullet\bullet}{Cl}}\colon$; chloro	$-CX_3$; trihalomethyl
$-\underset{\bullet\bullet}{\overset{\bullet\bullet}{O}}H$; phenolic hydroxyl	$-\underset{\underset{O}{\Vert}}{\overset{\overset{O}{\Vert}}{S}}-OH$; sulphonic acid	$-\underset{\bullet\bullet}{\overset{\bullet\bullet}{Br}}\colon$; bromo	
$-\underset{\bullet\bullet}{\overset{\bullet\bullet}{O}}CH_3$; methoxy	$-\overset{O}{\overset{\Vert}{C}}-H$; aldehyde	$-\underset{\bullet\bullet}{\overset{\bullet\bullet}{X}}\colon$; halo	

6.11.1 Activating and Deactivating Groups

An atom or group already present on a benzene ring not only directs the orientation of substitution of an incoming group but also influences the rate of the reaction.

If a substituted benzene derivative reacts more rapidly than benzene itself, then the substituent group is said to be an activating group. For example, anisole is 300,000 times more reactive than benzene for Friedel Crafts acylation reaction. Thus methoxy group is an activating group. On the other hand, if the benzene derivative reacts more slowly than benzene itself, then the substituent is called **deactivating** group. The bromination of nitrobenzene is more than 100,000 times slower than the bromination of benzene. Thus the nitro group is a deactivating group.



Reacts faster than benzene; A = activating groups

Reacts slower than benzene; D = deactivating group

A given group (or substitutent) is either activating in all electrophilic aromatic substitution reactions or deactivating in all such reactions.

The rate-determing step of an electrophilic aromatic substitution reaction is attack of the nucleophilic aromatic ring on the positively charged electrophile. Therefore, increasing the electron density of the benzene ring increases its nucleophilicity. The greater its nucleophilicity, the more readily it will attack the electrophile and the faster the electrophilic substitution reaction will take place. Therefore, substituents that are capable of donating electrons to the ring will increase the rate of electrophilic substitution reaction. Such substituents will be activating groups. Similarly, substituents that withdraw electrons from the ring will decrease the rate of electrophilic substitution. Such substitutents will be deactivating groups (Tables 6.1 and 6.2).

All *o*, *p*-directors with the exception of the halogens are activating groups. All have a lone pair of electrons, except alkyl groups. Thus +R groups and +I groups are *o*, *p*-directing groups and activating groups. The only exception is the halo group.

All *meta* directors and halogens are deactivating groups. All *meta* directors either possess a positive charge or the key atom (the atom directly attached to the ring) of the substituent is bonded with electronegative atom by multiple bond except —CCl_3 group. Thus –*R* and –I groups are *meta* directors and deactivating groups (Table 6.2).

6.12 THEORY OF SUBSTITUENT EFFECTS ON ELECTROPHILIC AROMATIC SUBSTITUTIONS

6.12.1 Theory of the Effect of Substituents on Reactivity

There are three ways by which substituents can donate electrons to a benzene ring and increase its reactivity towards electrophilic substitutions :

(i) Electron donation by hyperconjugation, *i.e.*, alkyl groups having at least one hydrogen on α- carbon.
(ii) Electron donation by inductive effect, *i.e.*, + I groups (alkyl groups).
(iii) Electron donation by resonance, *i.e.*, group should be + *R* group (the key atom should have at least one lone pair of electrons).

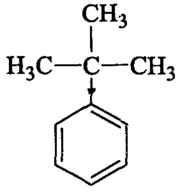
There are also three ways by which substituents can withdraw electrons from a benzene ring and decrease its reactivity towards electrophilic subsitutions :

(i) Electron withdrawal by reverse hyperconjugation (—CCl_3).
(ii) Electron withdrawal by inductive effect, *i.e.*, – I groups (—$\overset{\oplus}{N}R_3$ type groups).
(iii) Electron withdrawal by resonance, *i.e.*, group should be a—*R* groups.

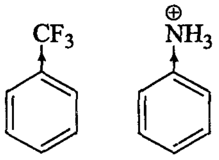
Table 6.2 *The effects of substituents on the reactivity of a benzene ring toward electrophilic substitution*

Activating substituents	Most activating		
↓	$-NH_2$	strongly activating	*ortho/para* directing
	$-NHR$		
	$-NR_2$		
	$-OH$		
	$-OR$		
	$-NH\overset{O}{\overset{\|}{C}}R$	moderately activating	
	$-O\overset{O}{\overset{\|}{C}}R$		
	$-R$	weakly activating	
	$-Ar$		
	$-CH{=}CH_2$		
Standard of comparison →	$-H$		
Deactivating substituents	$-CCl_3$	weakly deactivating	
↓	$-F$		
	$-Cl$		
	$-Br$		
	$-I$		
	$-\overset{O}{\overset{\|}{C}}H$	moderately deactivating	*meta* directing
	$-\overset{O}{\overset{\|}{C}}R$		
	$-\overset{O}{\overset{\|}{C}}OR$		
	$-\overset{O}{\overset{\|}{C}}OH$		
	$-\overset{O}{\overset{\|}{C}}Cl$		
	$-C{\equiv}N$	strongly deactivating	
	$-SO_3H$		
	$-\overset{+}{N}H_3$		
	$-\overset{+}{N}H_2R$		
	$-\overset{+}{N}HR_2$		
	$-\overset{+}{N}R_3$		
	$-NO_2$		
	most deactivating		

Inductive Electron Donation and Withdrawal : Alkyl group is the inductive electron donor group, whereas —$\overset{\oplus}{N}H_3$, —$\overset{\oplus}{N}R_3$ and —CX_3 are inductive electron withdrawal groups.

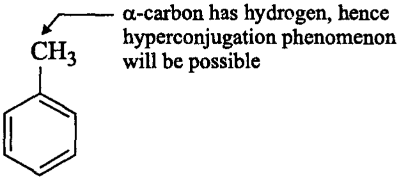


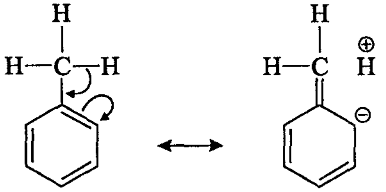
Substituent donates electrons
by inductive effect
(activating group)



Substituent withdraws electrons
by inductive effect
(deactivating group)

Hyperconjugative Electron Donation and Withdrawal : Substituent donates electron by hyperconjugation, hence it is an activating group.

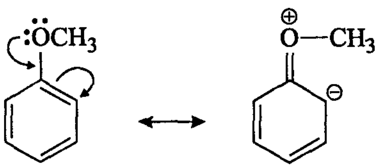




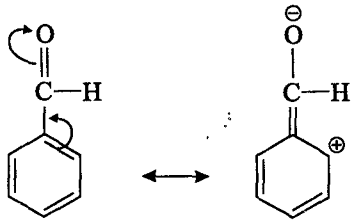
Resonance Electron Donation and Withdrawal :

(i) If the key atom has negative charge or has at least one lone pair of electrons, the group is always + *R* group. + *R* group donates electrons to the benzene ring by resonance effect.

(ii) If key atom has incomplete octet or key atom is bonded to an electronegative atom by multiple bond, then the group is – *R* group. – *R* group always withdraws electrons from the benzene ring by resonance effect.



Substituent donates electron by
resonance effect
(activating group)



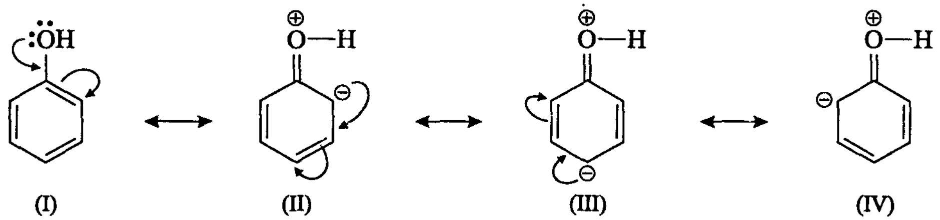
Substituent withdraws electrons by
resonance effect
(deactivating group)

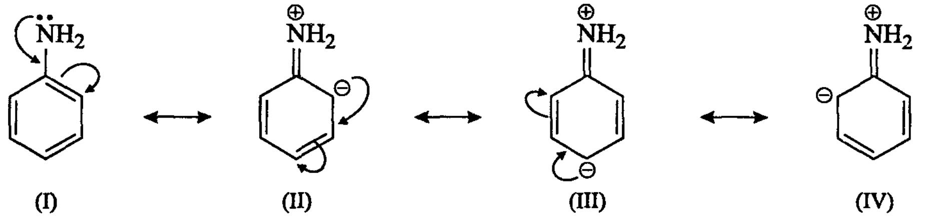
6.12.2 Theory of the Effect of Substituents on Orientation

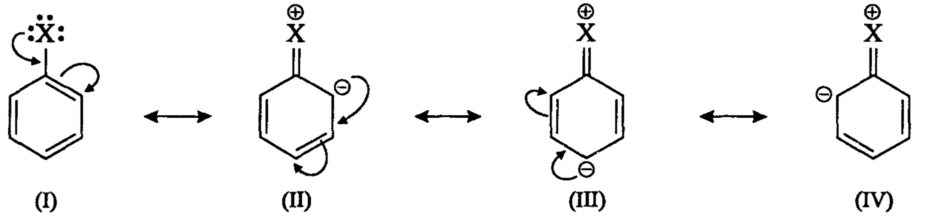
There are two ways of studying the relative reactivities of positions (*i.e.*, reaction at *o*- and *p*- or *m*-position) in substituted benzenes; one based on charge distribution (electronic explanation) and the other on the stability of the intermediate carbocation (*i.e.*, *sigma* complex).

(i) Electronic Explanation for *o*- and *p*- Directive Influence : From the examination of the electronic structure and polar characteristics of *o*- and *p*- directing groups, it is evident that with the exception of alkyl groups all of them posses at least one lone pair of electrons at the key atom. Also their polar characteristics are $-I$ and $+R$ type except alkyl groups which is $+I$ type only.

The lone pair of electrons present on key atom is in conjugation with the *pi* electrons of the ring and exhibits a strong $+R$ effect, thus increasing the overall electron density on the benzene ring. Although the $-I$ effect opposes the $+R$ effect but latter predominates **because resonance effect is primary where inductive effect is secondary in nature.** However, the relative increase of electron density is greater at *o*- and *p*-positions due to nature of conjugation as shown below, hence the substitution occurs at these positions.



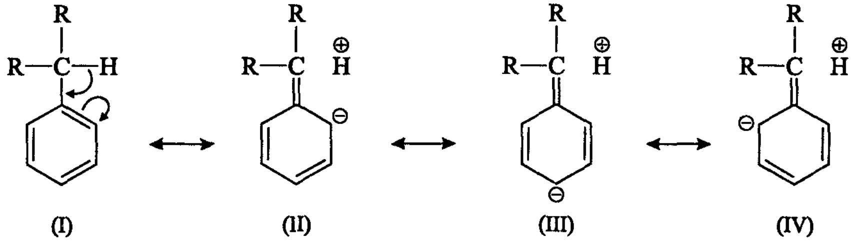




In the resonance forms (II–IV) the *ortho* and *para* positions have a greater electron density than *meta* position. Thus the electrophile ($\overset{\oplus}{E}$) would naturally attack at these positions.

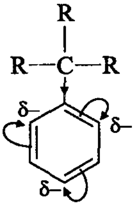
Effects of Alkyl Groups

Case 1 : When the alkyl group has at least one *alpha* hydrogen (*i.e.*, alkyl group may be 1° or 2° but not 3°). Such type of alkyl groups are *o*-, *p*- directing groups because of the hyperconjugation.



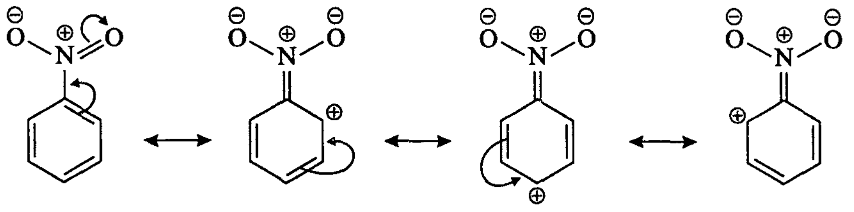
In the hyperconjugative forms (II–IV) the *ortho* and *para* positions have a greater electron density than the *meta* position. Thus the electrophile ($\overset{\oplus}{E}$) would naturally attack at these positions.

Case 2 : When the alkyl groups have no hydrogen on α carbon, it will not undergo resonance or hyperconjugative effect. However, the alkyl group undergoes the strong $+I$ effect which increases the electron density at *o*- and *p*- positions and hence directs the incoming groups to these positions.

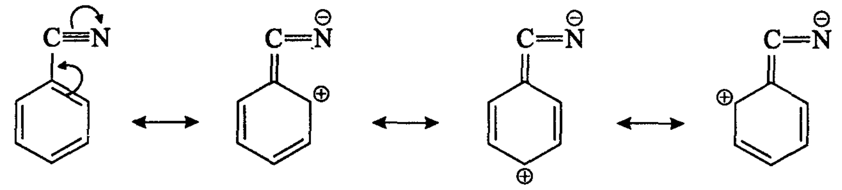


(ii) Electronic Explanation for *meta*-directing Groups : The polar characteristics of *m*-directing groups are $-I$ and $-R$ with the exception of $\overset{\oplus}{N}R_3$ and $—CX_3$ groups which exhibit only $-I$ effect. The $—CCl_3$ group also exhibits reverse hyperconjugative effect.

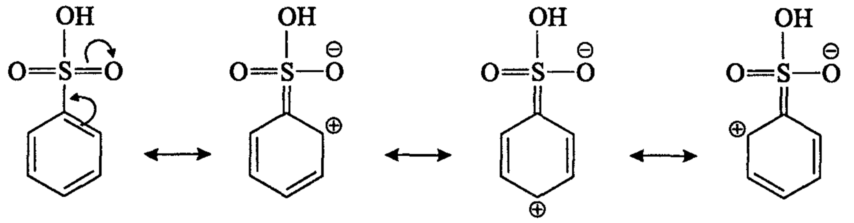
The groups like $—NO_2$, —CHO, —CN, —COOH, etc. have a *pi* bond conjugated to the benzene ring and strongly electron attracting atom linked to the key atom through this multiple bond. Due to conjugation electron attracting atom causes withdrawal of electrons away from the ring and towards the group by a $-R$ effect, this deactivates the nucleus. However, the effect is more pronounced at *o*- and *p*- positions leaving *m*- position as point of relatively high electron density. The $-I$ effect assists the $-R$ effect.



(I) (II) (III) (IV)



(I) (II) (III) (IV)



(I) (II) (III) (IV)

As the molecule is a resonance hybrid of various contributing structures, there is small positive charge at the *ortho* and *para* position (structures II–IV). The *meta* positions remain the position of relatively high electron density and attract electrophiles resulting in *m*- substitution.

6.12.3 Orientation Based on *Sigma* Complex Stability

Whether given group is *o/p*-directing group or *m*- directing group can also be explained by the stability of carbocation (*sigma* complex). When a substituted benzene undergoes an electrophilic substitution reaction, three different carbocation intermediates can be formed. Which one is actually formed depends on the relative stabilities of the carbocations. (Fig. 6.5). Comparison of the relative stabilities of these three carbocations allows us to determine the preferred pathway of the reaction because the more stable the carbocation, the less energy is required to make it. In other words, the product formation always takes place by formation of most stable reaction intermediate.

Case 1 : When group is – *I* group only, *i.e.*, Alkyl group.

When benzene reacts with an electrophile, the resulting *sigma* complex has the positive charge distributed over three secondary carbon atoms. In the case of *ortho* and *para* substitution of toluene, however, the positive charge is spread over two secondary carbons and one tertiary (3°) carbon (Fig. 6.6).

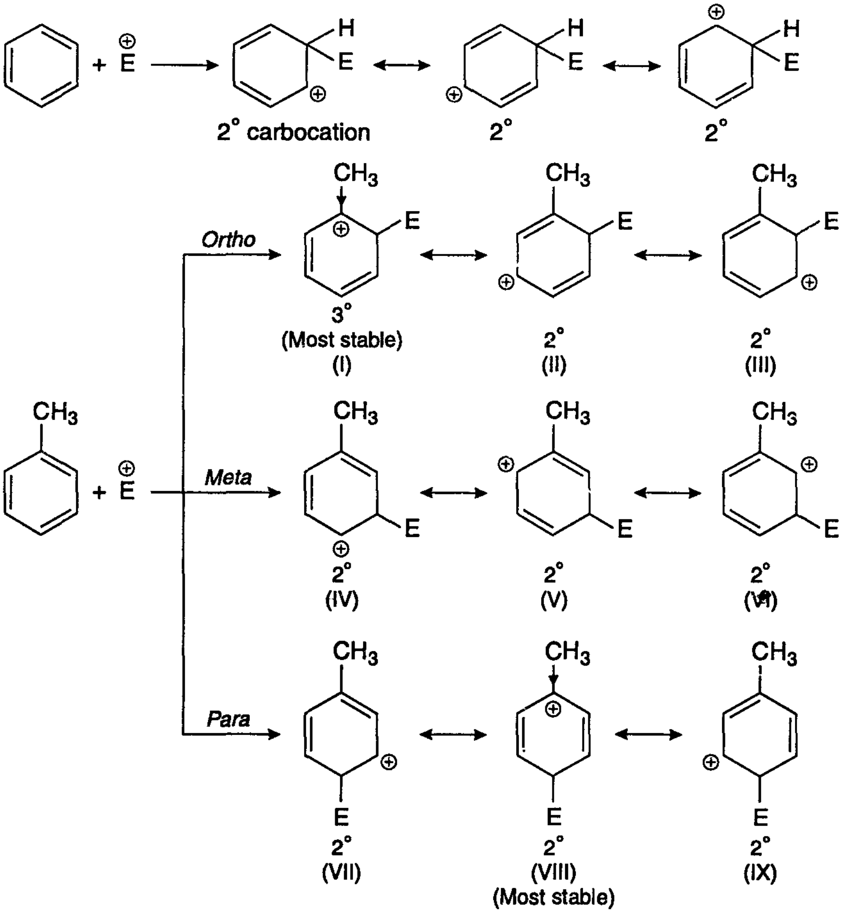


Fig. 6.6. The structures of the carbocation intermediates formed from the reaction of an electrophile with the toluene at the *ortho*, *meta* and *para* position.

If a substituent (*i.e.*, alkyl group) donates electrons by inductive effect, the indicated resonance contributors, (I) and (VIII) (Fig. 6.6) are most stable. This is because the substituent is attached directly to the positively charged carbon, which it can stabilise by inductive electron donation. These relatively stable resonance contributors are obtained only when the substituent is directed to an *ortho* or *para* position. Therefore, the most stable carbocation is obtained by directing the incoming group to the *ortho* and *para* positions. Thus any substituent that donates electrons inductively is an *ortho/para* director.

Case 2 : When group is + *R* group.

If a substituent donates electrons by resonance, the carbocation formed by putting the incoming electrophile on the *ortho* and *para* positions have a fourth resonating structure as a result of resonance electron donation by the substituent (Fig. 6.7). This is a specially stable resonance contributor because it is the only one whose all atoms have complete octets. Therefore, all groups that donate electrons by resonance are *ortho/para* directors.

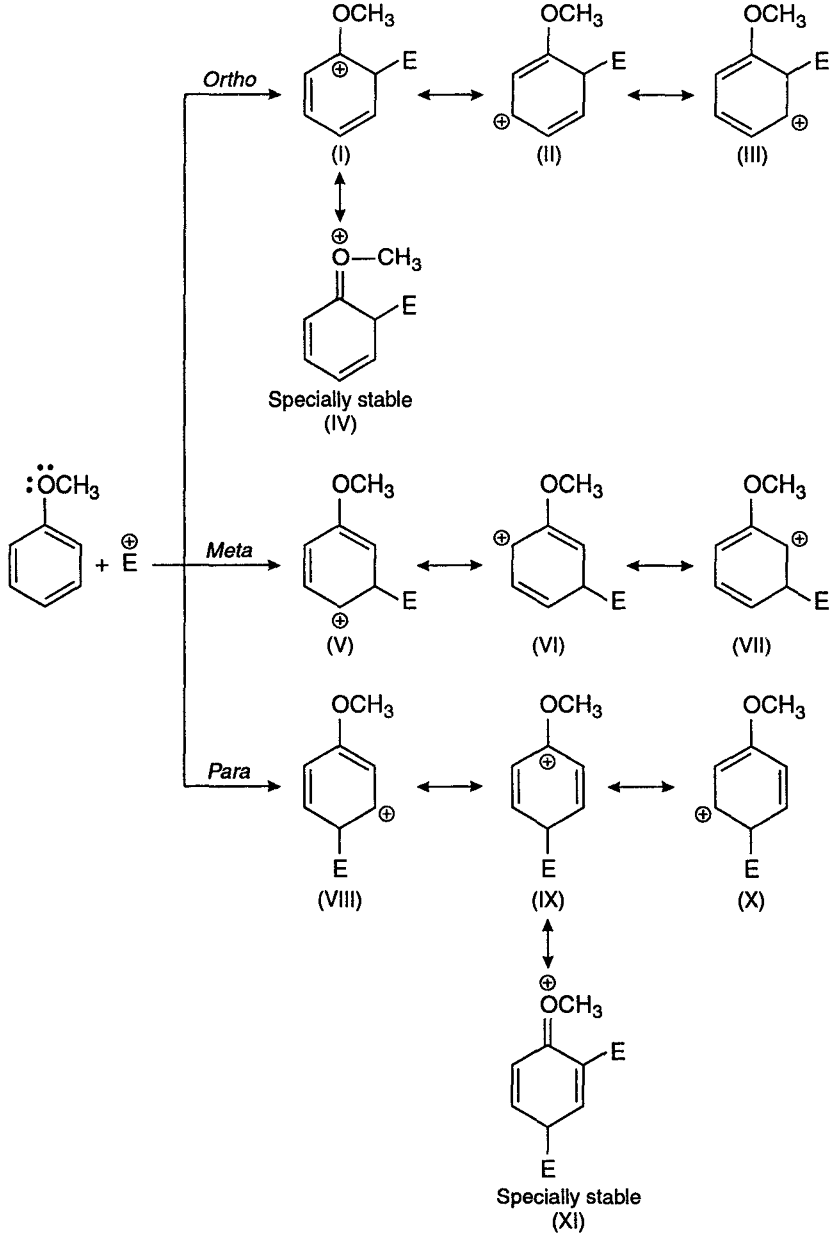


Fig. 6.7. The structures of the carbocation intermediates formed from the reaction of an electrophile with anisole at the *ortho*, *meta* and *para* position.

Case 3 : When group is $-I$ or $-R$ group.

Substituents (like $\overset{\oplus}{N}H_3$, $-CX_3$, NO_2, CHO, etc.) with $-I$ effect or $-R$ effect attached to the benzene ring withdraw electrons from the ring. All of these substituents withdraw electrons inductively.

(i) When group is –*I* group.

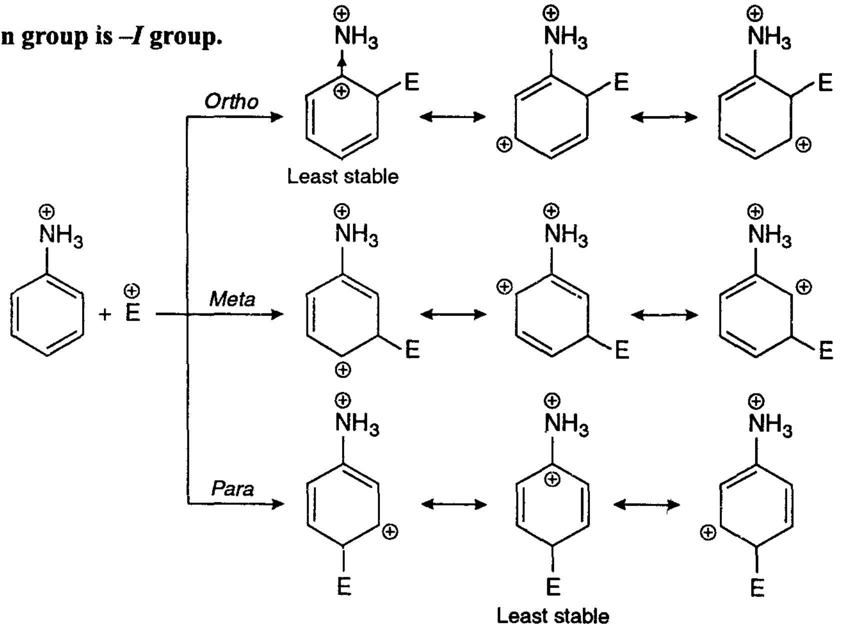


Fig. 6.8. Structures of the carbocation intermediates formed from the reaction of an electrophile with protonated aniline (–*I* group) at the *ortho*, *meta* and *para* positions.

(ii) When group is –*R* group.

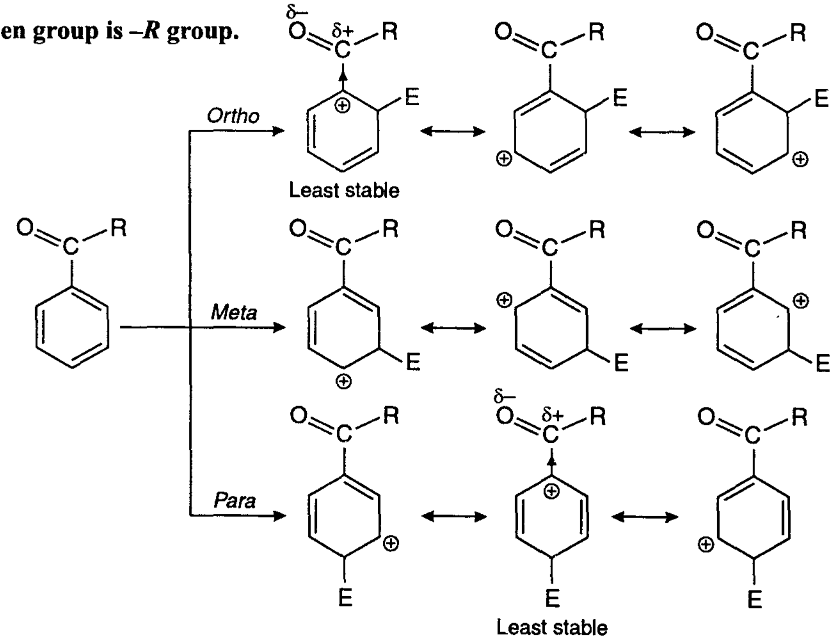


Fig. 6.9. Structures of the carbocation intermediates formed from the reaction of an electrophile with a substrate, having a –*R* group, at the *ortho*, *meta* and *para* positions.

and most withdraw electrons by reasonance as well. For all such substituents the indicated resonance contributors (Figs. 6.8 and 6.9) are the least stable. This is because the substituent is in a position to further increase the size of the positive charge on the carbon by inductive electron withdrawal. So the most stable carbocation occurs when the incoming electrophile is directed to the *meta* position.

Case 4 : Halogen Substituents : *Ortho*, *Para* Directing but Deactivating

We know that :

(i) All *meta* directing groups are deactivating groups.

(ii) All *ortho*, *para* directing groups except the halogens are activating groups.

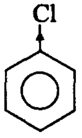
(iii) Halogens are *ortho/para* directing groups but are deactivating groups. Thus the halogens are exceptions to the general rules. We can explain this unusual combination of properties by considering that :

(1) The halogens are strongly electronegative and withdraw electron from a carbon atom through the *sigma* bond (– *I* effect).

(2) The halogens have non-bonding electrons that can donate electrons through *pi* bonding (+ *R* effect).

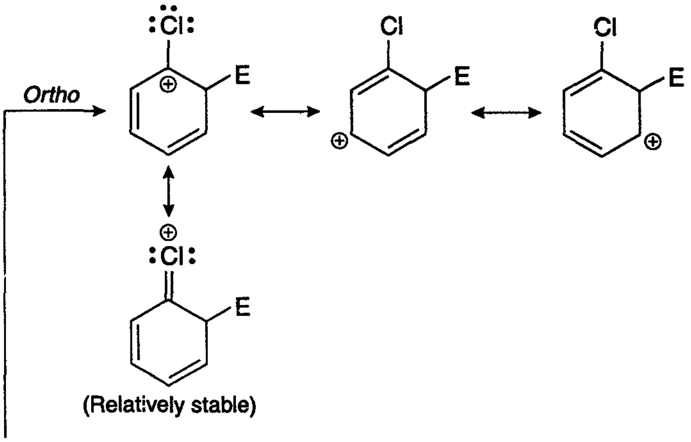
We can readily account for the behaviour of halo substituents, if we assume that **their electron withdrawing inductive effect influences reactivity and their electron donating resonance effect governs orientation.**

Let us apply these assumptions specially to chlorobenzene. The chlorine atom is highly electronegative. It has very strong – *I* effect. Thus we would expect a chlorine atom to withdraw electrons from the benzene ring and thereby deactivate it.



Inductive effect of chlorine atom deactivates ring

On the other hand, when electrophilic attack does take place, the chlorine atom stabilises the carbocation (arenium cation) resulting from *ortho* and *para* attack relative to that from *meta* attack. The chlorine atom does this by donating an unshared pair of electrons. These electrons give rise to relatively stable resonance structures contributing to the hybrids for the *ortho-* and *para-* substituted arenium ions. (Fig 6.10).



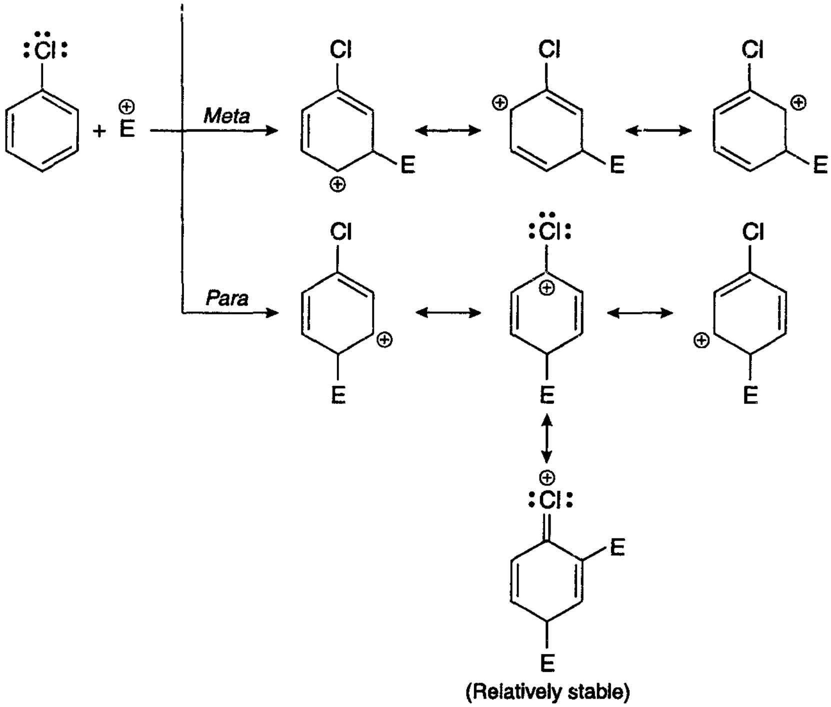


Fig. 6.10. Structures of the carbocation intermediates formed from the reaction of an electrophile with a halogenated benzene at the *ortho*, *meta* and *para* positions.

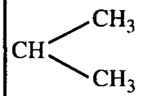
6.13 *ORTHO/PARA* RATIO

When a benzene derivative bears an *ortho/para* directing group, the ratio of the yield of the *ortho* product to that of the *para* product is known as *ortho/para* ratio. This ratio vary from reaction to reaction and substrate to substrate. Since there are two *ortho* positions and one *para* position relative to the substituent in a monosubstituted benzene, it may seem that the *o/p* ratio theoretically will be 2 : 1 in all reactions irrespective of any substituent; but this is not true. The products never form corresponding to that ratio. Several factors need consideration to explain the *o/p* ratios observed in aromatic substitution reactions. The main factors are the steric and electronic effects of the substituents already present on the benzene ring. The size of the attacking electrophile is also an important factor.

6.13.1 Steric Effect

Ortho position being very near to the substituent, the attacking electrophile experiences spatial congestion when it approaches the *ortho* position; but it does not experience the same when it attacks

Table 6.3 ***O/p ratio in the nitration of alkyl benzenes***

Substituent	% of *ortho* product	% of *para* product	*o/p* ratio
CH_3	58	37	1.57
C_2H_5	45	49	0.92
 $CH(CH_3)_2$	30	62	0.48
$—C(CH_3)_3$	16	73	0.22
Increasing size of the substituent			

the *para* position since this is far from the substituent. The larger the size of the substituent or that of the attacking electrophile, the greater is the spatial congestion at the *ortho* position and consequently the lower is the o/p ratio. This means that increasing spatial congestion at the *ortho* position the yield of the *ortho* product decreases and that of the *para* product increases (Table 6.3).

Table 6.3 reveals that as the size of the substituent increases down the series, the yield of *o*-nitro product decreases and that of the *para* product increases and as a consequence o/p ratio decreases.

It has also been found that as the size of the attacking electrophile increases, the o/p ratio decreases. Electrophilic substitution on chlorobenzene with electrophiles of different sizes shows that o/p ratio decreases as the size of the elecrophile increases (Table 6.4).

Table 6.4 Reactions on chlorobenzene and the o/p ratio

Attacking electrophile	% of *o*-product	% of *para* product	o/p ratio
$\overset{\oplus}{Cl}$	39	55	0.71
$\overset{\oplus}{NO_2}$	30	70	0.43
$\overset{\oplus}{Br}$	11	87	0.14
SO_3 ↓	1	99	0.01
Size of the electrophiles in increasing order			

6.13.2 Electronic Effect

The steric factor alone should not be held responsible for the observed o/p ratios in different reactions. The electronic effects should also be considered among other factors. When halobenzenes are nitrated under the same set of conditions, the yield of *ortho* product increases and that of the *para* product decreases despite the increase in the size of the substituents (Table 6.5).

Table 6.5 Electronic effect and the o/p ratio in the nitration of halobenzenes

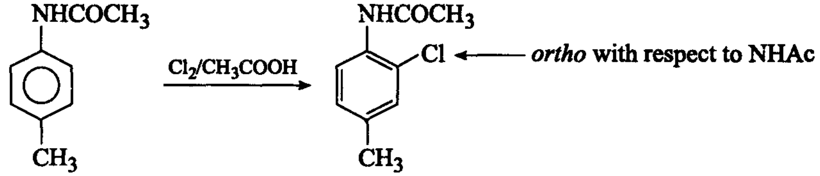
Substituent	% of *o* product	% of *para* product	o/p ratio
F	12	88	0.14
Cl	30	69	0.44
Br	37	62	0.60
I ↓	38	60	0.63
Increasing size decreasing-I power			

$-I$ group deactivates the benzene ring but the effect is the maximum on the *ortho* positions and it is practically nil on the *para* position due to the distance. In fluorobenzene the *ortho* positions being highly deactivated by the strong $-I$ effect of the fluorine atom, the attacking electrophile attacks the *para* position preferentially. In case of iodobenzene the $-I$ effect of the iodine atom being very small, it deactivates the *ortho* positions to a minimum extent and consequently an appreciable amount of the *ortho* product forms. Thus the o/p ratio increases on going from fluorobenzene to iodobenzene in the nitration of halobenzenes.

6.14 ORIENTATION IN DISUBSTITUTED BENZENES

Position of the third group entering the ring depends on the nature of two group already present in the ring.

Case I. When both the groups are activating groups, position of the third group is governed by the group which has higher activating power, *e.g.*,

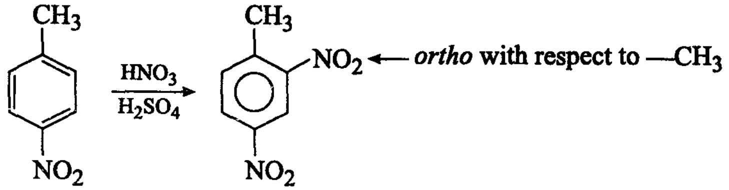


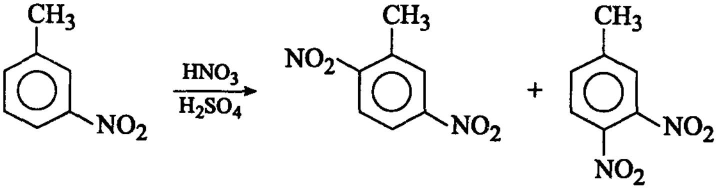
Activating power of NHAc is more than CH_3.

Activating power of groups in decreasing order is as follows :

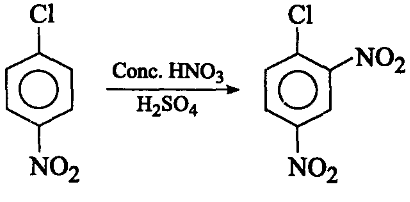
$\overset{\ominus}{O} > NR_2 > NHR > NH_2 > OH > OR > NHCOR > CH_3 >$ *prim*-alkyl > *sec*-alkyl > *t*-alkyl > C_6H_5

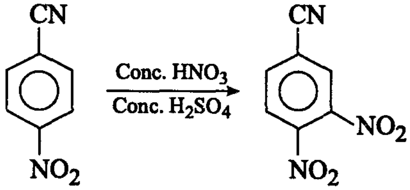
Case II. When one group is activating and the other group is deactivating group, position of incoming group is governed by activating group, *e.g.*,





Case III. When both the groups are deactivating groups, position of incoming group is decided by the group which has less deactivating power, *e.g.*,





Deactivating power of groups in decreasing order is as follows :

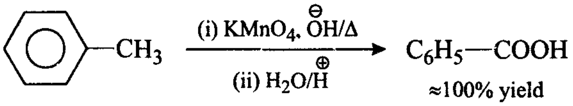
$\overset{\oplus}{N}R_3 > NO_2 > CF_3 > CN > SO_3H > CHO > COR > COOH > COOR >$
$CONH_2 > CCl_3 > F > Cl > Br > I$

6.15 SIDE CHAIN REACTIONS OF BENZENE DERIVATIVES

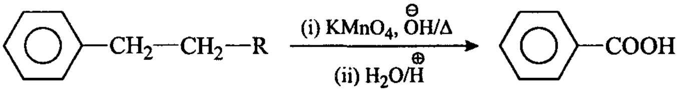
Although some reactions of phenyl substituted compounds are not affected by the presence of benzene ring, the aromatic ring becomes crucial in many other reactions. Let us consider some side-chain reactions that illustrate the effect of a nearly aromatic ring.

6.15.1 Side Chain Oxidation (Permanganate Oxidation)

Alkylbenzenes on oxidation with alkaline potassium permangnate give potassium salt of benzoic acid in almost quantitative yield.

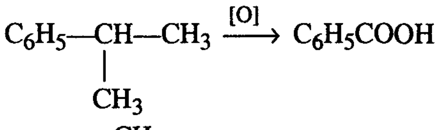


An important characteristic of side chain oxidations is that oxidation takes place initially at the benzylic carbon; alkyl groups longer than methyl are ultimately degraded to benzoic acid.

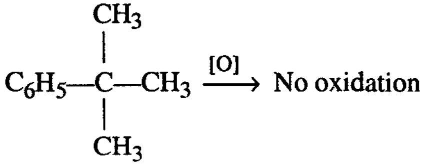


This oxidation begins with the abstraction of benzylic hydrogen by oxidising agent. Thus this oxidation is given only by those alkylbenzenes in which benzylic carbon has at least one hydrogen.

$$C_6H_5-CH_2-CH_3 \xrightarrow{[O]} C_6H_5COOH$$



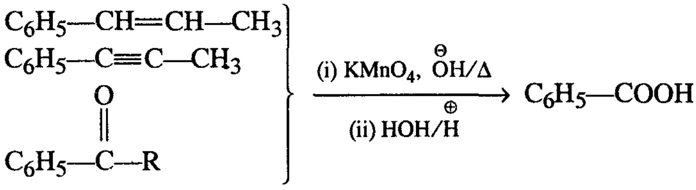
$$C_6H_5-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_3 \xrightarrow{[O]} C_6H_5COOH$$



$$C_6H_5-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3 \xrightarrow{[O]} \text{No oxidation}$$

The oxidising agent ultimately oxidises the benzylic carbon to a carboxylic group, and in the process, it cleaves the remaining carbon atoms of the side chain.

Side chain oxidation is not restricted to alkyl groups. Alkenyl, alkynyl and acyl groups are oxidised by hot alkaline potassium permanganate in the same way.



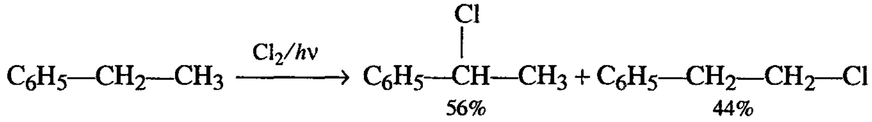
$$\left.\begin{array}{l} C_6H_5-CH{=}CH-CH_3 \\ C_6H_5-C{\equiv}C-CH_3 \\ C_6H_5-\overset{\displaystyle O}{\overset{\|}{C}}-R \end{array}\right\} \xrightarrow[\text{(ii) } HOH/\overset{\oplus}{H}]{\text{(i) } KMnO_4,\ \overset{\ominus}{O}H/\Delta} C_6H_5-COOH$$

The aromatic ring imparts extra stability to the nearest carbon (*i.e.*, benzylic carbon) atom of its side chains. The aromatic ring and benzylic carbon atom of a side chain can survive in a vigorous oxidation to give a carboxylate salt of benzoic acid.

6.15.2 Side Chain Halogenation

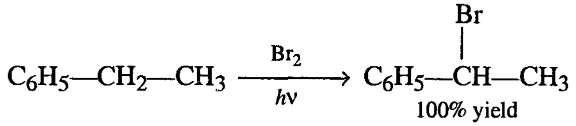
Alkylbenzenes undergo free radical halogenation more easily than alkanes. Halogenation mainly takes place at benzylic carbon atom. This is because reaction intermediate in this particular case is benzyi free radical which is stabilised by resonance due to the presence of benzene ring.

Although chlorine gives selective chlorination at benzylic carbon with alkyl benzenes, the chlorine radical is too reactive to give chlorination of other carbons also.



$$C_6H_5-CH_2-CH_3 \xrightarrow{Cl_2/h\nu} \underset{56\%}{C_6H_5-\overset{\displaystyle Cl}{\overset{|}{C}}H-CH_3} + \underset{44\%}{C_6H_5-CH_2-CH_2-Cl}$$

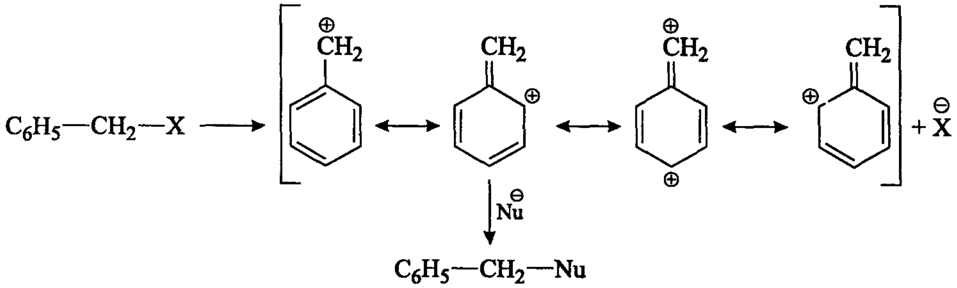
Bromine radicals are not as reactive as chlorine radicals, and bromination is more selective than chlorination. Bromine reacts exclusively at the benzylic position.



$$C_6H_5-CH_2-CH_3 \xrightarrow[h\nu]{Br_2} \underset{100\%\ \text{yield}}{C_6H_5-\overset{\displaystyle Br}{\overset{|}{C}}H-CH_3}$$

6.15.3 Nucleophilic Substitution of the Benzylic Position

(i) SN1 Reactions : A first order nucleophilic substitution requires ionisation of the halide to give a carbocation. In the case of benzyl halide, the carbocation is resonance stabilised. Thus benzyl halides are more reactive than alkyl halides.



(ii) SN2 Reactions : Benzyl halides are also more reactive than primary alkyl halides for SN2 reactions also. Benzyl halides are about 100 times as reactive as primary alkyl halides in SN2 reactions.

This enhanced reactivity is due to the presence of benzene ring at benzyl carbon. When benzyl halide undergoes SN2 reaction, the *p* orbital which is partially bonding with the nucleophile and the leaving group overlaps with the *pi* electrons of the ring. This stabilising conjugation lowers the energy of the transition state, increasing the reaction rate (Fig. 6.11).

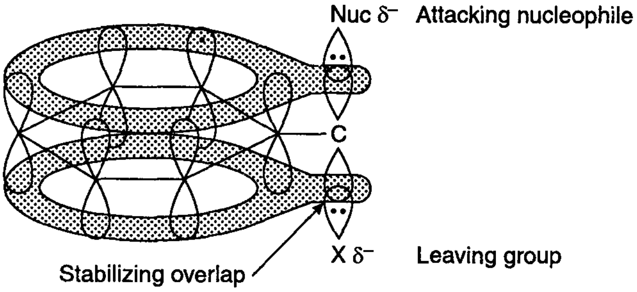


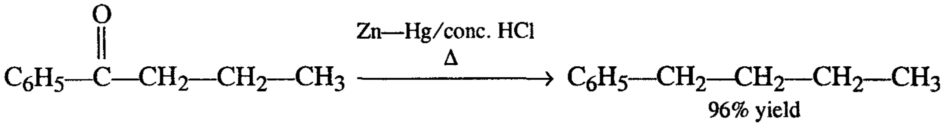
Fig. 6.11. The transition state for SN2 displacement of a benzylic halide is stabilized by conjugation with the π electrons in the ring.

6.15.4 Hydrogenolysis of Benzyl Alcohol

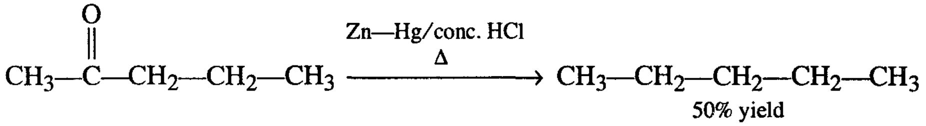
Although aliphatic alcohols are inert towards catalytic hydrogenation, benzylic alcohols are reduced to the corresponding hydrocarbons. Catalytic reduction where hydrogenation is used to break a single bond (*i.e.*, *sigma* bond) is called hydrogenolysis.

6.15.5 Clemmensen Reduction

Aryl ketones are more reactive than aliphatic ketones for Clemmensen reduction. The enhanced reactivity of aryl ketone is due to the presence of benzene ring on carbonyl carbon.



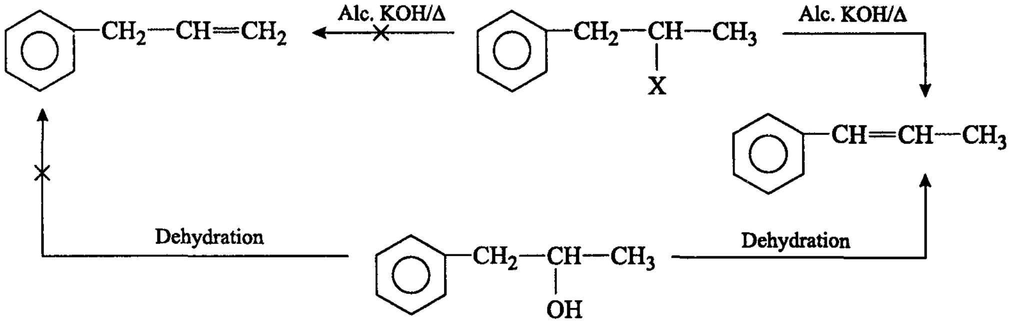
$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_2-CH_3 \xrightarrow[\Delta]{\text{Zn—Hg/conc. HCl}} \underset{\text{96\% yield}}{C_6H_5-CH_2-CH_2-CH_2-CH_3}$$



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_2-CH_3 \xrightarrow[\Delta]{\text{Zn—Hg/conc. HCl}} \underset{\text{50\% yield}}{CH_3-CH_2-CH_2-CH_2-CH_3}$$

6.15.6 Orientation of β-Eliminations

The orientation of eliminations in compounds having a side chain larger than two carbon atoms is greatly affected by the presence of an aromatic ring.



6.16 ALKYLBENZENES

6.16.1 Methods of Formation

(i) Wurtz-Fittig reaction : Fittig modified Wurtz reaction and found that crossed coupling takes place between an alkyl and aryl halide when they are treated with metallic sodium in ethereal solution to give an alkylbenzene mixed with diaryl and dialkyl derivatives.

$$C_6H_5-X + 2Na + X-R \xrightarrow{\text{ether}} C_6H_5-R + 2NaX$$

This method has an advantage over Friedel-Crafts reaction, as there is no isomerisation in the alkyl group during the course of reaction.

When aryl halide, *e.g.*, bromobenzene, is treated with metallic sodium, it gives biphenyl (*Fittig reaction*).

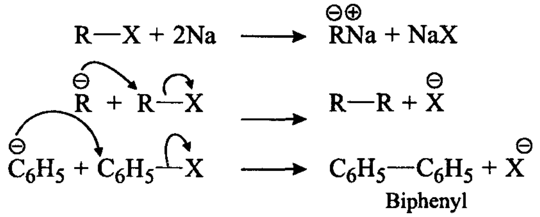
$$2C_6H_5-Br + 2Na \longrightarrow C_6H_5-C_6H_5 + 2NaBr$$

As for the Wurtz reaction, free radical and ionic mechanisms have been proposed for Wurtz-Fittig reaction. However, evidence favour ionic mechanism which is as follows :

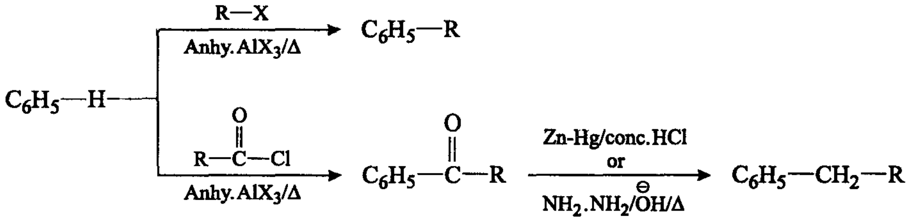
$$C_6H_5-X + Na \longrightarrow \underset{\text{Organometallic intermediate}}{\overset{\ominus}{C_6H_5}\overset{\oplus}{Na}} + NaX$$

$$\overset{\ominus}{C_6H_5} + R-X \longrightarrow C_6H_5-R + \overset{\ominus}{X}$$

This mechanism can similarly explain the formation of other products during the reaction :

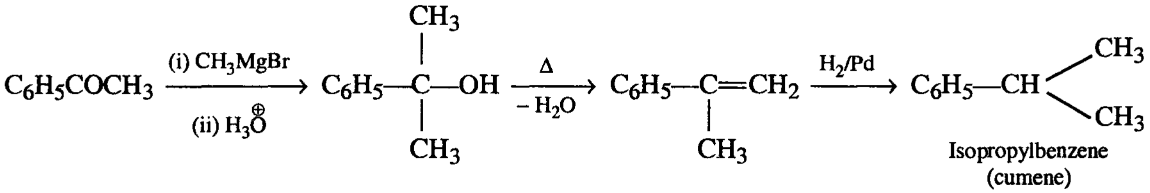


(ii) Friedel-Crafts reaction : As discussed in Section 6.9.



(iii) Grignard reaction : Grignard reaction is also useful for preparing alkylbenzenes with branched side chain as follows :

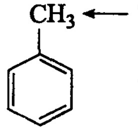
$$C_6H_5MgBr + X\text{—}R \longrightarrow C_6H_5\text{—}R + MgXBr$$



6.16.2 Chemical Reactions

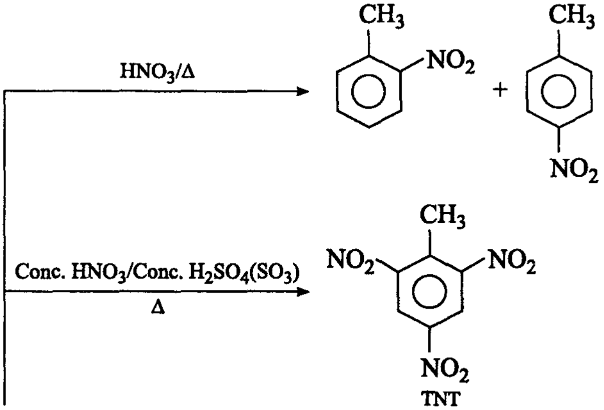
Monosubstituted alkylbenzene gives three types of reaction.

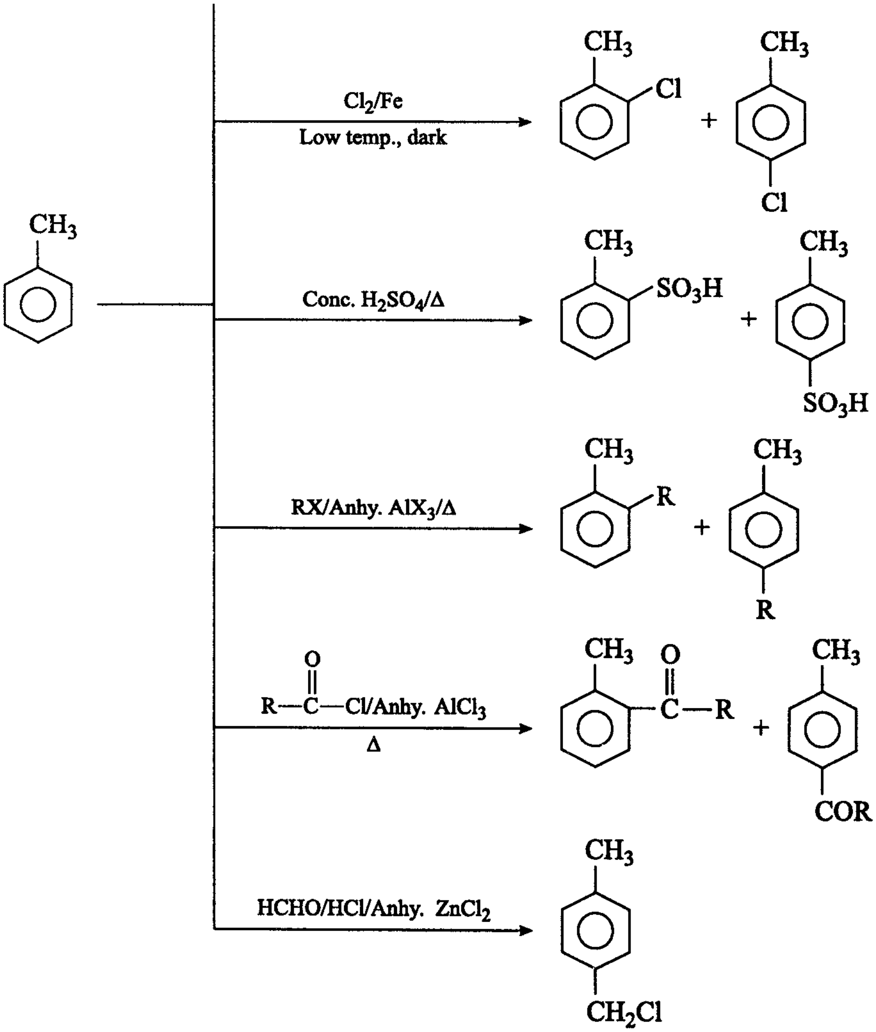
(1) Reaction due to benzene ring, *i.e.*, electrophilic aromatic substitution reaction.



This group is
(i) activating group and
(ii) *ortho-para* directing group

hence substitution reactions will take place at *ortho* and *para* positions. Major product in almost all cases is *para* due to steric effect. Electrophilic substitution reactions of toluene are given below :





(2) Properties Due to Side chain : (i) Free radical halogenation at Benzylic carbon :

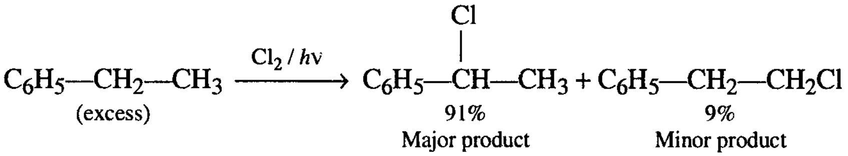
(a) Chlorination : Toluene undergoes chlorination in the presence of sunlight, and the nature of product depends on the molar ratio of toluene and chlorine. The chlorinated products on hydrolysis give benzyl alcohol, benzaldehyde and benzoic acid.

$$\text{(i)}\quad \underset{\text{excess}}{C_6H_5\text{—}CH_3} \xrightarrow{Cl_2/h\nu} \underset{\text{Benzyl chloride}}{C_6H_5\text{—}CH_2\text{—}Cl} \xrightarrow{\overset{\ominus}{O}H} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}$$

$$\text{(ii)}\quad \underset{1\text{ mole}}{C_6H_5\text{—}CH_3} + \underset{2\text{ mole}}{Cl_2} \xrightarrow{h\nu} \underset{\text{Benzal chloride}}{C_6H_5\text{—}CHCl_2} \xrightarrow{\overset{\ominus}{O}H} \underset{\text{Benzaldehyde}}{C_6H_5CHO}$$

$$\text{(iii)}\quad C_6H_5\text{—}CH_3 + \underset{\text{(excess)}}{Cl_2} \xrightarrow{h\nu} \underset{\text{Benzotrichloride}}{C_6H_5\text{—}CCl_3} \xrightarrow[\text{(ii) } H_3\overset{\oplus}{O}]{\text{(i) }\overset{\ominus}{O}H} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

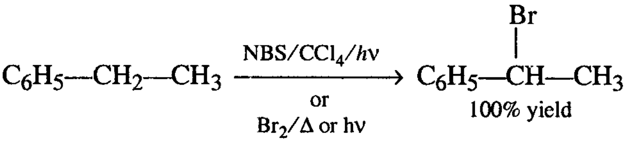
Chlorine as chlorinating agent is most reactive and least selective reagent hence chlorination reaction is not very useful reaction.



$$\underset{\text{(excess)}}{C_6H_5-CH_2-CH_3} \xrightarrow{Cl_2\,/\,h\nu} \underset{\substack{91\% \\ \text{Major product}}}{C_6H_5-\overset{\overset{\displaystyle Cl}{|}}{C}H-CH_3} + \underset{\substack{9\% \\ \text{Minor product}}}{C_6H_5-CH_2-CH_2Cl}$$

(b) Bromination : Bromination reaction can be carried out either by Br_2 or by NBS. Br_2 is less reactive, hence more selective reagent. Bromination takes place only at benzylic carbon and product is always monobromo derivative.

$$C_6H_5-CH_3 \xrightarrow[\substack{\text{or} \\ NBS/CCl_4/h\nu}]{Br_2/h\nu \text{ or } \Delta,} \underset{100\%}{C_6H_5-CH_2-Br}$$

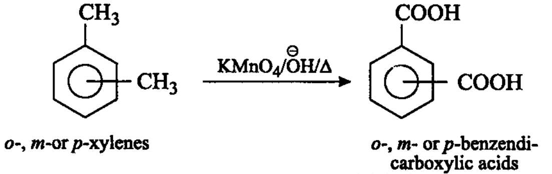


$$C_6H_5-CH_2-CH_3 \xrightarrow[\substack{\text{or} \\ Br_2/\Delta \text{ or } h\nu}]{NBS/CCl_4/h\nu} \underset{100\% \text{ yield}}{C_6H_5-\overset{\overset{\displaystyle Br}{|}}{C}H-CH_3}$$

(ii) Side chain oxidation (a) Strong oxidising agents oxidise alkyl benzenes into benzoic acid. The oxidation can be carried out by hot $KMnO_4/\overset{\ominus}{O}H/\Delta$. Benzene ring is not oxidised under these conditions.

$$C_6H_5-CH_3 \xrightarrow{KMnO_4/\overset{\ominus}{O}H/\Delta} \underset{100\% \text{ yield}}{C_6H_5-COOH}$$

$$C_6H_5-CH_2-CH_2-CH_3 \xrightarrow{KMnO_4/\overset{\ominus}{O}H/\Delta} C_6H_5-COOH$$

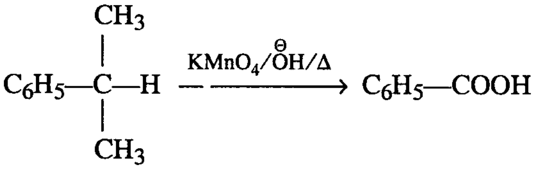


o-, *m*-or *p*-xylenes

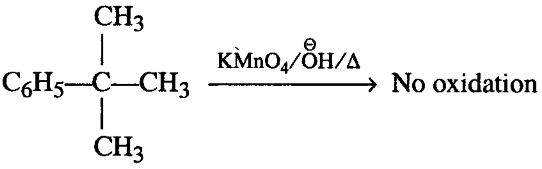
o-, *m*- or *p*-benzendicarboxylic acids (phthalic acid, isophthalic acid or teriphthalic acid)

Note :

1. Alkyl benzene can only be oxidised when benzyl carbon has atleast one hydrogen (*i.e.*, benzyl carbon should not be quaternary)

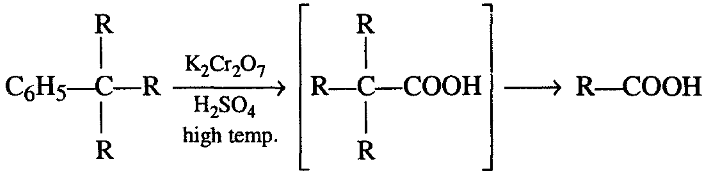


$$C_6H_5-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-H \xrightarrow{KMnO_4/\overset{\ominus}{O}H/\Delta} C_6H_5-COOH$$



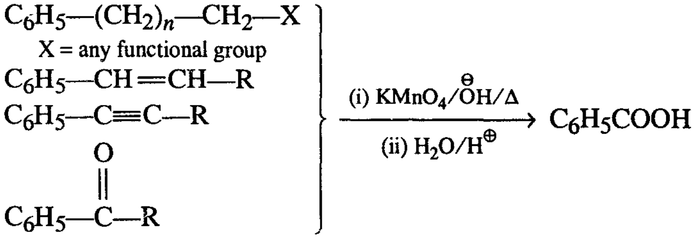
$$C_6H_5-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3 \xrightarrow{KMnO_4/\overset{\ominus}{O}H/\Delta} \text{No oxidation}$$

2. If side chain has no α-hydrogen then benzene ring is cleaved. This reaction takes place at very high temperature.



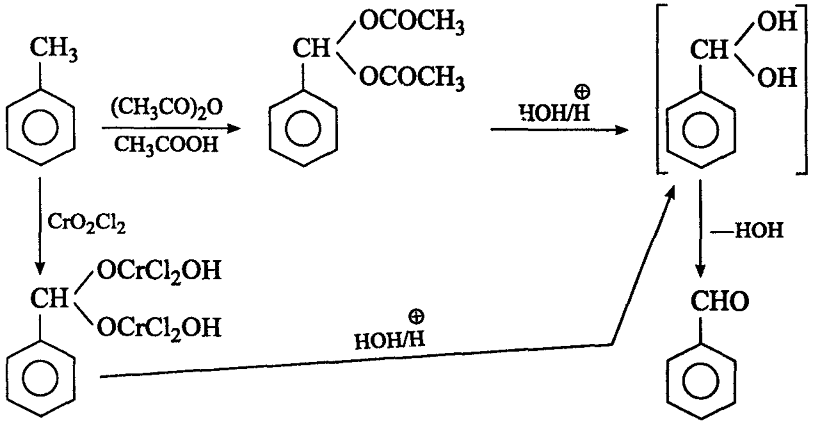
$$C_6H_5-\overset{\displaystyle R}{\underset{\displaystyle R}{C}}-R \xrightarrow[\text{high temp.}]{K_2Cr_2O_7 \;/\; H_2SO_4} \left[R-\overset{\displaystyle R}{\underset{\displaystyle R}{C}}-COOH \right] \longrightarrow R-COOH$$

3. Side chain oxidation is not restricted to alkyl groups. Alkenyl, alkynyl, acyl and alkyl substituted groups are oxidised to benzoic acid.



$$\left.\begin{array}{l} C_6H_5-(CH_2)_n-CH_2-X \\ \text{X = any functional group} \\ C_6H_5-CH{=}CH-R \\ C_6H_5-C{\equiv}C-R \\ C_6H_5-\overset{\displaystyle O}{\overset{\|}{C}}-R \end{array}\right\} \xrightarrow[\text{(ii) } H_2O/H^{\oplus}]{\text{(i) } KMnO_4/\overset{\ominus}{O}H/\Delta} C_6H_5COOH$$

(b) Methyl group of aromatic ring is also oxidised by
(i) CrO_3/acetic anhydride or
(ii) CrO_2Cl_2 (chromyl chloride) or
(iii) SeO_2

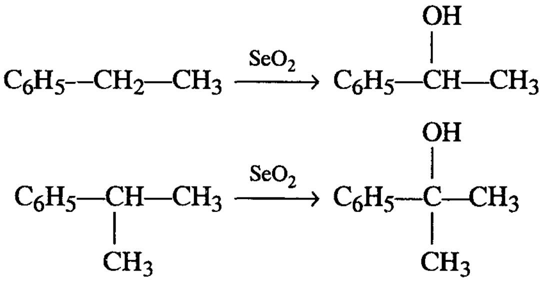


Note :
(1) Conversion of toluene into benzaldehyde by chromyl chloride is known as **Etard reaction.**
(2) Chromyl chloride also oxidises terminal methyl group of alkyl benzene into CHO group.

$$C_6H_5-CH_2-(CH_2)_n-CH_3 \xrightarrow[\text{(ii) } HOH/\overset{\oplus}{H}]{\text{(i) } CrO_2Cl_2/CS_2} C_6H_5-CH_2-(CH_2)_n-CHO$$

Selenium dioxide gives benzylic oxidation with alkyl benzene. In this reaction one of the benzylic hydrogen is replaced by —OH group.

$$C_6H_5-CH_2-H \xrightarrow{SeO_2} C_6H_5-CH_2-OH$$



$$C_6H_5{-}CH_2{-}CH_3 \xrightarrow{SeO_2} C_6H_5{-}\overset{\overset{OH}{|}}{C}H{-}CH_3$$

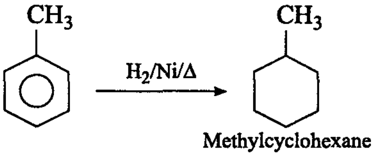
$$C_6H_5{-}\underset{\underset{CH_3}{|}}{C}H{-}CH_3 \xrightarrow{SeO_2} C_6H_5{-}\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}{-}CH_3$$

(c) Oxidation of benzene ring : The benzene ring of an alkylbenzene can be converted to a carboxylic group by ozonolysis followed by treatment with hydrogen peroxide.

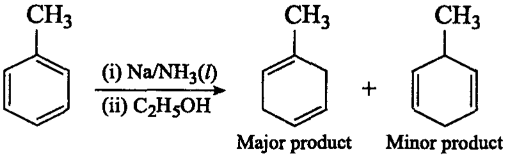
$$R{-}C_6H_5 \xrightarrow[\text{(ii) } H_2O_2]{\text{(i) } O_3/CH_3COOH} R{-}COOH$$

(3) Reduction : Toluene gives two types of reduction :

(i) Total reduction



(ii) Birch reduction

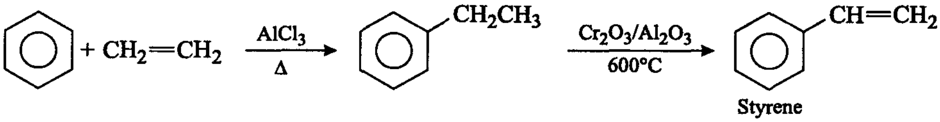


6.17 ALKENYLBENZENES

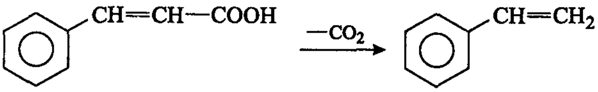
6.17.1 Methods of Formation

Methods of preparation of alkenylbenzenes are similar to β-elimination reactions employed for the formation of alkenes. Some of the common methods are illustrated by the synthesis of styrene.

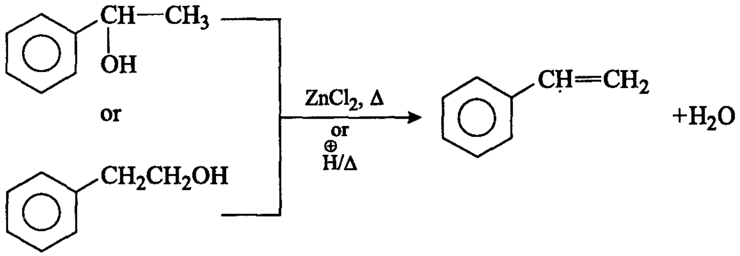
(i) Dehydrogenation of the side chain :



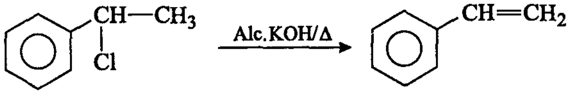
(ii) Decarboxylation of carboxylic acids having an unsaturated side chain : Laboratory preparation of styrene involves heating of cinnamic acid in the presence of a little hydroquinone which prevents polymerisation.



(iii) Dehydration of hydroxyalkylbenzenes :



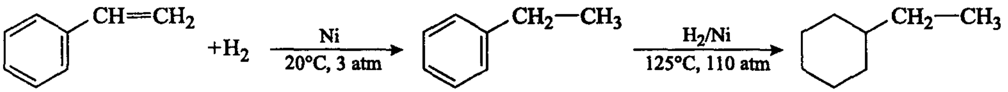
(iv) Dehydrohalogenation of haloalkylbenzenes :



6.17.2 Chemical Reactions

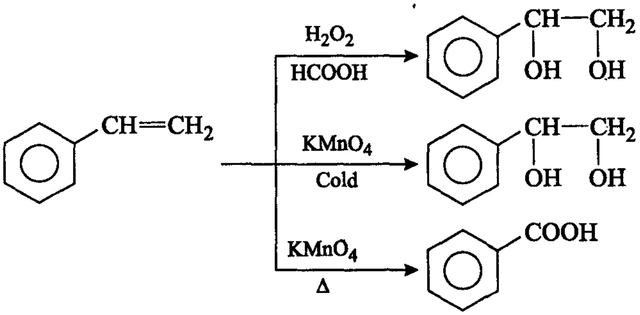
Alkenylbenzenes exhibit electrophilic additions due to unsaturated side chain and electrophilic substitution reactions due to aromatic nucleus.

(i) Hydrogenation :

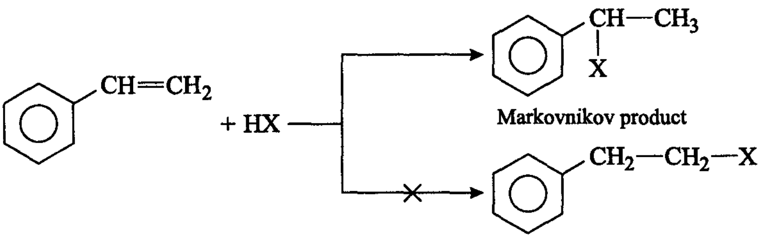


The side chain double bond of the styrene can be reduced preferentially by choosing the proper reaction conditions.

(ii) Oxidation :

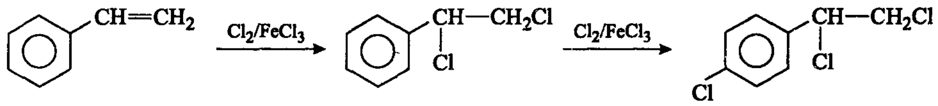


(iii) Addition of halogen acids :

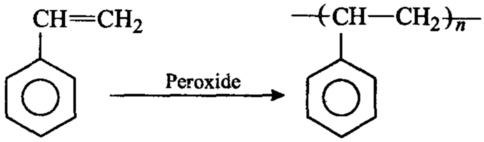


In the presence of peroxide or light *anti*-Markovnikov product is obtained, when HBr is added to styrene.

(iv) Addition of halogens :



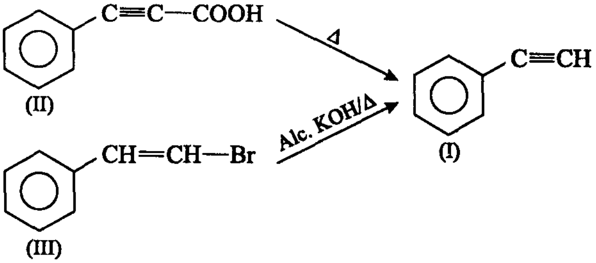
(v) Polymerisation : In the presence of peroxides, styrene undergoes free radical polymerisation resulting in the formation of polystyrene which is an industrially important plastic.



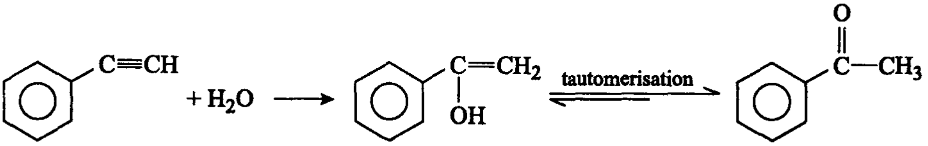
Polystyrene

6.18 ALKYNYLBENZENES

The simplest compound of this class, phenylacetylene (I) may be prepared by decarboxylation of phenylpropionic acid (II) or by dehydrobromination of β-bromostyrene (III) :

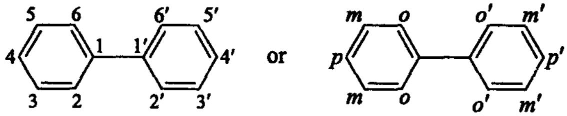


Similar to acetylene, it also shows acidic properties and forms metallic salts. On reduction with Zn dust and acetic acid it gives styrene. It can be hydrated in the presence of mercuric perchlorate and perchloric acid in aqueous dioxane to give acetophenone.



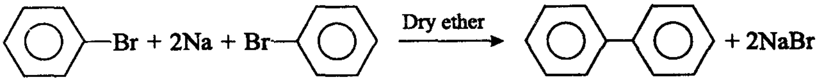
6.19 BIPHENYL (DIPHENYL)

Biphenyl is the simplest and most important example of an aromatic hydrocarbon in which the two rings are directly linked to each other. It occurs in coal-tar. The structure of biphenyl, including the numbering of this system, is given on the next page :

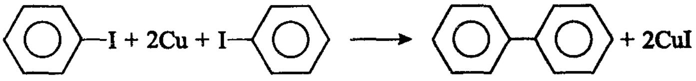


6.19.1 Methods of Formation

(i) Fittig reaction : This is carried out by treating bromobenzene with metallic sodium in ethereal solution.

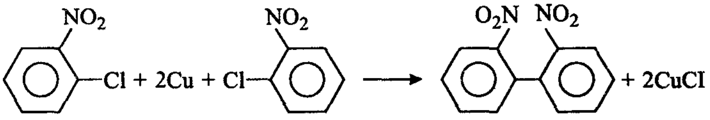


(ii) Ullmann biaryl synthesis : Iodobenzene on heating with copper or copper bronze in a sealed tube affords biphenyl.

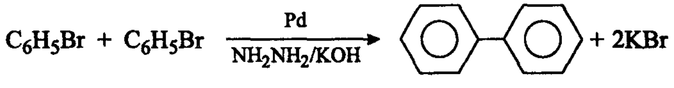


This reaction usually fails with aryl chlorides and aryl bromides unless some strong electron withdrawing group is present in the *ortho* or *para* position.

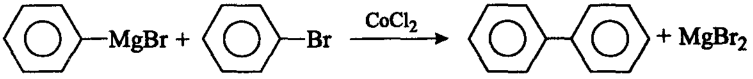
This reaction is preferably carried out in dimethylformamide (DMF).



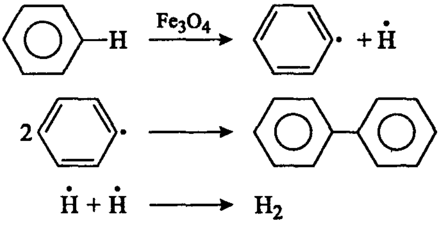
(iii) Biphenyl is formed by refluxing bromobenzene with hydrazine in alcoholic KOH solution in the presence of Pd catalyst.



(iv) Biphenyl is formed by reaction between phenylmagnesium bromide and bromobenzene in the presence of small amount of cobaltous chloride.



(v) Industrial preparation of biphenyl involves pyrolytic coupling of benzene in the vapour phase (1000°–1100°) in the presence of a little moisture and Fe_3O_4. The reaction is called intermolecular dehydrogenation and may take place *via* free radical coupling.

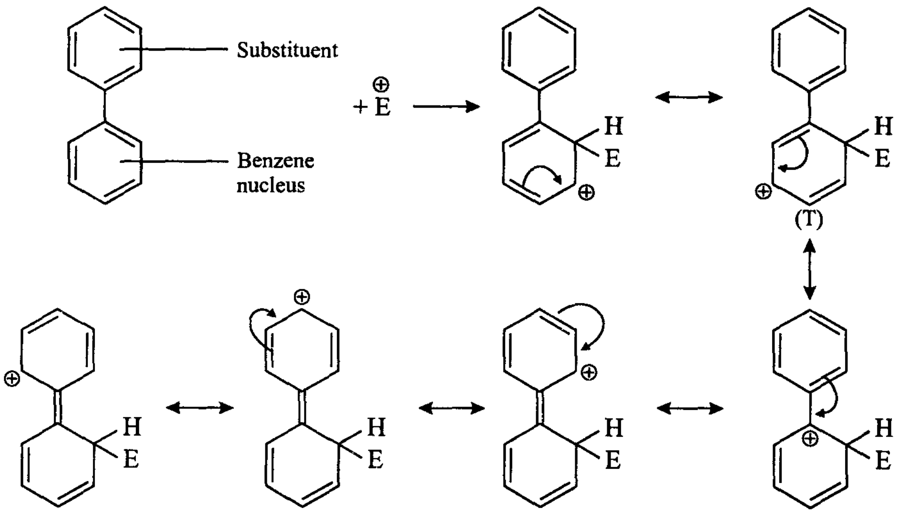


6.19.2 Properties and Reactions :

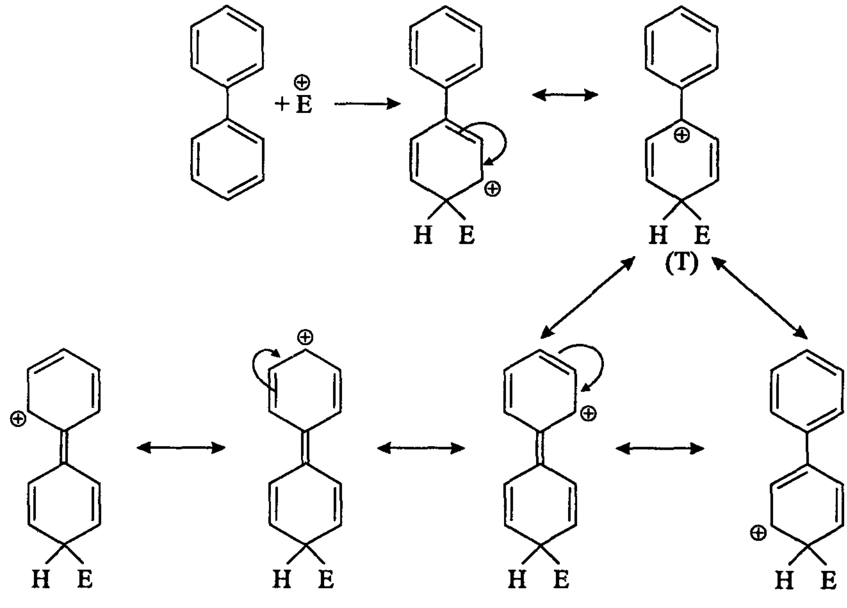
It is colourless crystalline solid m.p. 71°C. It has a characteristic odour. It is insoluble in water but soluble in organic solvents like alcohol and ether.

Diphenyl exhibits the usual electrophilic substitution reactions. In a broader sense, the molecule can be regarded as a benzene derivative having a phenyl substituent. The phenyl group (phenyl substituent) is *o* and *p*-directing and this activates the other benzene ring for electrophilic substitution. **Although phenyl groups are electron withdrawing (– *I*) they might seem to be deactivating and *m*-directing but due to the resonance effect (+ *R*), these are *o*, *p*-directing.** Orientation effect of one benzene ring on the other can best be explained as follows :

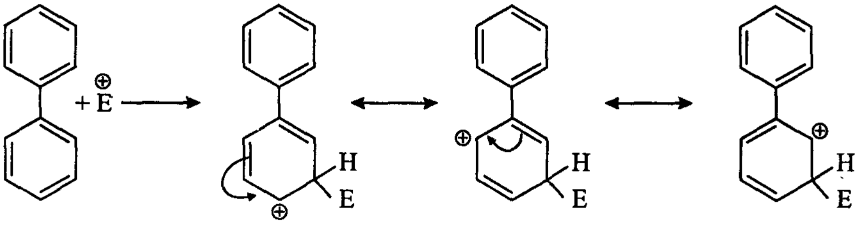
***ortho* attack**



***Para* attack**

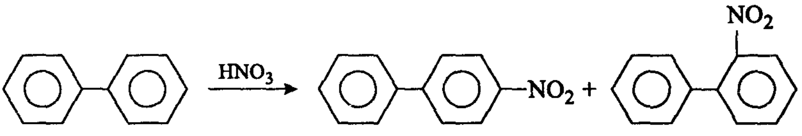


***Meta* attack**



The tendency of biphenyl to undergo substitution at *ortho* and *para* positions can be understood in terms of the **Wheland intermediates (σ complexes).** In the case of *ortho* and *para* there is one structure (marked T) in each case where the positive charge is located on the carbon atom to which the phenyl group is attached, whereas no such intermediate is possible in case of *meta* attack. The structures marked T are more stable, firstly because they are benzylic carbocations whereas all other forms are secondary carbocations, and secondly because of the *p*-π conjugation there is delocalisation of positive charge from this carbon to the ring. In other words, the charge is spread over both rings (due to T) in *ortho* and *para* substitution. In *meta* substitution charge spreading is confined to only one ring.

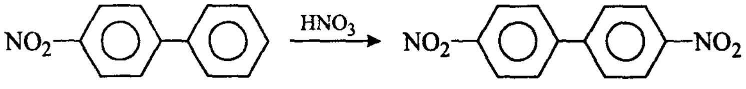
For monosubstitution reactions of biphenyl the substituent enters mainly the *p*-position and to a lesser extent the *ortho* position. For example, on nitration the main product is 4-nitrobiphenyl together with a small amount of 2-nitrobiphenyl.



Major product Minor product

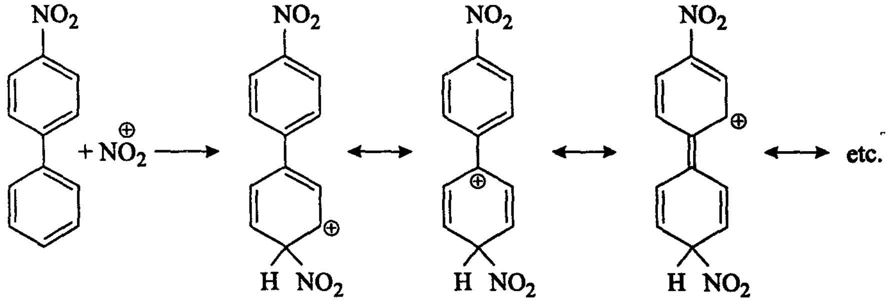
The second substituent enters the unsubstituted phenyl ring either at *para* or *ortho* position, irrespective of the electron withdrawing or electron releasing nature of the first substituent.

The reason for such a disubstitution at *para* or *ortho* positions rather than disubstitution at *m*-position is the greater stability of carbocation intermediate. In the former the charge is spread over both rings. In *meta* substitution charge spreading is confined to only one ring.

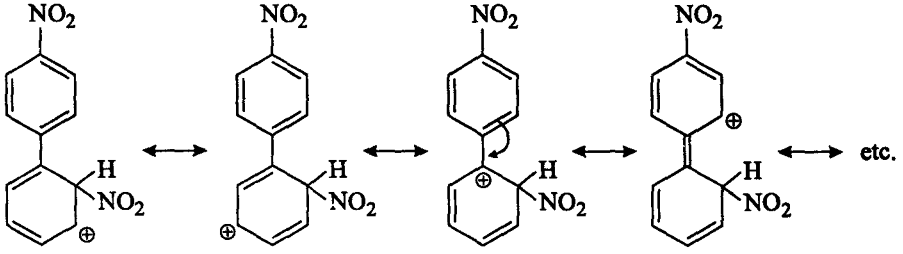


4, 4'-dinitrobiphenyl

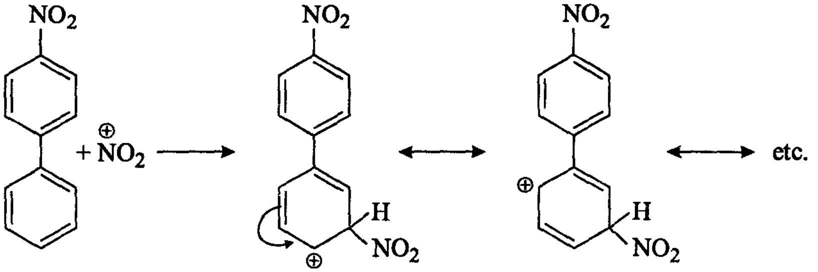
***para* attack**



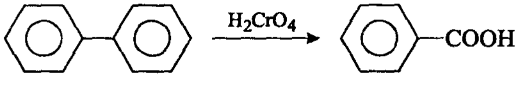
***ortho* attack**



***meta* attack**

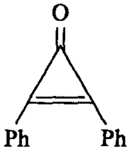


Oxidation : On oxidation with chromic acid it forms small amount of benzoic acid, most of the hydrocarbon being oxidised completely to carbon dioxide and water.



VERY SHORT ANSWER QUESTIONS

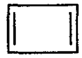
1. Which of the following has the highest resonance energy?
   Cyclobutadiene, Cyclooctatetraene and Cycloheptatrienyl cation.
2. Explain why cyclopentadienone is less stable than cyclopropenone and cycloheptatrienone?
3. 3-Chlorocyclopropene reacts with $SbCl_5$ to form a salt but chlorocyclopropane does not. Explain why?
4. Although the following compound contains a keto group, it does not undergo nucleophilic addition reactions. Explain.

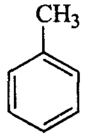


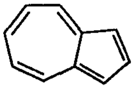
5. Predict the product of Friedel-Crafts reaction with isobutyl chloride.
6. Write the structure of the major bromination product of *o*-acetamidoanisole.
7. Which of three isomeric xylenes will undergo sulphonation preferentially. Explain.
8. Give the structure of the major product formed when toluence is subjected to Birch reduction.
9. Mesitylene reacts with HF/SbF_5 in liquid SO_2 to form a coloured crystalline complex. Suggest a suitable structure of the product.
10. Benzene has three carbon-carbon double bonds but it fails to give Baeyer's test. Explain why?
11. Cyclooctatetraene reacts with two equivalents of potassuim to give an unusually stable compound. Write the structure and account for its unusual stability.

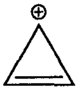
PROBLEMS WITH SOLUTIONS

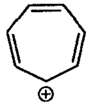
1. Determine whether the following compounds are aromatic, anti-aromatic or non-aromatic. Explain your answers.

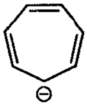
(a) 

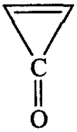
(b) 

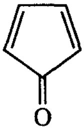
(c) 

(d) 

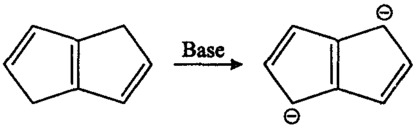
(e) 

(f) 

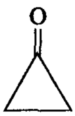
(g) 

(h) 

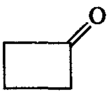
2. 2, 4-Pentadien-1-ol has hydroxyl group at allylic carbon. The compound protonates and loses water radily to give the corresponding carbocation with conc. H_2SO_4. On the other hand, its cyclic counterpart cyclopentadienol does not protonate and lose water to give cyclopentadienyl cation with conc. H_2SO_4. Explain.
3. Write resonance forms of the dianion formed by the following reaction and explain its ease of formation.

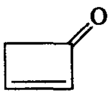


4. Benzene reacts with covalent thallium tri-fluoroacetate to form phenylthalium trifluoroacetate. Give mechanism for this electrophilic substitution reaction.
5. (a) Write contributing structures for σ complex (*i.e.*, intermediate arenium ion) from reaction C_6H_5—G with $\overset{\oplus}{E}$ at the *ortho*, *meta* and *para* positions.
   (b) Classify the group G when it is an electron-donating group. What will be the effect of the stability of the σ complex in these cases.
   (c) Also classify electron-withdrawing G groups in terms of their structures and electronic effect and give an example of each.
6. Explain why activating power of —$\overset{\ominus}{O}$ is more than the —OH.
7. Explain why nitroso group is *ortho*, *para* directing group but is deactivating group although key atoms is bonded with electronegative atom (*i.e.*, oxygen) with a multiple bond.
8. Which of the following has maximum dipole moment.

(a) 

(b) 

(c) 

(d) 

9. Which of the following is most reactive towards ring nitration with mixed acid (conc. HNO_3 + conc. H_2SO_4) ?
   (a) Toluene (b) Aniline (c) Chlorobenzene (d) Acetophenone
10. Which of the following is *meta* directing ?
   (a) —F (b) —$NHCOCH_3$ (c) —CF_3 (d) —$NHCH_3$
11. In the following reaction :

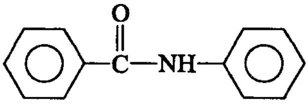
$$C_6H_5\text{—}CH_3 \xrightarrow{SeO_2} (X)$$

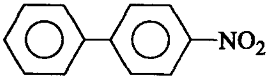
(X) will be :

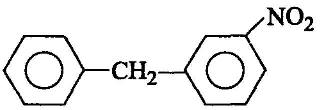
(a) $C_6H_5—CH_2OH$ (b) $C_6H_5—CHO$

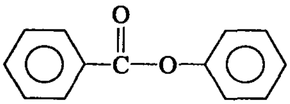
(c) $C_6H_5—COOH$ (d) mixture of C_6H_5CHO and C_6H_5COOH

12. Give the structure of the major mononitro product formed on nitration of each of the following :

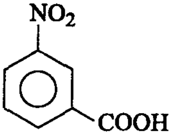
(a)


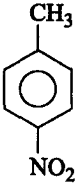
(b)


(c)


(d)


13. For each of the following compounds, indicate the ring carbon that would be preferably nitrated with conc. HNO_3/conc. H_2SO_4.

(a)


(b)


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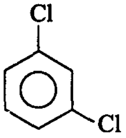
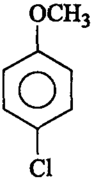
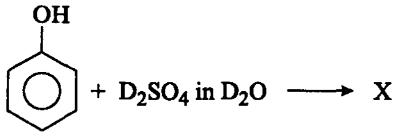
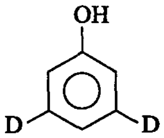


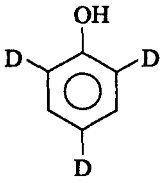
(d)


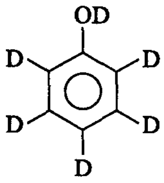
14. Consider the following reaction :

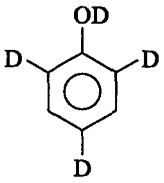


The product X is :

(a)


(b)


(c)


(d)


15. Arrange the chemical species in each of the following sets in increasing order of percentage of *meta* electrophilic substitution :

(a) $PhCH_2Cl$, $PhCHCl_2$, $PhCCl_3$. (b) $Ph\overset{\oplus}{N}Me_3$, $PhCH_2\overset{\oplus}{N}Me_3$, $PhCH_2CH_2\overset{\oplus}{N}Me_3$.

(c) $PhCOCH_3$, $PhNHCOCH_3$, $PhCCl_3$.

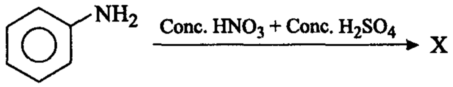
16. Give the principal monosubstitution product in each of the following reactions and indicate whether the reaction is faster (F) or slower (S) than with benzene :

(a) Nitration of PhNHCOMe (b) Nitration of Ph—Ph

(c) Bromination of PhI (d) Sulphonation of $PhCHMe_2$

(e) Chlorination of $PhCMe_3$ (f) Bromination of $PhCBr_3$

17.



The product *X* in the above reaction will be :

(a) *o*-Nitroaniline (b) *p*-Nitroaniline

(c) *m*-Nitroaniline (d) A mixture of *o*- and *p*-nitroanilines.

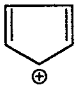
18. Give the major product of the reaction of benzene with :

(a) $CH_3CH{=}CH_2$ (HF, 0°C) (b) Cyclohexanol (BF_3, 60°C)

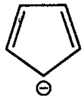
(c) $CH_3CH_2CH_2Cl/AlCl_3$ (d)

/$AlCl_3$

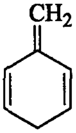
19. Characterize the following chemical species as aromatic, nonaromatic or antiaromatic :



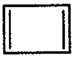
I



II

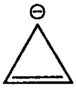


III



IV

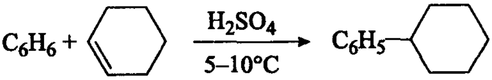
V



VI

20. Draw all the possible aromatic ions having the molecular formula C_4H_4.

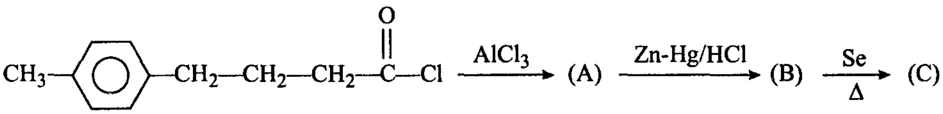
21. (a) Give the mechanism of the given reaction :



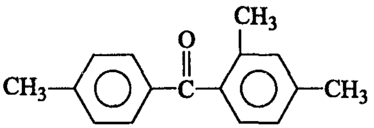
(b) Explain why the same product formed when cyclohexanol is use in place of cyclohexene?

22. (a) What product is formed when 2-methy-2-butene is added to large excess of benzene containing HF and the Lewis acid BF_3? By what mechanism it is forward?

(b) Complete the following reaction

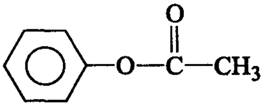


(c) How the given compound can be prepared by Friedel-Crafts acylation reaction?

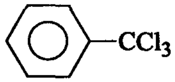


23. Predict the predominant products that would result from bromination of each of the following compounds.

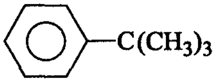
(a)



(b)



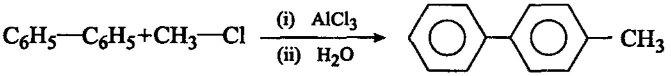
(c)



(d) $C_6H_5-\overset{\ominus}{O}$

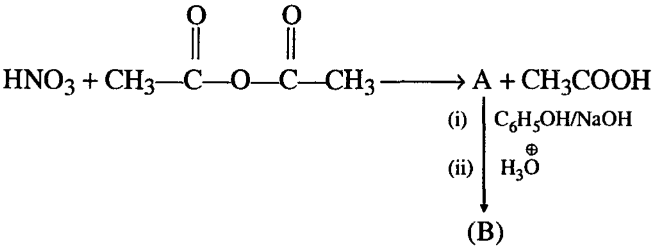
(e) $C_6H_5-\overset{\oplus}{N}(C_2H_5)_3$

24. Biphenyl undergoes the Friedel-Crafts reaction as shown by the given reaction :



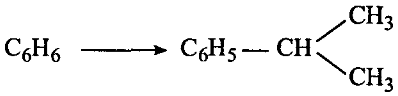
(a) On the basis of the above reaction, what is the directing effect of the phenyl group?
(b) Explain the directing effect of the phenyl group.

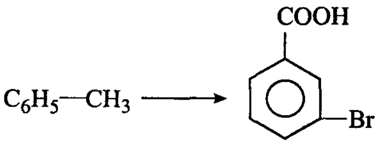
25. Complete the following reactions :

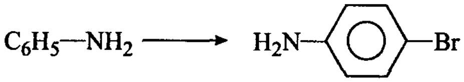


$$HNO_3 + CH_3\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}O\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}CH_3 \longrightarrow A + CH_3COOH \xrightarrow[\text{(ii) } H_3\overset{\oplus}{O}]{\text{(i) } C_6H_5OH/NaOH} (B)$$

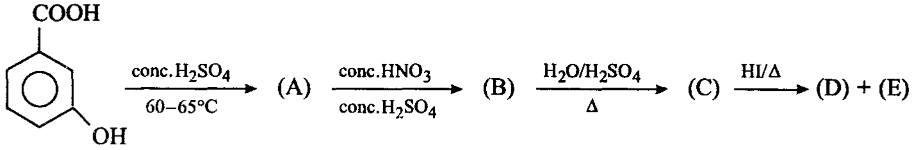
26. How the following conversions can be achieved?

(a) 

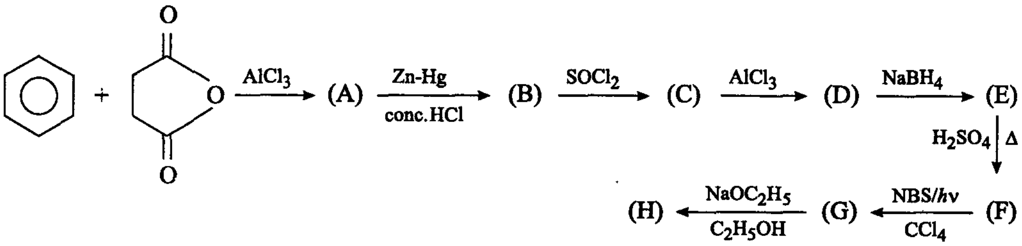
(b) 

(c) 

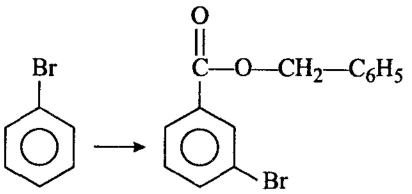
27. Propose structures for compounds (A), (B), (C), (D) and (E)

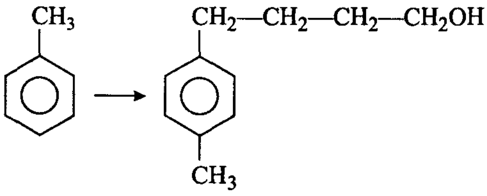


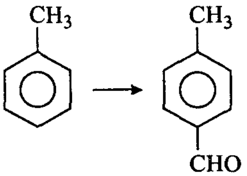
28. Propose structures for compounds (A) to (H)

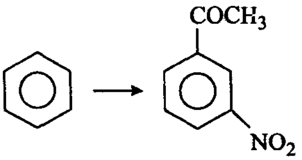


29. Propose syntheses of the following compounds from the given starting materials :

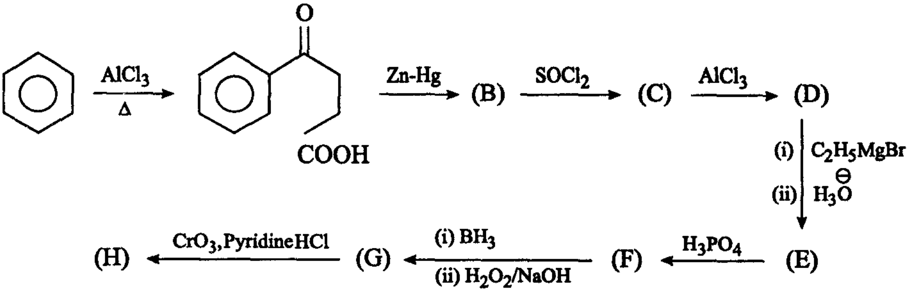
(a) 

(b) 

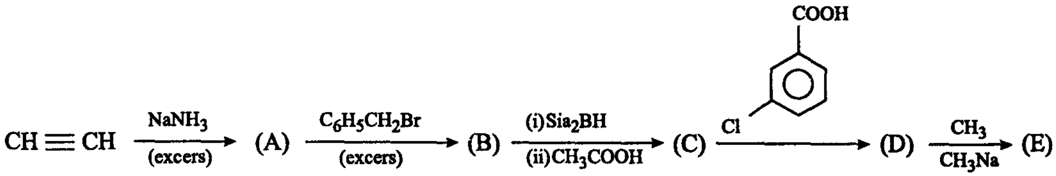
(c) 

(d) 

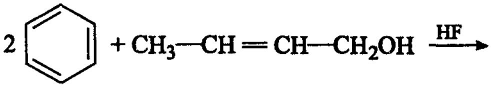
30. Identify (A) to (H) in the given sequence of reactions :



31. Identify (A) to (E) in the given flow chart :



32. Complete the following reaction and give its mechanism



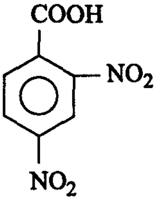
33. Benzene gives Diels-Alder addition reaction with very reactive alkynes such as (A). The reaction takes place at very high temperature. Give the structure of the adduct of bezene with (A).

$$\underset{(A)}{CF_3-C\equiv C-CF_3}$$

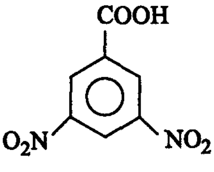
34. Using benzene and any necessary organic reagents, suggest efficient syntheses of :

(a) *Ter*-butylbenzene
(b) Isobutylbenzene
(c) Neopentylbenzene
(d) Mono-deuterated benzene

35. Show how to convert toluence to the following two isomeric carboxylic acids.



(a)



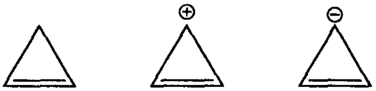
(b)

36. Aniline is more reactive than phenoxide ion, phenol and phenyl ethers for electrophilic substitutions. Explain.

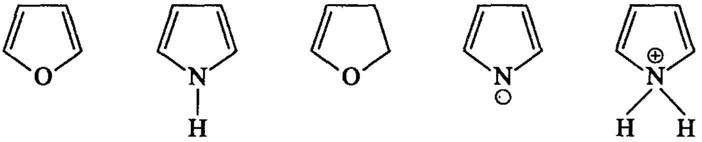
PROBLEMS FOR SELF ASSESSMENT

1. The following molecules and ions are grouped according to similar structures. Classify each molecule or ion as aromatic, antiaromatic or nonaromatic. For the aromatic and antiaromatic species, give the number of *pi* electrons in the ring.

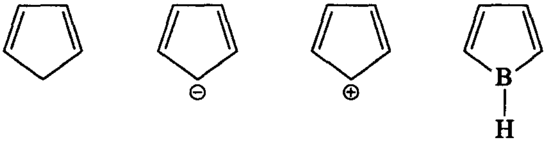
(a)



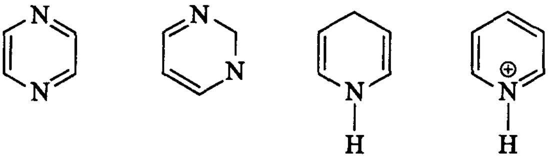
(b)



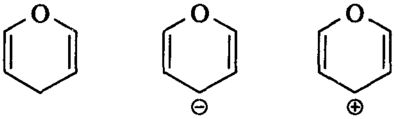
(c)



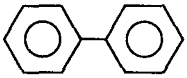
(d)



(e)



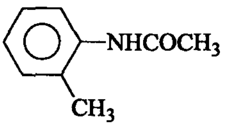
2. Biphenyl has the following structure :



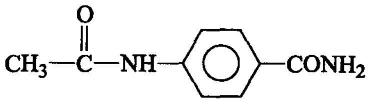
   (a) Is biphenyl a fused polynuclear aromatic hydrocarbon ?
   (b) How many *pi* electrons are there in the two aromatic rings of biphenyl ?
   (c) The heat of hydrogenation of biphenyl is about 100 kcal/mole. Calculate the resonance energy of biphenyl.

3. Predict the mononitration products of the following compounds :
   (a) *o*-nitrotoluene
   (b) *m*-chlorotoluene
   (c) *o*-bromobenzoic acid
   (d) *p*-methoxybenzoic acid

(e)

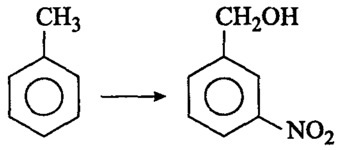


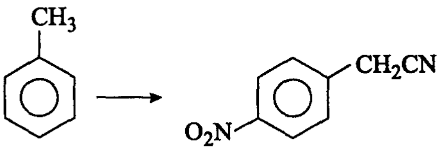
(f)

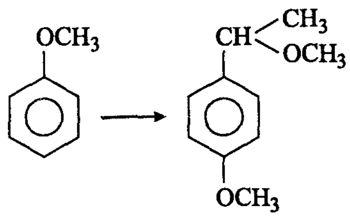


4. Predict the product and give mechanism for the following reactions :
   (a) Benzene + Cyclohexene $\xrightarrow{HF}$
   (b) Benzene + *tert*-butyl alcohol $\xrightarrow{BF_3}$
   (c) *tert*-Butylbenzene + 2-methylpropene $\xrightarrow{HF}$

5. Show how would you synthesise the following compounds, using the indicated compounds as starting materials.

(a)


(b)


(c)


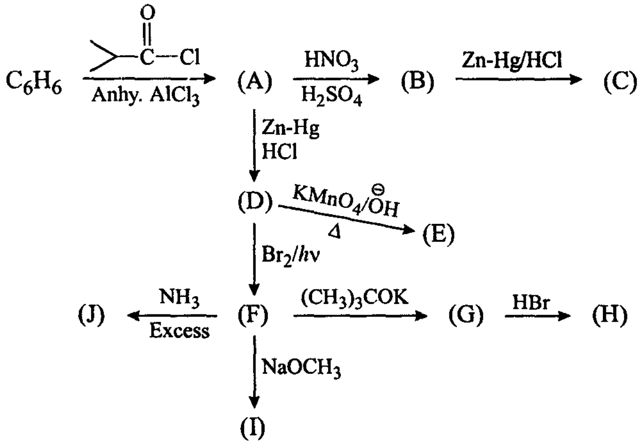
6. Briefly define the following terms and give examples :

(a) Activating group (b) Deactivating group (c) *ortho-para* director (d) *ortho-para* ratio
(e) Birch reduction (f) Hydrogenolysis

7. Predict the major products that will be formed when isopropylbenzene reacts with the following reagents :

(a) *n*-Propylchloride/Anhy. aluminium chloride (b) SO_3 and H_2SO_4
(c) Hot conc. $KMnO_4/\overset{\ominus}{OH}$ (d)Acetyl chloride/Anhy. $AlCl_3$
(e) 1 Eq of bromine and $h\upsilon$ (f) $Br_2/FeBr_3$

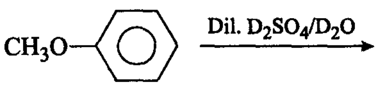
8. Identify (A) to (J) in the given reaction sequence :

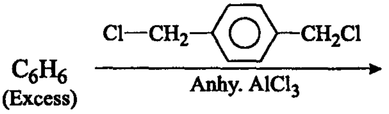


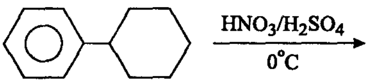
9. Outline synthesis of each of the following compounds, starting with benzene and any other reagents :

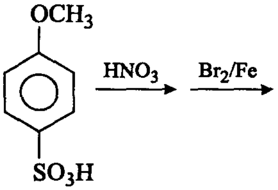
(a) *p*-Nitrotoluene (b) *p*-Dichlorobenzene
(c) *p*-Chloroacetophenone (d) *p*-Dibromobenzene
(e) *p*-Chloroethylbenzene (f) 1, 3, 5-Trinitrobenzene
(g) Methylcyclohexane (h) Cyclopentylbenzene.

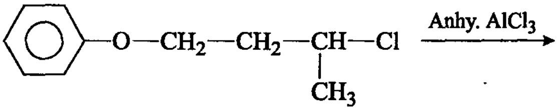
10. Give the structures of the principal organic product(s) of each of the following reactions :

(a)


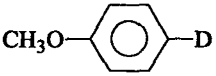
(b)


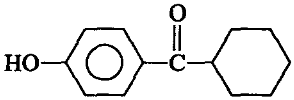
(c) 

(d) 

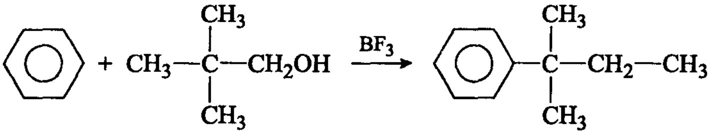
(e) 

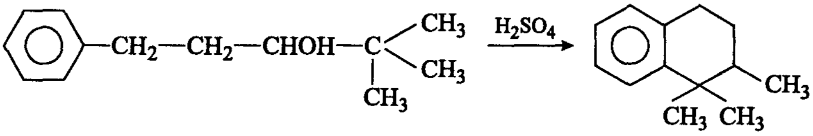
11. Outline a synthesis of each of the following compounds from anisole and any other reagents :

(a) 

(b) 

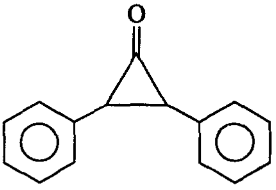
12. Using the arrow formalism, give a detailed mechanism for each of the following reactions :

(a) 

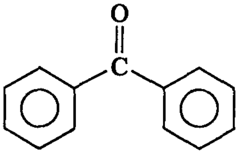
(b) 

13. Explain why triphenylmethane (*pKa* = 31) is more acidic than toluene (*pKa* = 41).

14. Explain why dipole moment of ketone (A) is more than the Ketone (B)



(A)
$\mu = 5.08$ D



(B)
$\mu = 2.97$ D

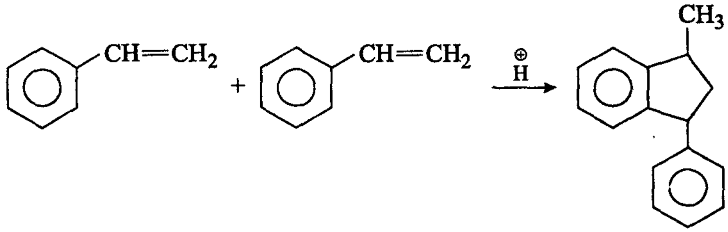
15. The heat of hydrogenation of cyclooctene to cyclooctane is − 23·3 kcal/mole. That for 1, 3, 5, 7-cyclooctatetraene is − 100·9 kcal/mole. On the basis of the above results calculate the resonance energy of cyclooctatetraene.

16. The heat of formation of benzene C_6H_6, *i.e.*, $(CH)_6$ is + 19·82 kcal/mole. The heat of formation of cyclooctatetraene C_8H_8, *i.e.*, $(CH)_8$ is 71·23 kcal/mole. On the basis of these results calculate the resonance energy of benzene.

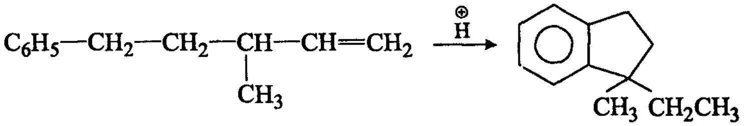
17. Methyl group in toluene is *ortho*, *para* directing whereas trifluoromethyl group in trifluoromethylbenzene is *meta* directing. Explain why?

18. Write a reasonable mechanism, showing all intermediates involved for the given reaction.

(a)

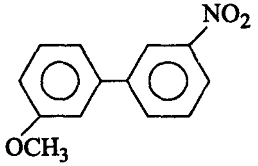


(b)

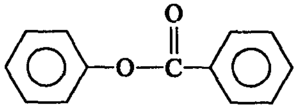


19. Give the product(s) obtained from the reaction of each of the following compounds with $Br_2/FeBr_3$.

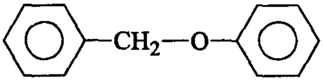
(a)



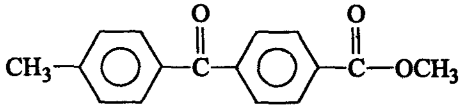
(b)



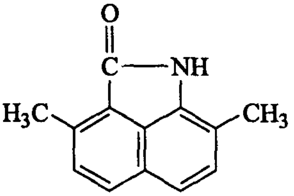
(c)



(d)

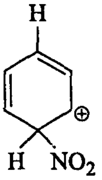


(e)

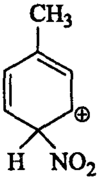


20. Using resonance contributors, answer the following :

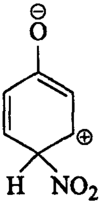
(a) Which is a more stable carbocation intermediate?



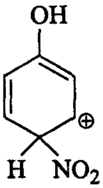
or



(b)



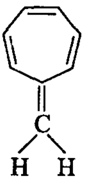
or

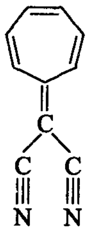


21. When Dewar benzene is treated with H_2SO_4, benzene is formed. Suggest a mechanism for this conversion.

22. Experimentally it has been found that cyclononatetraenyl anion and cyclooctatetraenyl dianion can be prepard and are reasonably stable species. Cyclononatetraene anion is obtained when cyclononatetraene is treated with NaH in DMSO. Cyclooctatetraenyl dianion is formed when cyclooctatetraene reacts with 2 equivalents of potassium metal in THF. Write the equations for the reactions mentioned here, and explain the source of the stability of the anions.

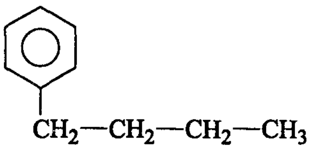
23. Heptafulvenes are compounds in which a carbon atom of the cycloheptatriene ring is doubly bonded to a carbon outside the ring. The parent compound (A) is highly unstable, but substitution of two cyano groups for the hydrogen atoms on the double bond outside the ring (compound B) gives a stable compound. How will you explain these results ?

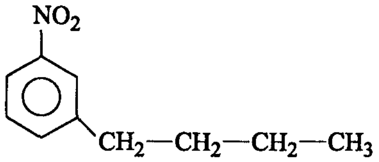

(A)

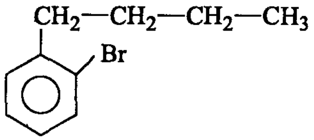


(*Hint.* Resonance contributors of both compounds will give the answer of the problem.)

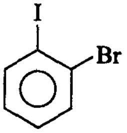
24. Provide synthesis of the following compounds, as free of other isomers as possible. You may use benzene inorganic reagents and organic reagents containing no more than four carbons.

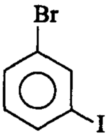
(a)


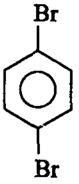
(b)


(c)


25. Provide syntheses for the following compounds free of other isomers.

(a)


(b)


(b)


26. Give evidence to show that aromatic electrophilic substitution is a two-step process and that the removal of proton is not the rate-determining step.

27. What are σ and π complexes ? Discuss their role in aromatic electrophilic substitution.

28. How do you account for the observation that in *o/p* directing systems, usually the *ortho* substitution occurs to a lesser extent than expected ? Are there exceptions to this general rule?

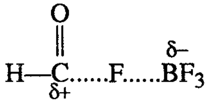
29. Sketch a suitable mechanism for the following reaction :

$$C_6H_5C(CH_3)_3 + Br_2 \xrightarrow{AlBr_3} C_6H_5Br + (CH_3)_2C{=}CH_2$$

30. Predict the product(s) and outline the mechanism for each of the following reactions :

(i) $C_6H_6 + ICl \xrightarrow{FeX_3}$ (ii) $C_6H_6 + F\text{—}CHO \xrightarrow{BF_3}$

Hint. (i) $\overset{\delta+}{I}......Cl......\overset{\delta-}{FeX_3}$



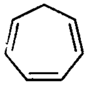
(ii) $H\text{—}\underset{\delta+}{\overset{\overset{O}{\|}}{C}}......F......\overset{\delta-}{BF_3}$

31. Explain the following :

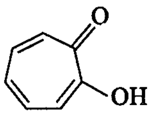
(a) An aqueous solution of tropylium bromide on treatment with $AgNO_3$ gives precipitate of AgBr.

(b) Cycloheptatrienyl cation is stabler than 1, 3, 5-heptatriene.

(c) 1, 3, 5-cycloheptatriene (**I**) is nonaromatic, whereas tropolone (**II**) is aromatic.



(I)



(II)

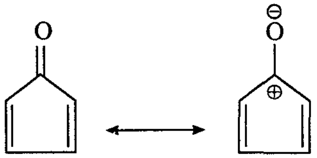
32. Unlike other electrophilic substitution reactions, polyalkylation is a side reaction in Friedel-crafts alkylation. Explain why?

(*Hint.* Alkyl group introduced during first alkylation activates the ring for further alkylation. On the other hand, groups introduced in other electrophilic substitutions deactivate the ring for further substitution.)

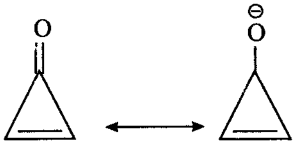
ANSWER TO VERY SHORT ANSWER QUESTIONS

1. Cycloheptatrienyl cation being aromatic has the highest resonance energy.

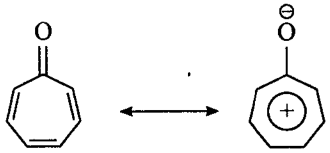
Due to aromatic character, the carbon-oxygen bond in the above compound does not have a true carbonyl group, hence does not undergo nucleophilic addition reactions.

2. 

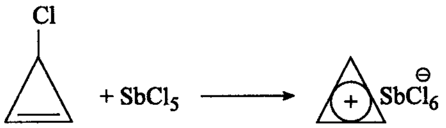
(antiaromatic, less stable)



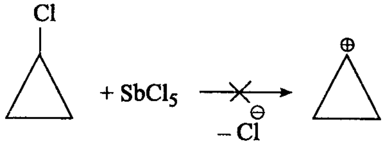
(aromatic, more stable)



(aromatic, more stable)

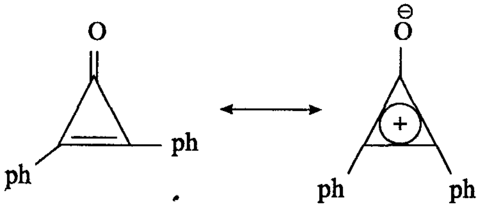
3. 

(aromatic, more stable and is easily formed)



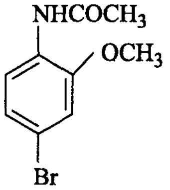
(not aromatic, less stable and is not easily formed)

4\.



5\. $(CH_3)_2CH—CH_2Cl \xrightarrow{AlCl_3} (CH_3)_2CH—\overset{\oplus}{C}H_2 \xrightarrow{\text{Rearrangement}} (CH_3)_3\overset{\oplus}{C} \xrightarrow{C_6H_6} C_6H_5C(CH_3)_3$

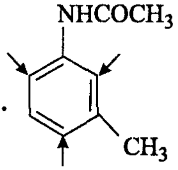
6\.



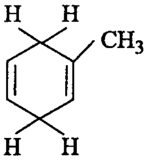
Because NHCOCH$_3$ group is a stronger activating group than OCH$_3$.

Only in *m*-xylene both the CH$_3$ groups increase the electron density at *o*, *p* positions whereas in other isomers only one CH$_3$ group does so, therefore, *m*-xylene being most reactive undergoes sulphonation preferentially.

7\.

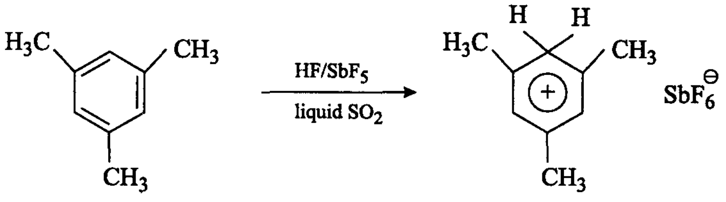


8\.



In Birch reduction electron-donating groups are mainly found at the non-reduced positions of the product, whereas electron-withdrawing groups at the reduced positions of the product.

9\.



σ-complex is formed

10\. Baeyer's test involves the hydroxylation of unsaturated compounds. In the case of benzene the hydroxylation will result in the loss of aromaticity thereby decreasing the stability of the benzene ring. Thus, benzene fails to give Baeyer's test.

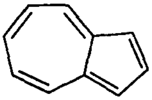
11. Cyclooctatetraene reacts with two equivalents of potassium to give cyclooctateraenyl dianion which satisfies Hückel rule, therefore, it is aromatic, hence quite stable.

cyclooctatetraene

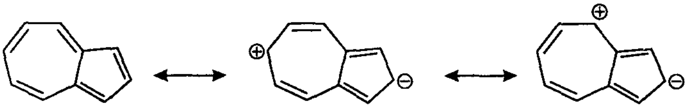
Cyclooctatetraenyl dianion
(10 π electrons, aromatic)

SOLUTIONS OF PROBLEMS

1. (a) Compound is cyclic, planar, conjugated having ($4n$) π electrons, hence it is antiaromatic.
   (b) Compound is cyclic, planar, conjugated having ($4n + 2$) π electrons, hence compound is an aromatic compound.
   (c)

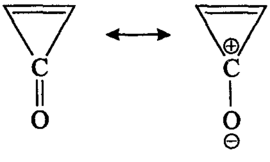


Neither cyclopentadiene nor cycloheptatriene ring alone is aromatic. Its charge resonance structures (1) and (2) show a preponderance of negative charged in the five membered ring, making it similar to the aromatic cyclopentadienyl anion. In these structures the seven membered ring bears a positive charge, giving it the aromatic character of the cycloheptatrienyl cation.



(1) (2)

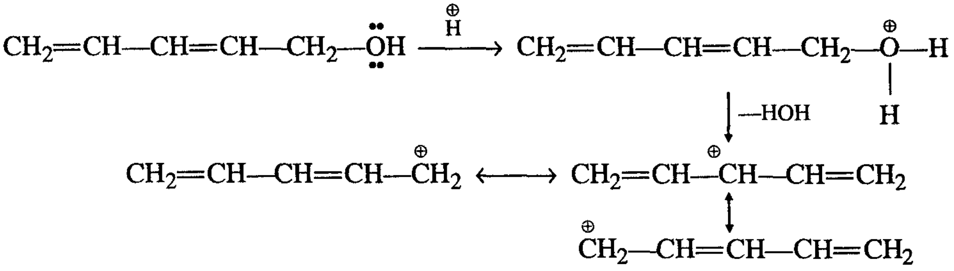
   (d) It is aromatic because it has ($4n + 2$) π conjugated electrons.
   (e) It is aromatic because it has ($4n + 2$) π conjugated electrons.
   (f) It is antiaromatic because it has ($4n$) π conjugated electrons.
   (g) This compound has C=O group in which oxygen is highly electronegative. Thus carbon of the C=O group bears positive charge. Hence it is aromatic in nature. The compound has ionic character (high dipole moment) because in this form it is highly stabilised by aromaticity.



($4n + 2$)π electrons

   (h) The given compound is antiaromatic because it has ($4n$) π electrons.

2. Consider the case of 2, 4-pentadien-1-ol :



$$\mathrm{CH_2{=}CH{-}CH{=}CH{-}CH_2{-}\ddot{O}H \xrightarrow{\overset{\oplus}{H}} CH_2{=}CH{-}CH{=}CH{-}CH_2{-}\overset{\oplus}{\underset{H}{O}}{-}H}$$

$$\downarrow -\mathrm{HOH}$$

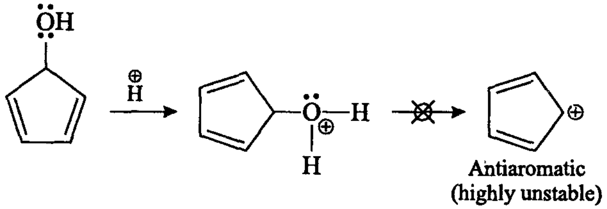
$$\mathrm{CH_2{=}CH{-}CH{=}CH{-}\overset{\oplus}{C}H_2 \longleftrightarrow CH_2{=}CH{-}\overset{\oplus}{C}H{-}CH{=}CH_2}$$

$$\updownarrow$$

$$\mathrm{\overset{\oplus}{C}H_2{-}CH{=}CH{-}CH{=}CH_2}$$

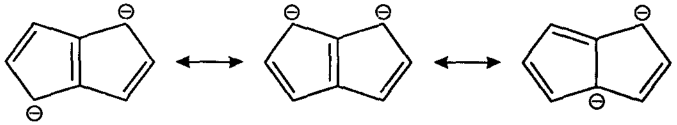
The carbocation is stable due to delocalisation of positive charge, hence loss of water takes place readily in this case :

Consider the case of cyclopentadienol :



Since cyclopentadienyl cation is highly unstable due to antiaromaticity, hence its formation is not favoured.

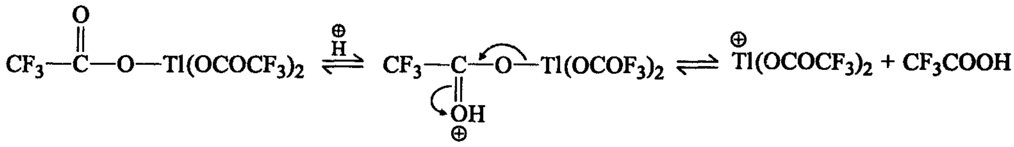
3. Resonance forms of dianion.



The dianion is aromatic having 10 π conjugated electrons. That is why formation of dianion is spontaneous process.

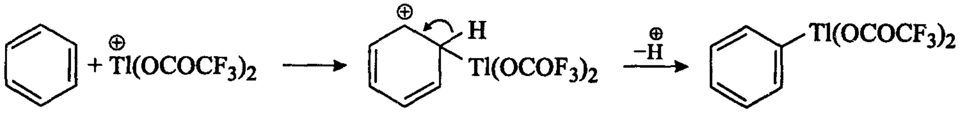
4. Mechanism of the reaction is as follows :

Step I : Formation of electrophile



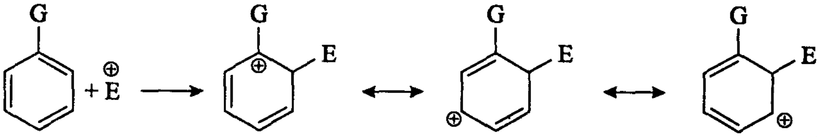
$$CF_3-\overset{\overset{O}{\|}}{C}-O-Tl(OCOCF_3)_2 \overset{\overset{\oplus}{H}}{\rightleftharpoons} CF_3-\underset{\underset{\overset{OH}{\oplus}}{\|}}{C}-O-Tl(OCOF_3)_2 \rightleftharpoons \overset{\oplus}{Tl}(OCOCF_3)_2 + CF_3COOH$$

Step II : Electrophilic substitution

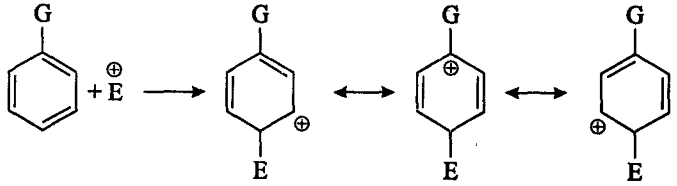


5. (a) Contributing structures for σ complex :

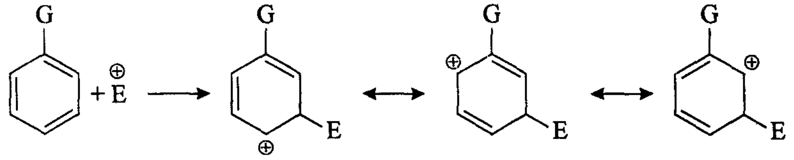
Case I : Attack of electrophile at *ortho* position.



Case II : Attack of *para* position.



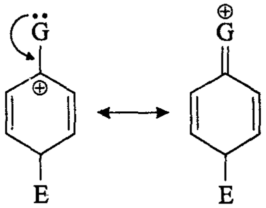
Case III : Attack at *meta* position.



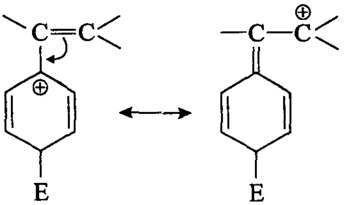
(b) If group G is an electron donating then it may be of three types :

1. G has an unshared pair of electrons on the atom bonded to the ring, which can be delocalised to the ring by extended *pi* bonding. Thus G may be

$$-\ddot{N}H_2,\ -\underset{\cdot\cdot}{\ddot{O}}H,\ -R,\ -\ddot{N}HAc,\ -\underset{\cdot\cdot}{\ddot{X}}:,\ -\underset{\cdot\cdot}{\ddot{S}}-,\ \text{etc.}$$

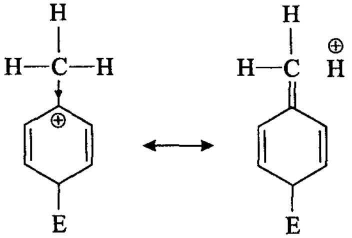


2. The atom bonded to the ring participates in an electron rich *pi* bond, $>C{=}C<$, C_6H_5 and Ar. Such groups increase stability of σ complex when electrophile attacks either on *ortho* or on *para* positions.



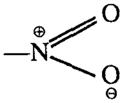
3. G has no unshared pair and is electron donating by induction or on by hyperconjugation, *i.e.*, alkyl groups.

   Such groups increase stability of *sigma* complex when electrophile attacks either at *ortho* or at *para* position.



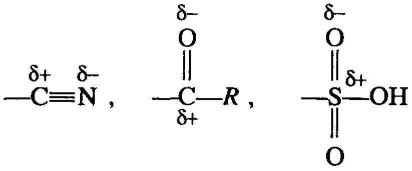
(c) The key atom should have no unshared pair of electrons. The key atom should have some positive charge. The positive charge may be :

(i) Full ($-\overset{\oplus}{N}H_3$, $-\overset{\oplus}{C}H_2$, etc.)

(ii) A positive formal charge : 

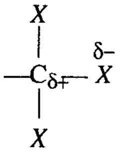
$-\overset{\oplus}{N}(=O)-\overset{\ominus}{O}$

(iii) A δ+ from being *pi* bonded to a more electronegative atom, *i.e.*,



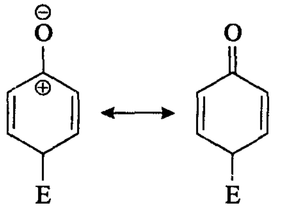
$\overset{\delta+}{-C}\equiv\overset{\delta-}{N}$, $-\underset{\delta+}{C}(=\overset{\delta-}{O})-R$, $-\overset{\delta+}{S}(=\overset{\delta-}{O})(=O)-OH$

(iv) σ bonded to several electronegative atoms, *e.g.*,



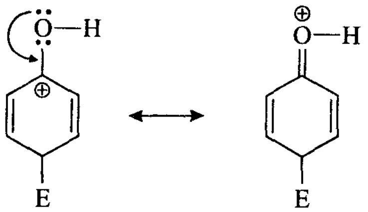
$-\underset{\delta+}{C}X_2-\overset{\delta-}{X}$

6. Both groups are activating and *o/p* directing groups. Let us consider the resonating structures of σ complex in both the case (when electrophile attacks either at *ortho* or at *para*)



(A)
Very stable uncharged
intermediate

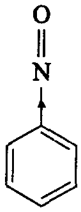
whereas —OH gives charged intermediate.



(B)
Stable intermediate because
octet of all atoms are complete.
But this intermediate is charged.

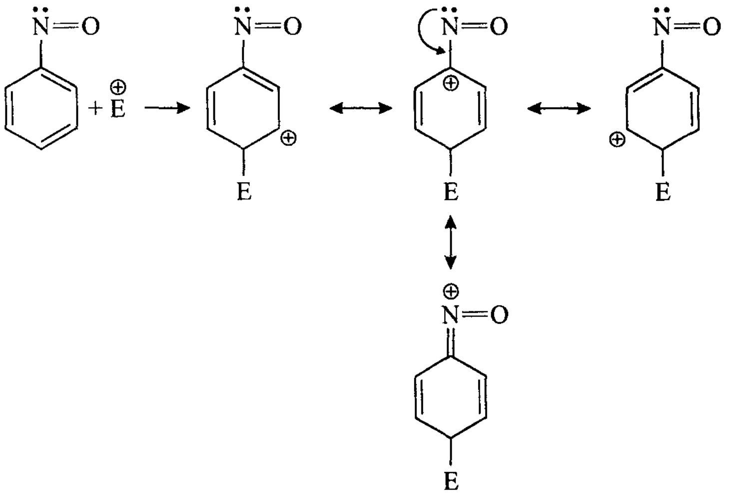
Hence (A) is more stable than (B). Therefore, activating power of $-\overset{\ominus}{O}$ is more than the —OH.

7. The nitroso group deactivates the ring inductively by attracting electrons because both nitrogen and oxygen are highly electronegative in nature.

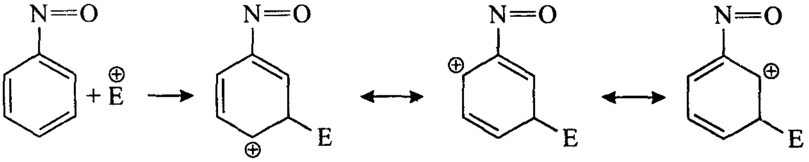


Inductive effect of —N═O group deactivates ring

On the other hand, when electrohilic attack does take place, the —NO group stabilises the σ complex resulting from *ortho* and *para* attack relative to that from *meta* attack.



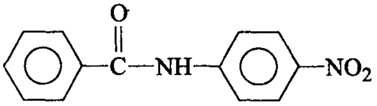
Very stable because all atoms have complete octet.



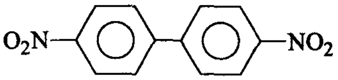
Less stable because all the three structures have an atom having incomplete octet. The atom is the carbon having positive charge.

8. (b) **9.** (a) **10.** (c) **11.** (a)

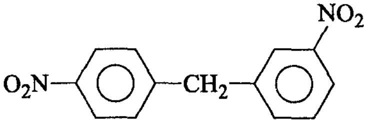
12. (a)



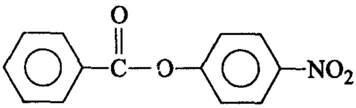
(b)



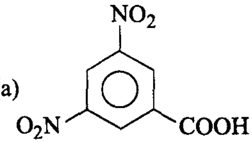
(c)



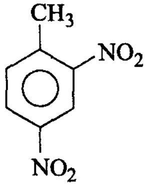
(d)



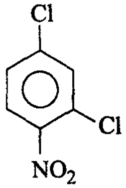
13. (a)



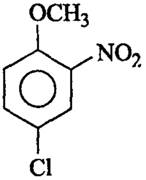
(b)



(c)



(d)

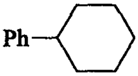


14. (d)

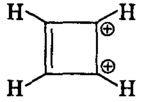
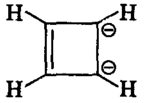
15. (a) $PhCH_2Cl$, $PhCHCl_2$, $PhCCl_3$.
(b) $PhCH_2CH_2\overset{\oplus}{N}Me_3$, $PhCH_2\overset{\oplus}{N}Me_3$, $Ph\overset{\oplus}{N}Me_3$.
(c) $PhNHCOCH_3$, $PhCCl_3$, $PhCOCH_3$.

16. (a) $p\text{-}O_2NC_6H_4NHCOMe$ (F); (b) $p\text{-}O_2NC_6H_4Ph$ (F);
(c) $p\text{-}BrC_6H_4I$ (S); (d) $p\text{-}HSO_3C_6H_4CHMe_2$ (F)
(e) $p\text{-}ClC_6H_4CMe_3$ (F) (f) $m\text{-}BrC_6H_4CBr_3$ (S)

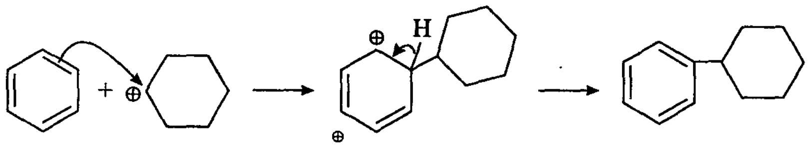
17. (c)

18. (a) $PhCH(CH_3)_2$ (b) Ph  (c) $PhCH(CH_3)_2$ (d) $PhCH_2CH_2OH$

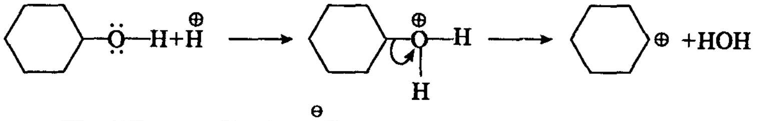
19. I, IV and VI are antiaromatic; II and V are aromatic; and III is nonaromatic.

20.  and 

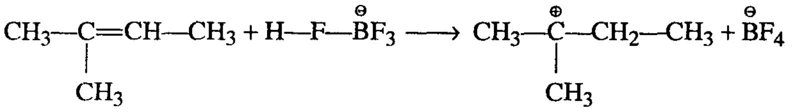
21. (a) 



(b) Cyclohexanol in the presence of $\overset{\oplus}{H}$ gives the same carbocation which is formed by cyclohexene. Due to this reason cyclohexanol gives the same product.

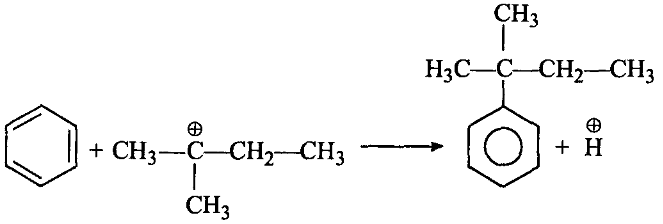
22. (a) **First step :** 

$$HF + BF_3 \rightleftharpoons H{-}F{-}\overset{\ominus}{B}F_3$$

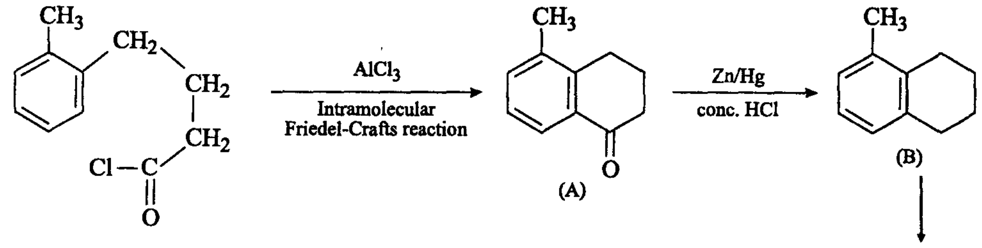


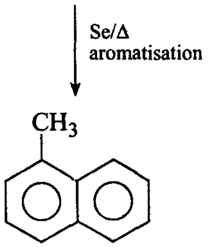
$$CH_3{-}\underset{CH_3}{\underset{|}{C}}{=}CH{-}CH_3 + H{-}F{-}\overset{\ominus}{B}F_3 \longrightarrow CH_3{-}\underset{CH_3}{\underset{|}{\overset{\oplus}{C}}}{-}CH_2{-}CH_3 + \overset{\ominus}{B}F_4$$

Second step :

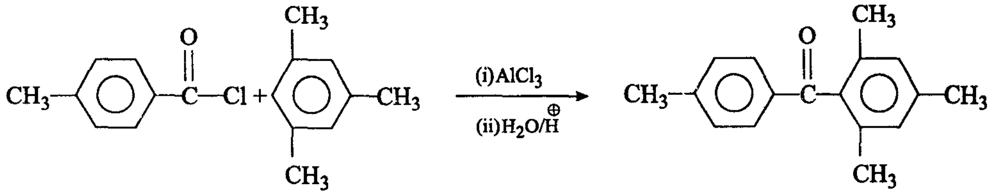


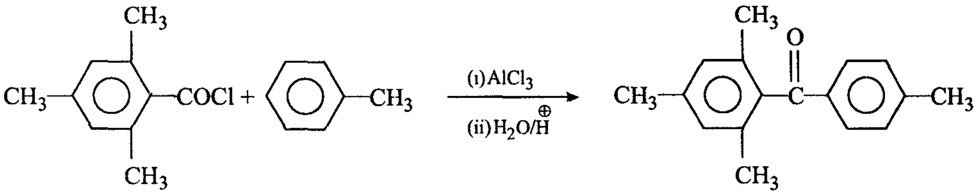
Third step : $\overset{\ominus}{B}F_4 + \overset{\oplus}{H} \rightleftharpoons HF + BF_3$

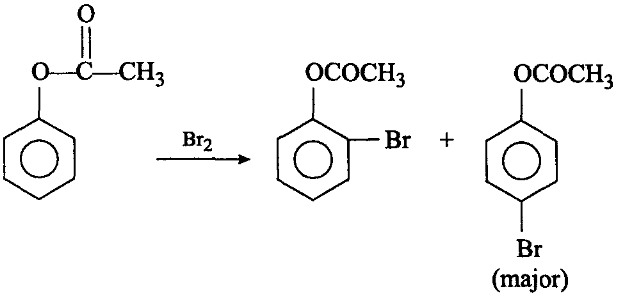
(b) 

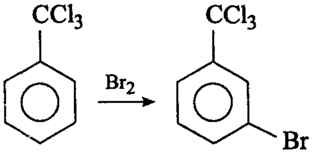


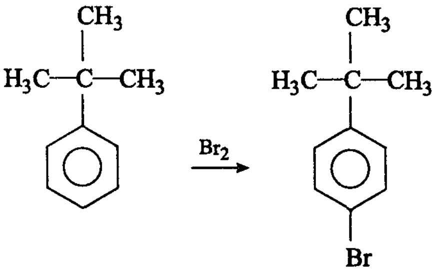
(c) The given compound can be prepared by either of the two methods :

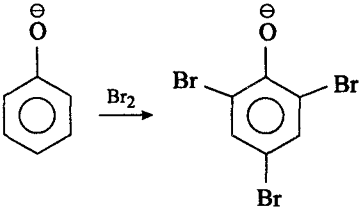
(I)


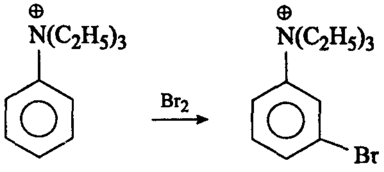
OR (II)


23. (a)


(b)


(c)


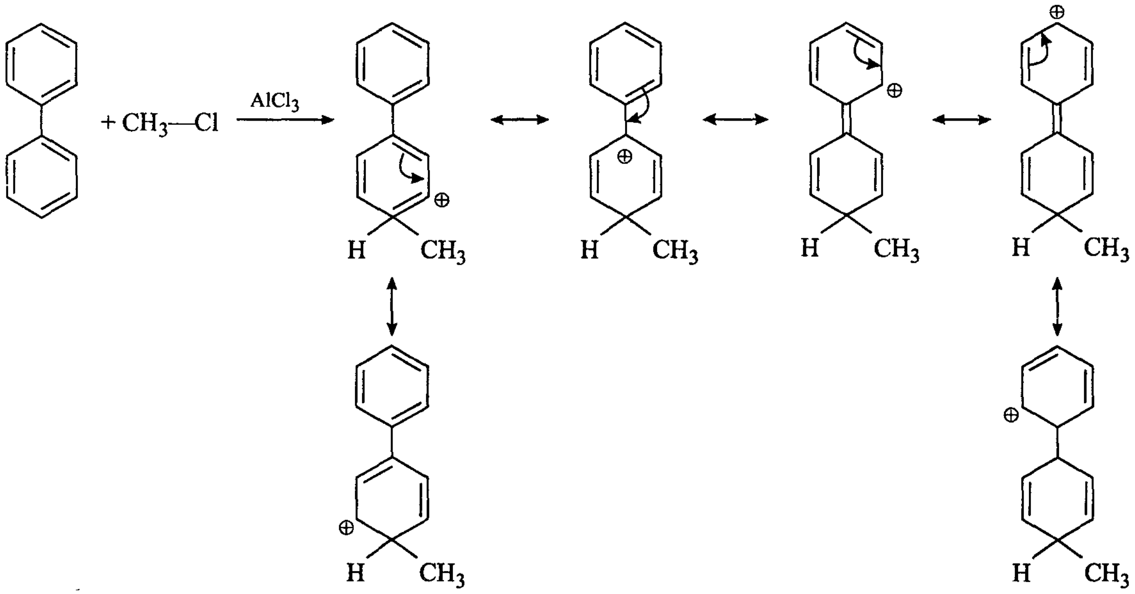
(d)


(e)


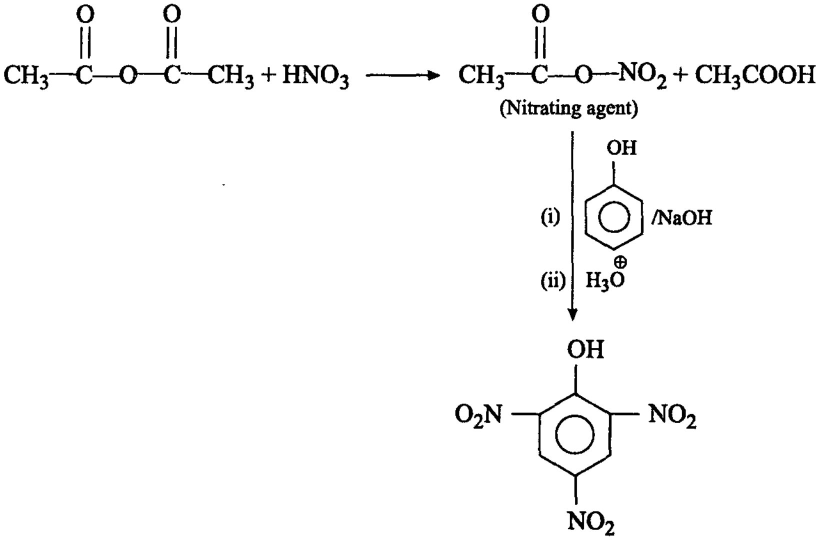
(c) The given compound can be prepared by either of the two methods :

24. (a) Because substitution occurs at *para* position to the phenyl group, the phenyl group is an *ortho*, *para*-direction group.

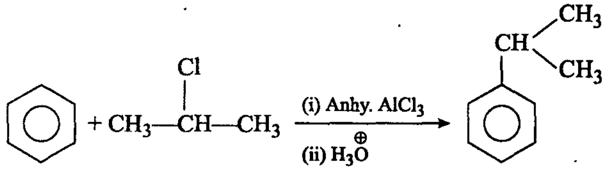
(b) The following resonance structures show that the electrons of the phenyl group can be used to



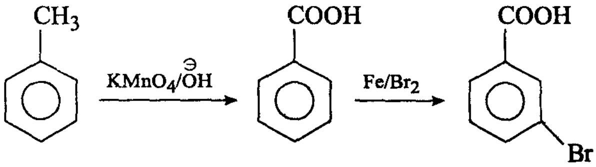
25.



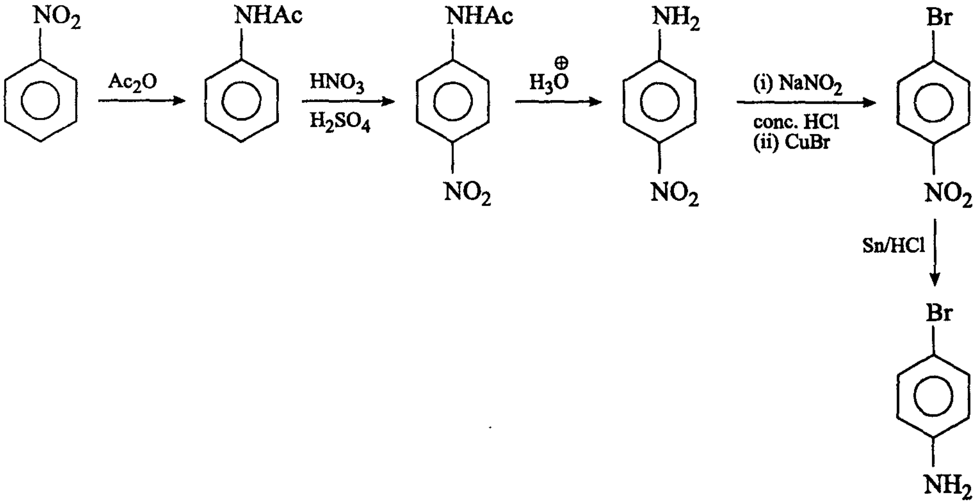
26. (a)



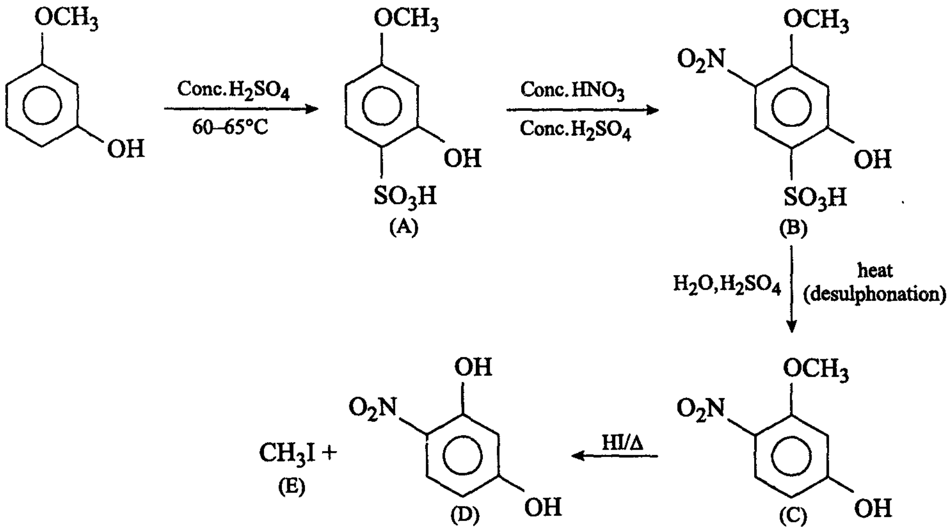
(b)


CH3
KMnO4/OH
COOH
Fe/Br2
COOH
Br

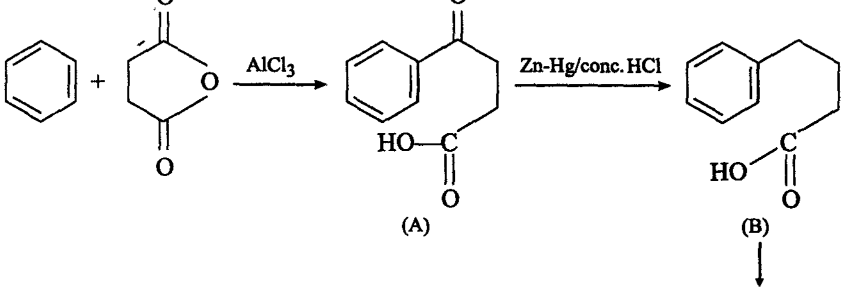
(c)

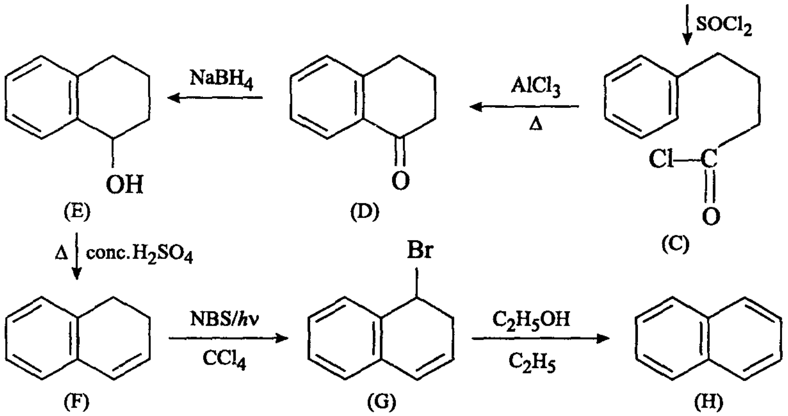

NO2
Ac2O
NHAc
HNO3
H2SO4
NHAc
NO2
H3O
NH2
NO2
(i) NaNO2
conc. HCl
(ii) CuBr
Br
NO2
Sn/HCl
Br
NH2

27.

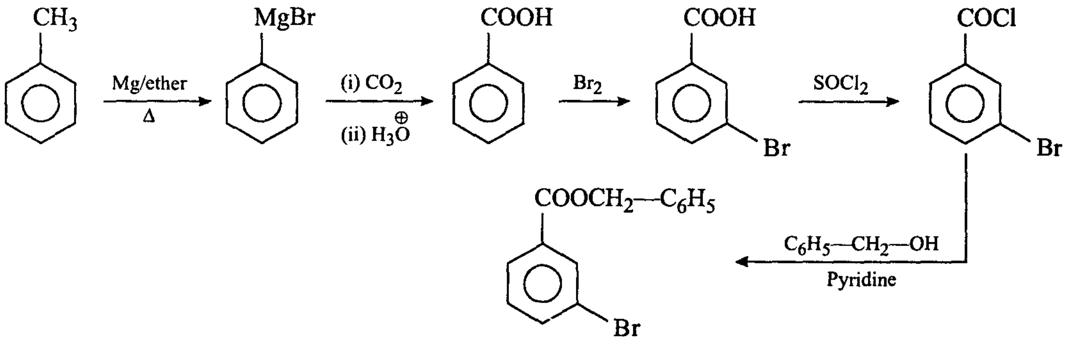

OCH3
OH
Conc.H2SO4
60–65°C
OCH3
OH
SO3H
(A)
Conc.HNO3
Conc.H2SO4
OCH3
O2N
OH
SO3H
(B)
H2O,H2SO4
heat
(desulphonation)
OCH3
O2N
OH
(C)
HI/Δ
OH
O2N
OH
(D)
CH3I +
(E)

28.

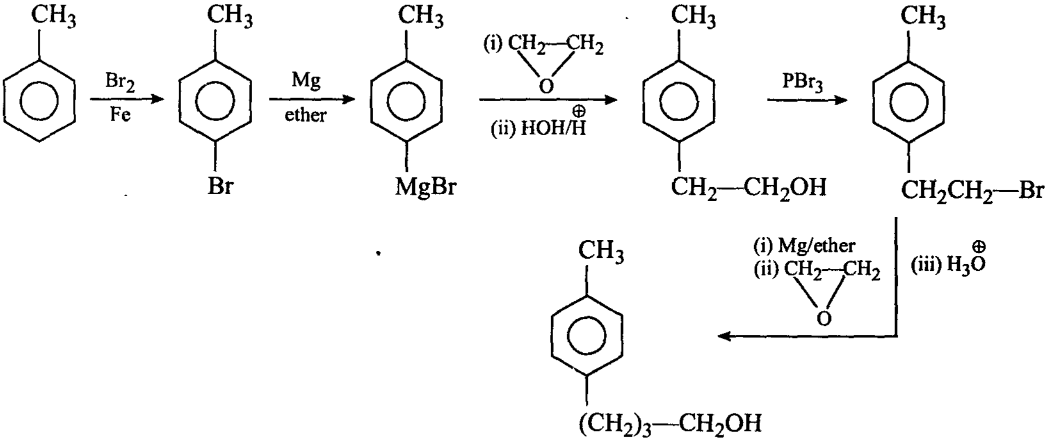

+
O
O
O
AlCl3
O
HO—C
O
(A)
Zn-Hg/conc.HCl
HO
C
O
(B)


$SOCl_2$
$NaBH_4$
$AlCl_3$
Δ
OH
O
Cl—C
O
(E)
(D)
(C)
Δ
conc. H_2SO_4
Br
NBS/hν
CCl_4
C_2H_5OH
C_2H_5
(F)
(G)
(H)

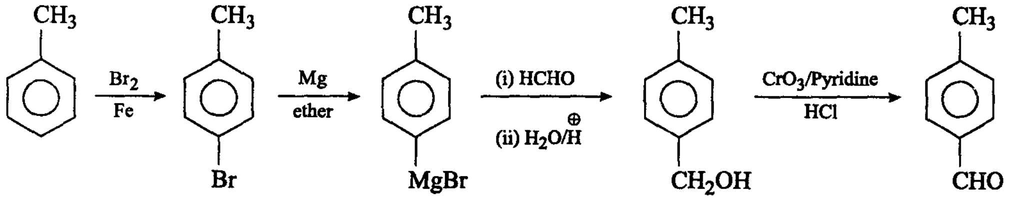
29.


CH_3
Mg/ether
Δ
MgBr
(i) CO_2
(ii) $H_3\overset{\oplus}{O}$
COOH
Br_2
COOH
Br
$SOCl_2$
COCl
Br
$COOCH_2—C_6H_5$
Br
$C_6H_5—CH_2—OH$
Pyridine

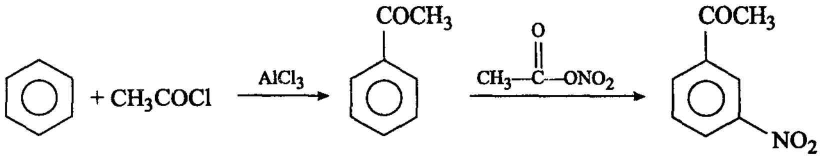
(b)


CH_3
Br_2
Fe
CH_3
Br
Mg
ether
CH_3
MgBr
(i) $CH_2—CH_2$ O
(ii) $HOH/\overset{\oplus}{H}$
CH_3
$CH_2—CH_2OH$
PBr_3
CH_3
$CH_2CH_2—Br$
(i) Mg/ether
(ii) $CH_2—CH_2$ O
(iii) $H_3\overset{\oplus}{O}$
CH_3
$(CH_2)_3—CH_2OH$

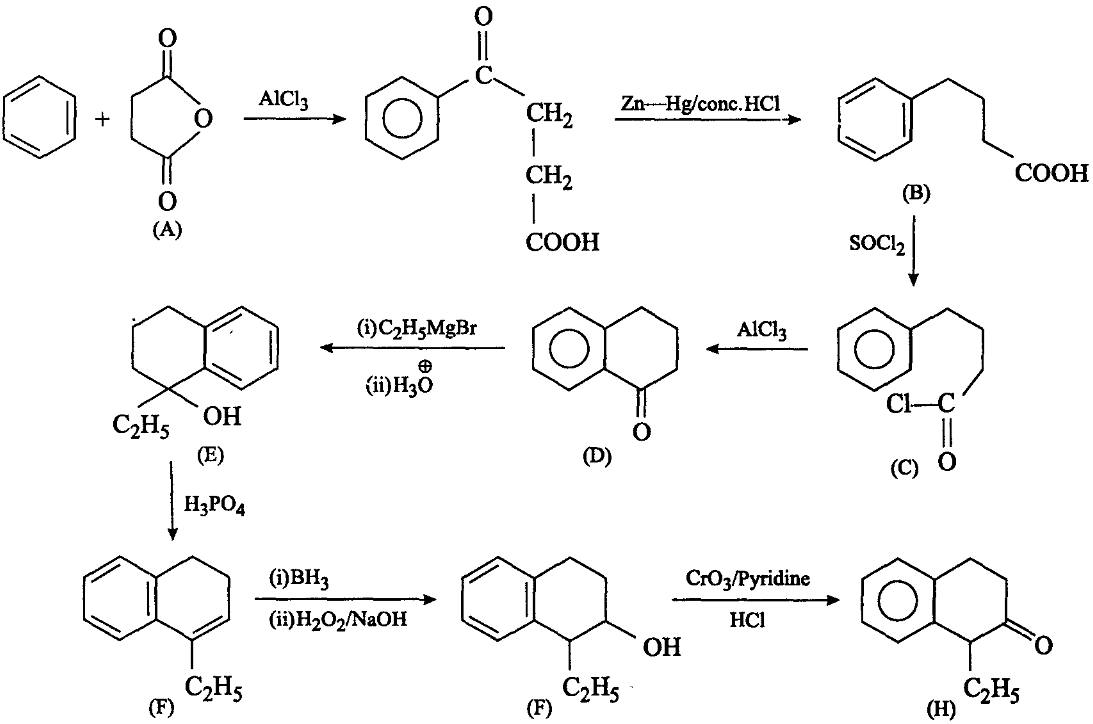
(c)


CH_3
Br_2
Fe
CH_3
Br
Mg
ether
CH_3
MgBr
(i) HCHO
(ii) $H_2O/\overset{\oplus}{H}$
CH_3
CH_2OH
CrO_3/Pyridine
HCl
CH_3
CHO

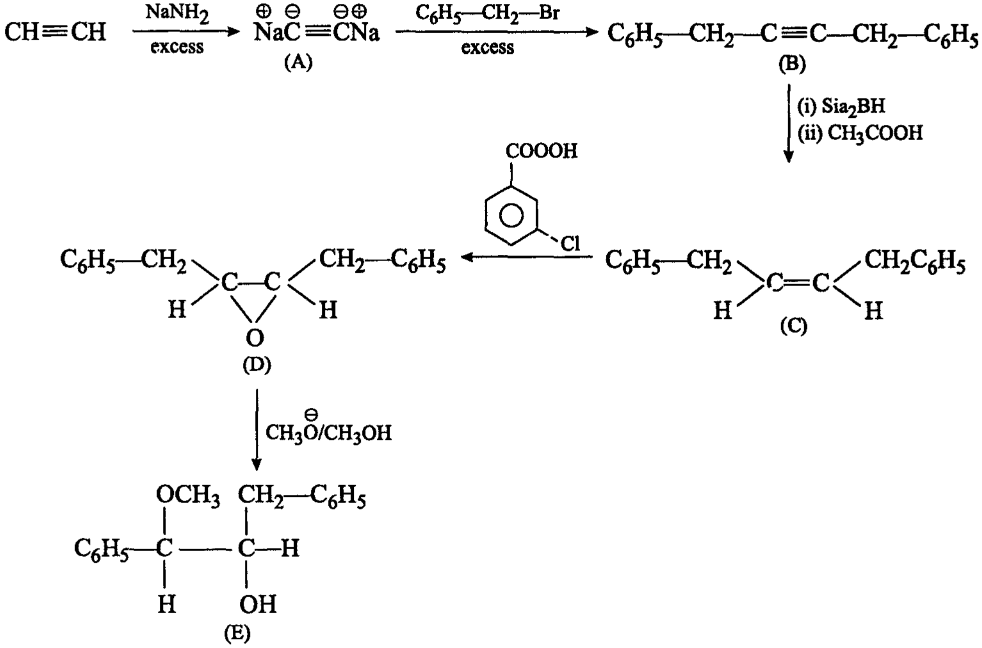
(d)


+ CH3COCl
AlCl3
COCH3
CH3—C(=O)—ONO2
COCH3
NO2

30.

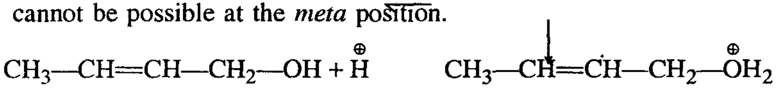

+
O
O
O
(A)
AlCl3
O
C
CH2
CH2
COOH
Zn—Hg/conc.HCl
COOH
(B)
SOCl2
Cl—C
O
(C)
AlCl3
O
(D)
(i)C2H5MgBr
(ii)H3O⊕
C2H5
OH
(E)
H3PO4
C2H5
(F)
(i)BH3
(ii)H2O2/NaOH
OH
C2H5
(F)
CrO3/Pyridine
HCl
O
C2H5
(H)

31.


CH≡CH
NaNH2
excess
⊕ ⊖ ⊖⊕
NaC≡CNa
(A)
C6H5—CH2—Br
excess
C6H5—CH2—C≡C—CH2—C6H5
(B)
(i) Sia2BH
(ii) CH3COOH
C6H5—CH2
H
C=C
CH2C6H5
H
(C)
COOOH
Cl
C6H5—CH2
H
C—C
O
CH2—C6H5
H
(D)
CH3O⊖/CH3OH
OCH3
CH2—C6H5
C6H5—C
C—H
H
OH
(E)

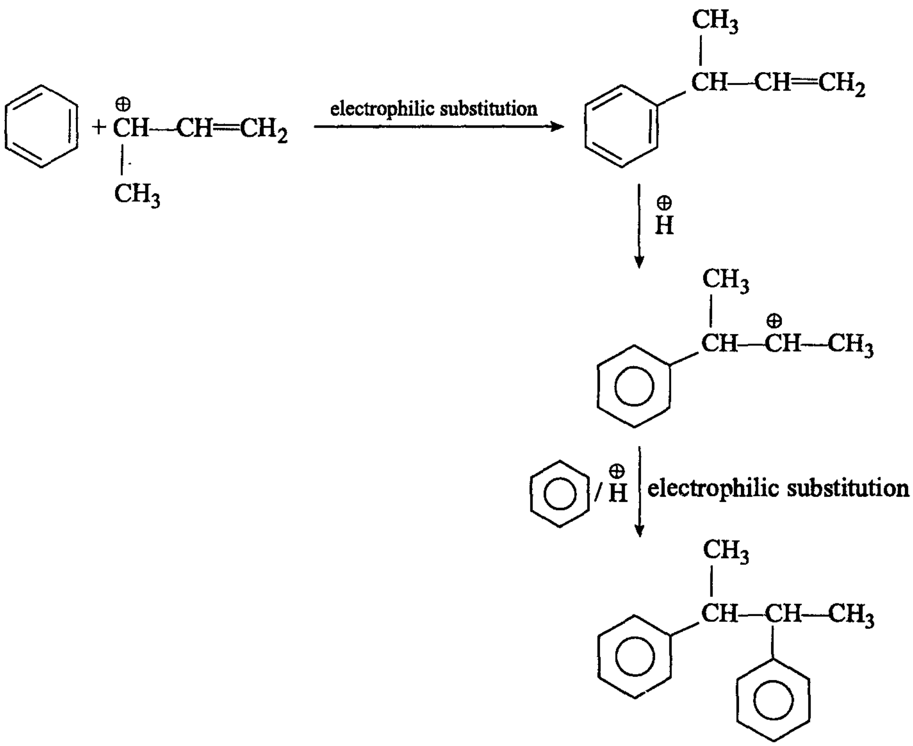
stabilished the complex when substitution occurs at the *para* position. This type of delocalisation cannot be possible at the *meta* position.

32. (i)

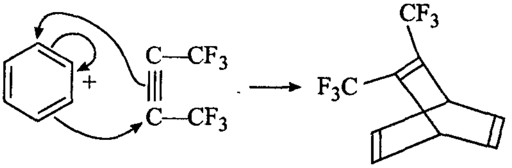


$$CH_3-CH=CH-CH_2-OH + \overset{\oplus}{H} \rightleftharpoons CH_3-CH=\dot{C}H-CH_2-\overset{\oplus}{O}H_2$$

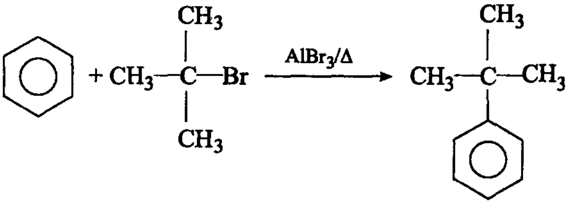
(ii)



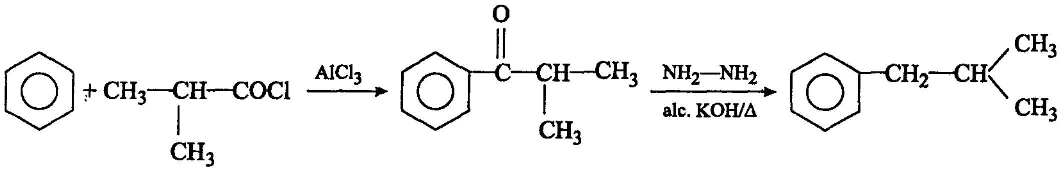
33.



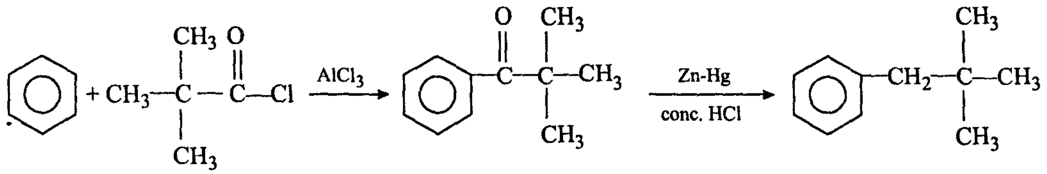
34. (a)



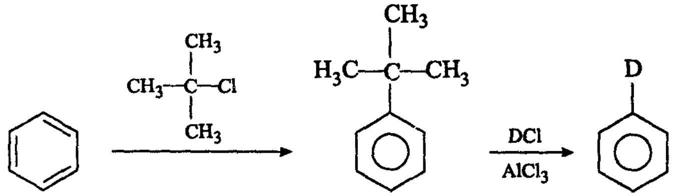
(b)



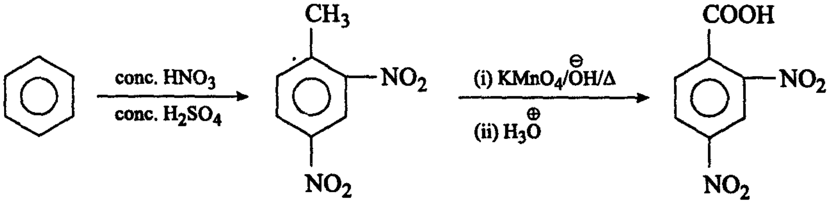
(c)



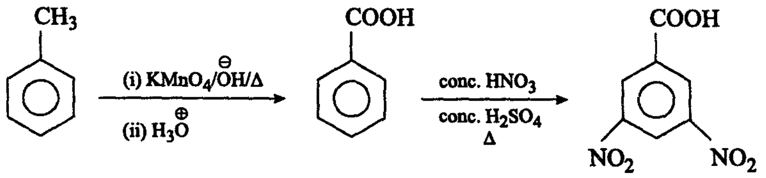
(d)



35. (a)



(b)



36. Aniline is more reactive than phenoxide ion because nitrogen is less electronegative than oxygen, the lone pair is higher in energy and so much available to interact with the π system than is the lone pair on oxygen.

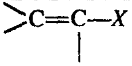
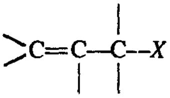
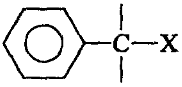
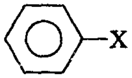
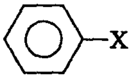
Compound	Rate of bromination relative to benzene
C_6H_6	1
$C_6H_5—OCH_3$	10^9
$C_6H_5H(CH_3)_2$	10^{14}

Chapter 7

HALOGEN COMPOUNDS : ALKYL AND ARYL HALIDES

7.0 INTRODUCTION

Organic halogen compounds are hydrocarbons in which one or more hydrogens have been replaced by halogen atoms. These compounds can be classified into groups that show similar chemical properties.

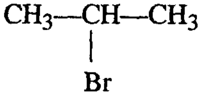
Class	General structure	Example
Haloalkanes	$R—X$	$CH_3—CH_2—X$
Vinyl halides		$CH_2=CH—X$
Allyl halides		$CH_2=CH—CH_2—X$
Benzyl halides		$C_6H_5—CH_2—X$
Aryl halides		

7.1 NOMENCLATURE OF ALKYL HALIDES

According to common naming system alkyl halides are named as alkyl derivatives of hydrogen halides, *e.g.*,

$CH_3—CH_2—Cl$

Ethyl chloride



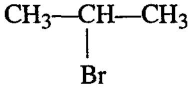
$CH_3—\underset{\displaystyle Br}{\underset{|}{CH}}—CH_3$

Isopropyl bromide

According to IUPAC naming system alkyl halides are named as haloalkanes. The longest carbon chain bearing the substituents is chosen and the compound is named as the derivative of the corresponding alkane. The carbon chain is numbered from one end to the other to indicate the positions of the substituents. The end chosen for starting the numbering of the carbon atoms is such that the sum of the numbers indicating the positions of the substituents is minimum. The following are the illustrative examples with common names in parentheses :

CH_3-CH_2-Cl

Chloroethane
(Ethyl chloride)

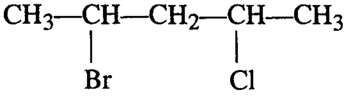


$CH_3-\underset{Br}{\underset{|}{CH}}-CH_3$

2-Bromopropane
(Isopropyl bromide)

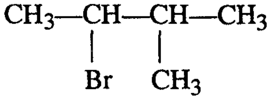
$CH_3-CH_2-CHCl_2$

1, 1-Dichloropropane



$CH_3-\underset{Br}{\underset{|}{CH}}-CH_2-\underset{Cl}{\underset{|}{CH}}-CH_3$

2-Bromo-4-chloropentane
not
4-Bromo-2-chloropentane



$CH_3-\underset{Br}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_3$

2-Bromo-3-methylbutane
not
3-Bromo-2-methylbutane

7.2 CLASSIFICATION OF HALOALKANES OR ALKYL HALIDES

Haloalkanes can be classified into following three categories :

(I) Monohaloalkanes (II) Dihaloalkanes and

(III) Polyhaloalkanes (trihalo-, tetrahaloalkanes, etc.)

MONOHALOALKANES

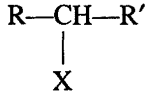
(i) These are halogen derivatives of alkanes having general formula $C_nH_{2n+1}X$
where $X = F, Cl, Br$ or I

(ii) Monohaloalkanes are of three types :

(a) Primary alkyl halides in which halo group is present on primary carbon atom, *i.e.*,

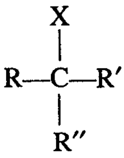
$$R-CH_2-X$$

(b) Secondary alkyl halides in which halo group is present on secondary carbon atom, *i.e.*,



$$R-\underset{X}{\underset{|}{CH}}-R'$$

(c) Tertiary alkyl halides in which halo group is present on tertiary carbon atom, *i.e.*,



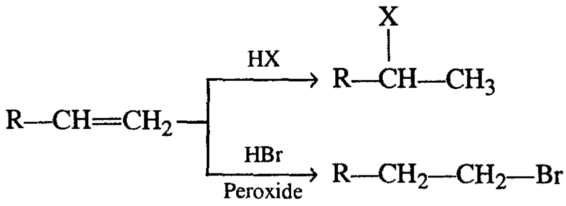
$$R-\overset{X}{\overset{|}{\underset{R''}{\underset{|}{C}}}}-R'$$

7.3 METHODS OF PREPARATION OF MONOHALOALKANES

Alkyl halides can be prepared by following methods :

7.3.1 Addition Reaction of Alkenes

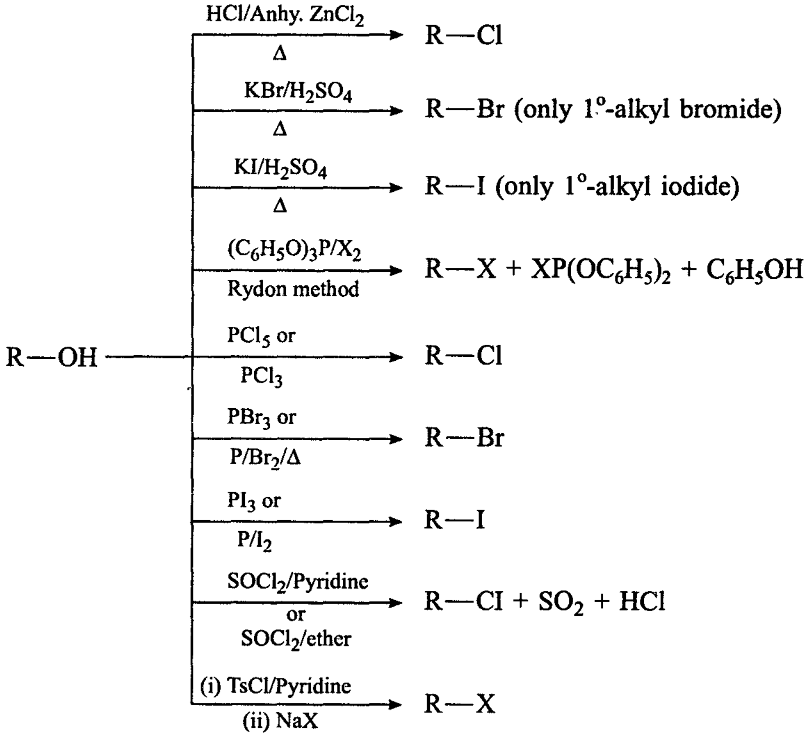
Alkene on addition with HX gives alkyl halide. Nature of alkyl halide depends on the structure of alkene.



$$R-CH{=}CH_2 \left\{ \begin{array}{l} \xrightarrow{HX} R-\overset{X}{\overset{|}{CH}}-CH_3 \\ \xrightarrow[\text{Peroxide}]{HBr} R-CH_2-CH_2-Br \end{array} \right.$$

7.3.2 Nucleophilic Substitution Reaction of Alcohols

Alcohol gives nucleophilic substitution reaction with following reagents to give alkyl halide.



$$R{-}OH \xrightarrow[\Delta]{HCl/Anhy.\ ZnCl_2} R{-}Cl$$
$$R{-}OH \xrightarrow[\Delta]{KBr/H_2SO_4} R{-}Br \text{ (only 1°-alkyl bromide)}$$
$$R{-}OH \xrightarrow[\Delta]{KI/H_2SO_4} R{-}I \text{ (only 1°-alkyl iodide)}$$
$$R{-}OH \xrightarrow[\text{Rydon method}]{(C_6H_5O)_3P/X_2} R{-}X + XP(OC_6H_5)_2 + C_6H_5OH$$
$$R{-}OH \xrightarrow[PCl_3]{PCl_5 \text{ or}} R{-}Cl$$
$$R{-}OH \xrightarrow[P/Br_2/\Delta]{PBr_3 \text{ or}} R{-}Br$$
$$R{-}OH \xrightarrow[P/I_2]{PI_3 \text{ or}} R{-}I$$
$$R{-}OH \xrightarrow[\substack{\text{or} \\ SOCl_2/\text{ether}}]{SOCl_2/\text{Pyridine}} R{-}Cl + SO_2 + HCl$$
$$R{-}OH \xrightarrow[\text{(ii) NaX}]{\text{(i) TsCl/Pyridine}} R{-}X$$

7.3.3 Free Radical Halogenation of Alkane

Alkanes on halogenation (chlorination and bromination) give alkyl halides.

(a) $$\underset{\text{(excess)}}{R{-}H} + X_2 \xrightarrow{h\nu} R{-}X + HX$$

(b) $$R{-}H + SO_2Cl_2 \xrightarrow[\substack{\text{or} \\ \text{Peroxide}}]{h\nu} R{-}Cl + HCl + SO_2$$

Order of ease of replacement of a hydrogen atom is :

Tertiary > Secondary > Primary > CH_4.

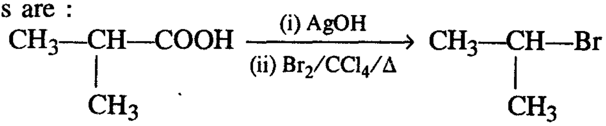
7.3.4 Hunsdiecker or Borodine-Hunsdiecker Reaction

Silver salt of acid reacts with X_2 (Cl_2 or Br_2) in the presence of CCl_4 to give alkyl chloride or bromide.

This reaction is one of the most important reaction in which **carboxylic group** is directly replaced by **halo** group.

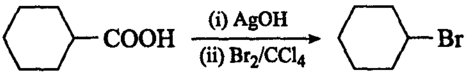
$$RCOOAg \xrightarrow{X_2/\Delta} R{-}X + AgX + CO_2$$

Some examples are :



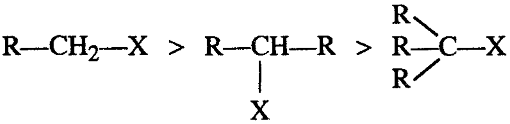
$$\underset{\substack{| \\ CH_3}}{CH_3{-}CH{-}COOH} \xrightarrow[\text{(ii) } Br_2/CCl_4/\Delta]{\text{(i) AgOH}} \underset{\substack{| \\ CH_3}}{CH_3{-}CH{-}Br}$$

$$C_6H_5{-}CH_2{-}COOH \xrightarrow[\text{(ii) }Cl_2/\Delta]{\text{(i) AgOH}} C_6H_5{-}CH_2{-}Cl$$



(a) Reaction takes place by free radical mechanism.

(b) The yield of halide in this reaction is as follows :



$$R{-}CH_2{-}X > R{-}\underset{\displaystyle X}{\underset{|}{CH}}{-}R > R_3C{-}X$$

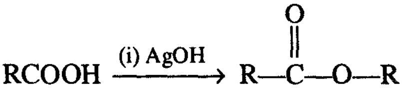
(c) One useful modification of this reaction is the use of HgO or $Pb(OAc)_4$ in place of silver salt.

$$2RCOOH \xrightarrow{X_2/HgO/\Delta} 2R{-}X + 2CO_2 + HgX_2 + H_2O$$

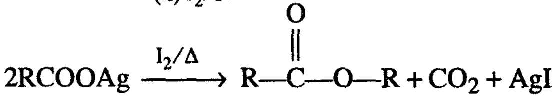
In the presence of $Pb(OAc)_4$, RI can also be prepared

$$RCOOH \xrightarrow[I_2/h\nu]{Pb(OAc)_4} R{-}I$$

(d) Silver salt of acid reacts with I_2 to give ester. This reaction is known as **Simonini reaction.**



$$RCOOH \xrightarrow[\text{(ii) }I_2/\Delta]{\text{(i) AgOH}} R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}R$$

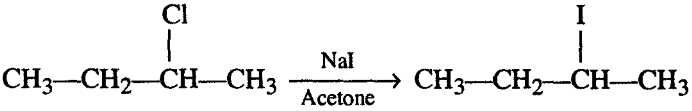


$$2RCOOAg \xrightarrow{I_2/\Delta} R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}R + CO_2 + AgI$$

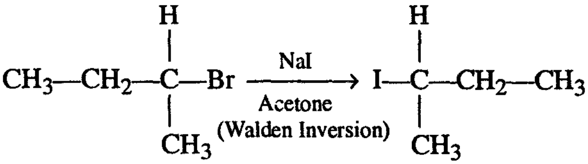
7.3.5 Conant-Finkelstein Reaction

Alkyl chloride and bromide react with NaI in the presence of acetone to give alkyl iodide. Thus this reaction is mainly used for the conversion of R—Br and R—Cl into R—I. This reaction is SN2 reaction. This reaction is given by primary and secondary alkyl halides whose β-carbon is either primary or secondary.

$$CH_3{-}Br \xrightarrow[\text{Acetone}]{\text{NaI}} CH_3{-}I$$



$$CH_3{-}CH_2{-}\overset{\displaystyle Cl}{\overset{|}{CH}}{-}CH_3 \xrightarrow[\text{Acetone}]{\text{NaI}} CH_3{-}CH_2{-}\overset{\displaystyle I}{\overset{|}{CH}}{-}CH_3$$



$$CH_3{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}{-}Br \xrightarrow[\substack{\text{Acetone}\\\text{(Walden Inversion)}}]{\text{NaI}} I{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}{-}CH_2{-}CH_3$$

7.3.6 Swart Reaction

Alkyl halide (chloride and bromide) react with AgF, SbF_3 or Hg_2F_2 to give alkyl fluoride. This reaction is known as Swart Reaction.

$$R{-}X + AgF \longrightarrow R{-}F + AgX\downarrow$$

This reaction is used for the preparation of alkyl fluoride.

7.4 PHYSICAL PROPERTIES OF HALOALKANES

The names, boiling points and densities of several haloalkanes are given in the Table 7.1.

Table 7.1 Physical properties of some haloalkanes

Compound	Boiling point °C	Density g/ml
Methyl chloride	–24	Gas
Methyl bromide	5	Gas
Methyl iodide	43	2.28
Methylene chloride (Dichloromethane)	40	1.34
Chloroform (Trichloromethane)	61	1.49
Carbon tetrachloride (Tetrachloromethane)	77	1.60

Except fluorine, halogen atoms are heavy compared to carbon or hydrogen atoms. The increase in the molecular weight as halogen atoms are substituted into hydrocarbon molecules causes an increase in the boiling points of a series of compounds.

Again because of the mass of halogen atom, the densities of liquid alkyl halides are often greater than those of other comparable organic compounds. Whereas most organic compounds are lighter than water, halogen containing compounds are heavier than water (density greater than 1). Haloalkanes do not form hydrogen bonds and are insoluble in water.

Alkyl halides are soluble in most organic solvents. They vary greatly in stability. Monofluoroalkanes are difficult to keep pure, on distillation they tend to lose HF to form alkenes. Chlorides are relatively stable and generally can be purified by distillation. However, higher molecular weight tertiary aryl/alkyl chlorides tend to lose HCl on heating and must be handled more carefully.

Chloroform slowly decomposes on exposure to light. This tendency is diminished by the presence of small amount of alcohol. Alkyl bromides and iodides are also light-sensitive. Upon exposure to light they slowly liberate the free halogen and turn brown or violet, respectively.

7.5 CHEMICAL REACTIONS OF ALKYL HALIDES

For a given halogen atom, the order of reactivity of an alkyl halide is as given below :

Tertiary alkyl halide > Sec. alkyl halide > Prim. alkyl halide

For a given alkyl group the order or reactivity in alkyl halides is :

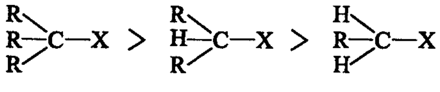
Iodides > Bromides > Chlorides > Fluorides

Among the primary alkyl halides the order of reactivity is :

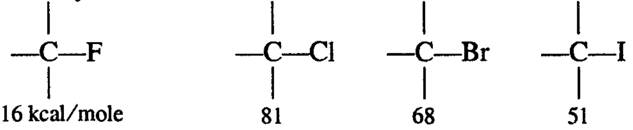
$$CH_3X > C_2H_5X > n—C_3H_7X > n—C_4H_9X, \text{ etc.}$$

These chemical characteristics can be explained by understanding the nature of C—*X* bond which is a highly polarised covalent bond. The halogen is far more electronegative than carbon and tends to pull the electrons away from carbon. Alkyl halides are, therefore, dipolar molecules with carbon as a positive end and halogen as the negative end of the dipole.

Since an alkyl group has + I effect, it would increase the electron density on the carbon atom (to which it is attached) of the C—*X* bond. The greater will be electron density on the carbon the greater would be electron repulsion towards halogen atom and consequently weaker would be the bond. Because the primary has one, secondary two, and tertiary three alkyl groups attached to carbon which is itself attached to halogen, the order of the reactivity of —C—*X* bond is :



The bond dissociation energy (given below) associated with the different C—*X* bonds gives the idea of their relative reactivity.

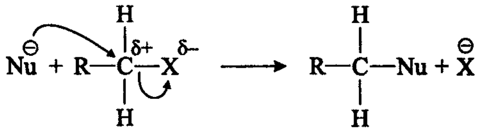


$$\text{—C—F}\quad 116\text{ kcal/mole}\qquad \text{—C—Cl}\quad 81\qquad \text{—C—Br}\quad 68\qquad \text{—C—I}\quad 51$$

Alkyl halides are reactive compounds and they undergo **substitution**, and **elimination** reactions. They also react with metals to form **organometallic compounds.**

7.6 NUCLEOPHILIC SUBSTITUTION REACTIONS

The C—*X* bond in alkyl halides is polar, withdrawal of electron pair towards halogen makes the carbon electron deficient, hence it becomes a good target for attack by nucleophiles.



In nucleophilic substitution two changes occur—breaking of the bond with **leaving group** and formation of bond with **nucleophile**. The principal mechanistic variations are associated with changes in the timing of the two processes. The following are the possible mechanisms of nucleophilic substitutions :

(1) Two step reaction (SN1 Mechanism, Substitution Nucleophilic Unimolecular)

First Step : Breaking of the C—*X* bond

Second Step : Making of the C—Nu bond

(2) One step reaction (SN2 Mechanism, Substitution Nucleophilic Bimolecular) : In this reaction the bond breaking and bond making are simultaneous.

Before discussing one step and two step reactions let us first discuss leaving group and incoming nucleophile of the reaction.

A general nucleophilic substitution reaction may be schematically represented as :

$$R\text{—L} + \overset{\ominus}{\text{Nu}} \longrightarrow R\text{—Nu} + \overset{\ominus}{\text{L}}$$

where L is a leaving group (or leaving nucleophile or nucleofuge) and Nu is an incoming nucleophile.

7.6.1 Incoming Nucleophile

An incoming nucleophile may either be negatively charged or it may be an uncharged species with unpaired of electrons :

$$\overset{\ominus}{\text{N}}\text{O}_2,\ \overset{\ominus}{\text{N}}_3,\ R\text{CO}\overset{\ominus}{\text{O}},\ \overset{\ominus}{\text{C}}\text{N},\ \overset{\ominus}{\text{I}},\ \overset{\ominus}{\text{B}}\text{r},\ \overset{\ominus}{\text{C}}\text{l},\ \overset{\ominus}{\text{O}}\text{H},\ \overset{\ominus}{\text{O}}\text{CH}_3,\ \text{H}_2\text{O},\ R\text{OH},\ \overset{\bullet\bullet}{\text{N}}\text{H}_3,\ R\overset{\bullet\bullet}{\text{N}}\text{H}_2,\ \overset{\ominus}{\text{S}}\text{H},\ \text{etc.}$$

The reactivity of nucleophile is called its nucleophilicity. The nucleophilicity increases with increasing polarisability. Nucleophilicity can be compared as given below :

(1) A species with a negative charge is a stronger nucleophile than a similar species without a negative charge. In particular, a base is a stronger nucleophile than its conjugate acid. Therefore, $\overset{\ominus}{\text{O}}\text{H}$ is a stronger nucleophile than HOH and $\overset{\ominus}{\text{S}}\text{H}$ is a stronger nucleophile than CH_3—S—CH_3.

(2) Nucleophilicity decreases on going from left to right in the period of the periodic table. Therefore, $\overset{\ominus}{\text{O}}\text{H}$ is more nucleophilic than $\overset{\ominus}{\text{F}}$; NH_3 is more nucleophilic than HOH; and $\overset{\ominus}{\text{C}}\text{H}_3$ is more nucleophilic than $\overset{\ominus}{\text{N}}\text{H}_2$.

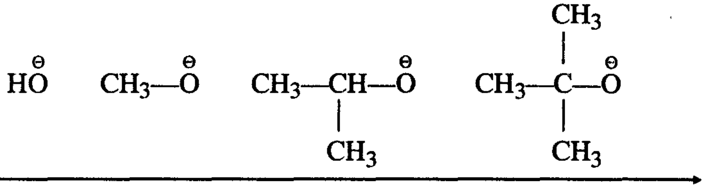
(3) Nucleophilicity increases on going down in the group of the periodic table. Therefore, $\overset{\ominus}{I}$ is more nucleophilic than $\overset{\ominus}{Br}$ which is more than $\overset{\ominus}{Cl}$.

Similarly :

$$Se\overset{\ominus}{H} > \overset{\ominus}{S}H > \overset{\ominus}{O}H$$

$$R_3\ddot{P} > R_3\ddot{N}$$

(4) Bulky group present on nucleophilic centre decreases nucleophilicity and increases basicity of the negatively charged species.



$H\overset{\ominus}{O} \quad CH_3-\overset{\ominus}{O} \quad CH_3-\underset{CH_3}{CH}-\overset{\ominus}{O} \quad CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{\ominus}{O}$

Basicity in increasing order; nucleophilicity in decreasing order

7.6.2 Leaving Groups or Leaving Nucleophiles

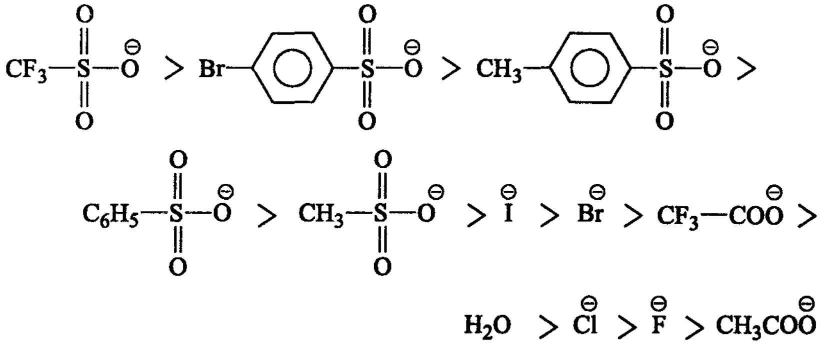
The leaving group must have the following three important characteristics :

(1) A leaving group is electron—withdrawing so that it creates a partial positive charge on the carbon atom.

(2) The leaving group should be stable after leaving with the bonding pair of electrons. In general, good leaving groups should be **weak bases**, and therefore, they are the conjugate bases of strong acids.

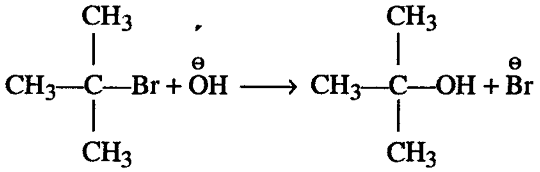
(3) Finally, the ability of a species to act as a good leaving group depends on its polarisability : That is its ability to continue bonding with a carbon atom while it is leaving. This bonding stabilises the transition state, minimising the activation energy.

The leaving power of some nucleophilic groups are given below in decreasing order :



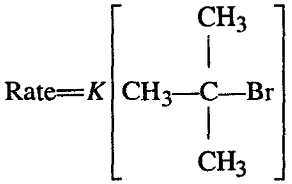
7.6.3 Two Step Process : (SN1 Mechanism or SN1 Reaction)

A typical example of this process is the hydrolysis of tertiary butyl bromide in the presence of sodium hydroxide.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br + \overset{\ominus}{O}H \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH + \overset{\ominus}{Br}$$

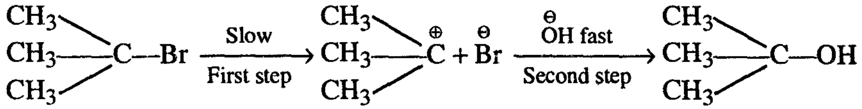
In this reaction, the rate of reaction is not increased by addition of NaOH even though hydroxide ions are consumed in the reaction. The rate of the reaction depends only on the concentration of the organic halide and hence, the first-order rate law is followed :



$$\text{Rate} = K\left[CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-Br\right]$$

This can be explained, if it is assumed that the reaction takes place in two steps. The first one being the ionisation of alkyl halide producing carbocation. This will obviously be a slow (rate determining) step as it involves breaking of a covalent bond.

This is followed by the fast (non-rate determining) step which involves addition of nucleophile to the reactive carbocation.



The energy profile diagram of SN1 mechanism is depicted in Fig. 7.1.

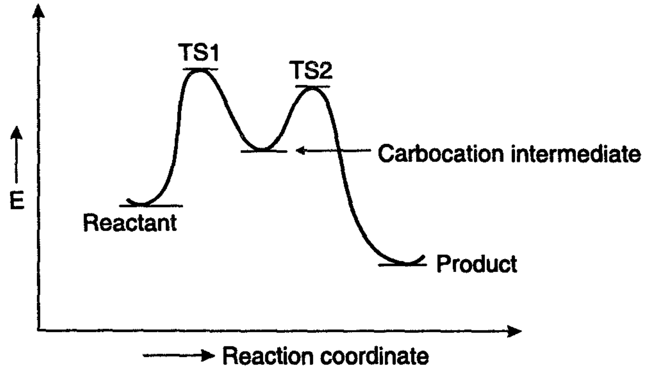


Fig. 7.1. Energy profile diagram of SN1 mechanism

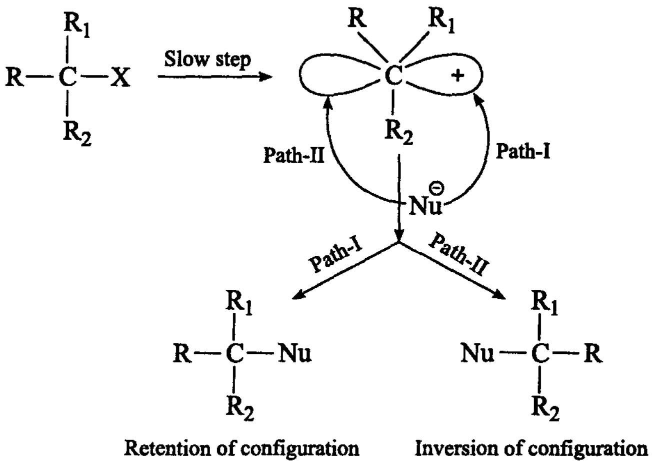
This two step mechanism (SN1 mechanism) of nucleophilic substitution is unimolecular because in the rate-determining step (slow first step) only the alkyl halide is undergoing covalency change. The nucleophile does not come into play until the fast second step.

Stereochemistry of SN1 Reaction : The reaction of alkyl halide in which halogen is bonded to a chiral carbon leads to the formation of enantiomers : One with the same relative configuration as the reacting alkyl halide and other with the inverted configuration.

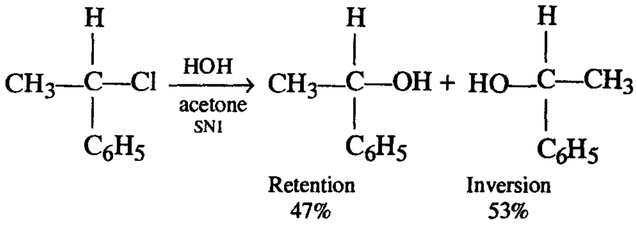
Formation of enantiomeric pair is due to the formation of carbocation whose geometry is planar.

The SN1 reaction that transforms an optically active substrate into an enantiomeric pair or racemic mixture is said to proceed with **racemisation.** If enantiomers are formed in equal amounts then reaction is said to proceed with complete racemisation. In the case of complete racemisation no optical activity is detected in the mixture.

Only very few reactions are known where optically active alkyl halides undergo complete racemisation (*i.e.* 50% retenion of configuration and 50% inversion of configuration). In most of the cases optically active alkyl halides undergoing SN1 reaction give partially racemised products instead of completely racemised products. The products usually consist of more inversion product than

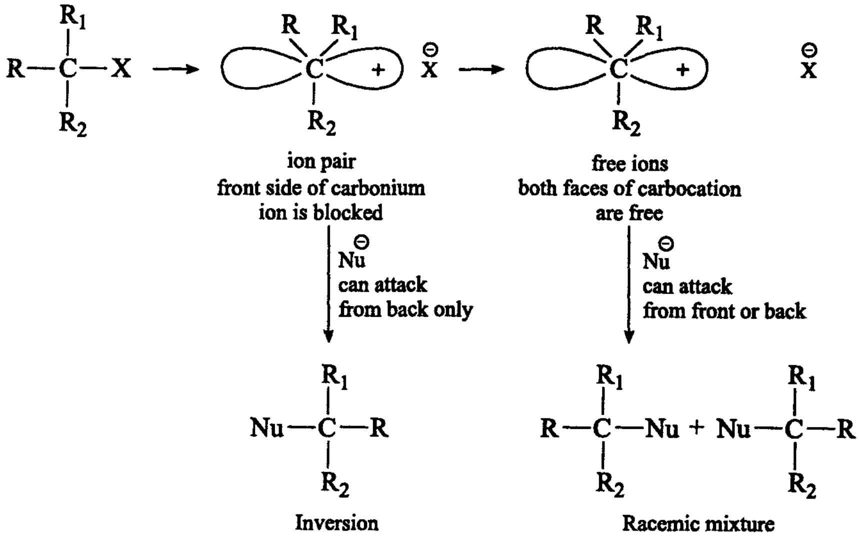


retention product. In most of the cases the product usually consists of 5–20% inverted product and 80–95% racemised species.



$$CH_3-\underset{C_6H_5}{\overset{H}{C}}-Cl \xrightarrow[\text{acetone, SN1}]{HOH} CH_3-\underset{C_6H_5}{\overset{H}{C}}-OH + HO-\underset{C_6H_5}{\overset{H}{C}}-CH_3$$

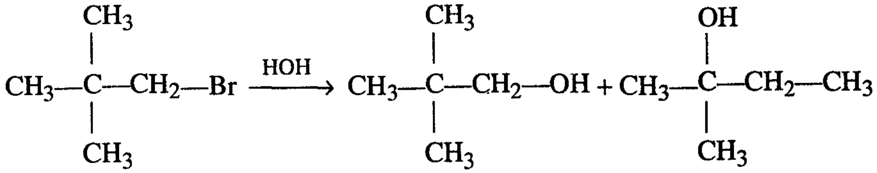
This result may occur if the carbocation is not sufficiently stable and if the leaving group is not far enough removed from the carbocation (it is present as ion pair). Ion pair blocks front face of carbocation for the attack of nucleophile. Thus attack of nucleophile on the ion pair can occur more easily at the backside producing more of inversion product and less of retention product. Partial racemisation proceeds as follows :



SN1 Reactions are Accompanied by Rearrangement

If carbocation is primary or secondary having at least three carbons then rearrangement takes place in carbocation. This leads to the formation of two or more products, one is normal and others are rearrangeds products.

For example :



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-Br \xrightarrow{HOH} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-OH + CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_2-CH_3$$

(Normal product) Rearranged product (Major product)

Factors Influencing SN1 Reaction Rate

(1) Effect of Substrate Structure on Rate : A carbocation being the intermediate in an SN1 reaction, its stability determines the rate of the reaction. The greater the carbocation stability, the higher is the rate. This is reflected in the reactivity order of alkyl halides towards SN1 reaction. The reactivity order is :

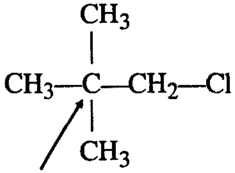
$$3° >> 2° > 1° > CH_3$$

Thus the SN1 mechanism will be most preferred in *tert*-halides and least preferred in case of primary alkyl halides.

If the carbon site having leaving group is highly crowded with bulky groups, it tends to get relief from the steric strain with 109° bond angle (sp^3) and it does so when it approaches 120° bond angle in the carbocation intermediate. In other words, the greater the crowding around the carbon having leaving group, the greater is the possibility of SN1 reaction.

$$CH_3-CH_2-CH_2-CH_2-X$$

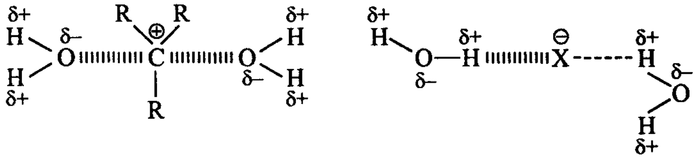
does not give SN1 reaction



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-Cl$$

Crowding around α-carbon gives SN1 reaction

2. Effect of Solvents on Rate : A solvent with high ionising power (*i.e.*, polar protic solvent) enhances the rate of SN1 reactions. Thus polar hydroxylic solvents like HOH, ROH, CH_3COOH, etc. are good solvents for SN1 reaction. This is because the negative pole of such species interacts with the incipient positive charge; while hydrogen bond is formed with the incipient negative charge through the $H^{\delta+}$ pole. In other words, polar protic solvent stabilises carbocation and hence increases rate of the reaction.



Ion-solvent interactions

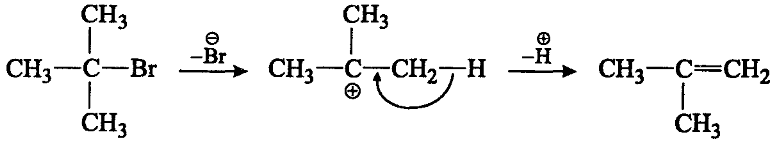
Non-polar, non-hydroxylic solvents retard the rate of an SN1 reaction.

3. Effect of Nucleophiles on Rate : Since the rate determining step of an SN1 reaction does not involve the incoming nucleophile, neither its nucleophilicity, nor its concentration has any effect on the rate of the reaction. So an SN1 reaction can proceed with weak nucleophiles of low concentration.

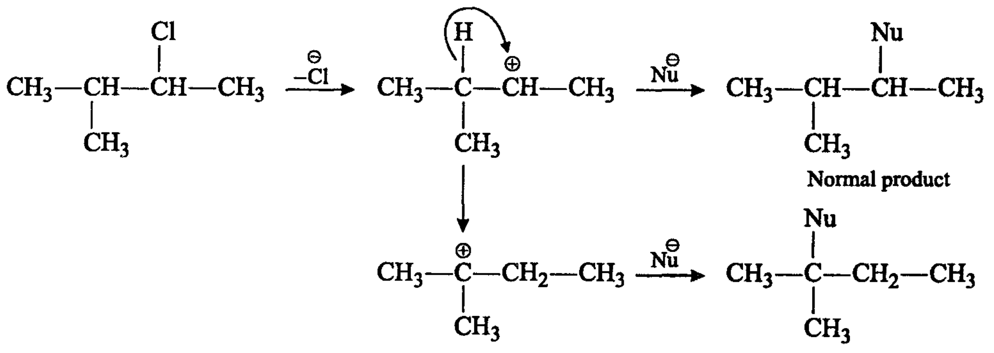
4. Effect of Leaving Groups on Rate : More is the leaving power of the group, more will be reactivity of the substrate for SN1 reaction. Thus reactivity order among the halide ions is :

$$\overset{\ominus}{I} > \overset{\ominus}{Br} > \overset{\ominus}{Cl} > \overset{\ominus}{F}$$

(1) Competitive Reactions : Carbocation is the intermediate in SN1 reaction. It may give up a $\overset{\oplus}{H}$ from the β-position with respect to the leaving group. This leads to the formation of a double bond and then the reaction is an elimination reaction (Chapter 5).



On the other hand, a carbocation may rearrange to give a stable carbocation.



Thus elimination and rearrangement reactions compete with substitution in SN1 reaction.

Strong nucleophiles being strong bases, they can abstract a H and thus favour elimination reaction. It is therefore, better to use weak nucleophiles in SN1 reactions.

7.6.4 One Step Process (SN2 Mechanism or SN2 Reaction)

A typical example of this process is the hydrolysis of methyl bromide in the presence of NaOH.

$$CH_3—Br + \overset{\ominus}{O}H \longrightarrow CH_3—OH + \overset{\ominus}{Br}$$

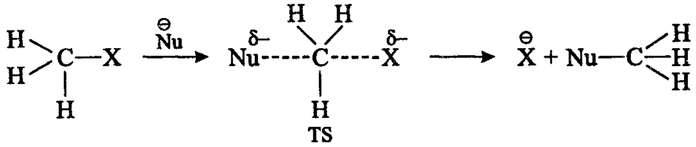
Kinetic studies have revealed that the reaction rate depends on the concentration of alkyl halide (CH_3Br) as well as the concentration of the nucleophile. Both the reactants being involved in the rate determining step.

$$\text{Rate} = K\,[CH_3Br]\,[\overset{\ominus}{O}H]$$

Increasing the concentration of either species will increase the reaction rate and vice-versa.

In this mechanism, the formation of carbon-nucleophile bond and cleavage of the carbon-halogen bond occurs simultaneously. In other words, the bond between carbon and nucleophile starts forming and at the same time the bond between carbon and halogen starts breaking. Such a reaction, therefore, involves a transition state in which the carbon atom appears to be pentavalent, *i.e.*, it is attached to three hydrogens by full covalent bonds and to the nucleophile and halogen atom by partial bonds. The three hydrogens acquire a coplanar geometry.

The nucleophile attacks the carbon from the side just opposite to that from which the halide is leaving. This is sterically favourable in that the nucleophile and halide do not hinder movement of each other as well as there is minimum repulsion between them.



The SN2 mechanism is bimolecular because both reacting species are undergoing covalency change in the rate determining step. The energy profile diagram of SN2 reaction is shown in Fig. 7.2.

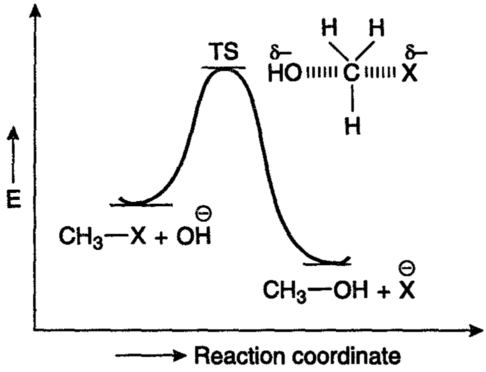
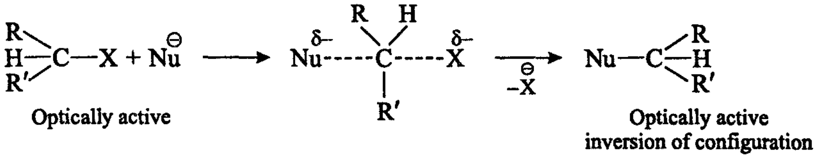


Fig. 7.2. Energy profile diagram of SN2 reaction

Stereochemistry of SN2 Reactions

In an SN2 reaction, the nucleophile enters as the halide is leaving. Consequently, the nucleophile attacks from the rear to avoid the path of the leaving group. If the alkyl halides is optically active, inversion of configuration will occur.



The nucleophile is attached just opposite side to the leaving group. Thus, the substitution product is still optically active but of opposite configuration to the alkyl halide.

Thus it can be said that an SN2 reaction proceeds with complete inversion of configuration usualy referred to as **Walden inversion.**

Factors Influencing SN2 Reaction Rate

(1) Effect of Substrate Structure on Rate : Electrical effect on the carbon site has the minimum to do with the SN2 reaction rate. The carbon atom usually bears a partial positive charge owing to the bond dipole of the C—*X* bond. Any thing that decreases the positive charge on the carbon site by giving electrons, decreases the reaction rate while anything that increases positive charge on the same by withdrawing electron, increses the rate of the reaction. Thus the reactivity order is :

$$CH_3—X > 1° > 2° > 3°$$

On the other hand, steric factor has profound effect on SN2 reaction rate. Availability of space for attack on the carbon site by the nucleophile decreases with the increasing steric hindrance and consequently the rate of the reaction diminishes largely. Since alkyl groups are larger than hydrogen atom, steric crowding increases in the direction from primary to tertiary alkyl halides and thus primary will be most reactive.

(2) Effect of Solvents on Rate : Polar hydroxyl solvents form hydrogen bond with the incoming nucleophile. Thus solvent molecules envelop the nucleophile. It becomes difficult for the nucleophile to attack the carbon site. Hence hydroxylic solvents retard the rate of an SN2 reaction. The rate, however, increases to a large extent in the presence of polar non-hydroxylic solvents like DMF (dimethylformamide) DMSO (dimethyl sulphoxide) and acetone.

(3) Effect of Nucleophiles on Rate : Since the single step SN2 reaction involves the substrate and the nucleophile, the rate of the reaction depends largely on the concentration of the nucleophile and on its nucleophilicity. Strong nucleophiles increase the rate of the SN2 reaction while weak nucleophiles decrease it.

(4) Effect of Leaving Groups on Rate : The rate of an SN2 reaction is dependant on the nature of the leaving group. Groups of lower basicity and higher polarisibility increase the rate of the reaction. Thus the reactivity order among the halide ions is :

$$\overset{\ominus}{I} > \overset{\ominus}{Br} > \overset{\ominus}{Cl} > \overset{\ominus}{F}$$

7.6.5 Competitive Reaction : Elimination reaction (Chapter 5) competes with the SN2 reaction. A strong base usually abstracts a proton from the β-carbon with respect to the leaving group and simultaneously leaving group itself leaves to species to form an alkene. If the reaction is carried out at low temperature in the presence of strong nucleophile (which is weak base) elimination reaction may be stopped.

7.6.6 Comparison of SN1 and SN2 Substitutions

SN2	SN1
(1) One step mechanism	(1) Two step mechanism
(2) Bimolecular reaction	(2) Unimolecular reaction
(3) Product formation takes place by TS	(3) Product formation takes place by carbocation intermediate
(4) No carbocation rearrangement	(4) Carbocation rearrangement
(5) Reaction is favoured by polar aprotic solvents	(5) Reaction is favoured by polar protic solvents
(6) Given mainly by methyl halides	(6) Given mainly by tertiary alkyl halides
(7) Reactivity of RX; $CH_3X > 1° > 2° > 3°$	(7) Reactivity of RX; $3° > 2° > 1° >$ methyl
(8) Mechanism is favoured when nucleophile is an anion	(8) Mechanism is favoured when nucleophile is neutral
(9) Reaction velocity depends on the con- centration of nucleophile, *i.e.*, mechanism is favoured by high concentration of nucleophile	(9) Reaction velocity is independent of the concentration of nucleophile.
(10) Inversion of configuration	(10) Racemisation

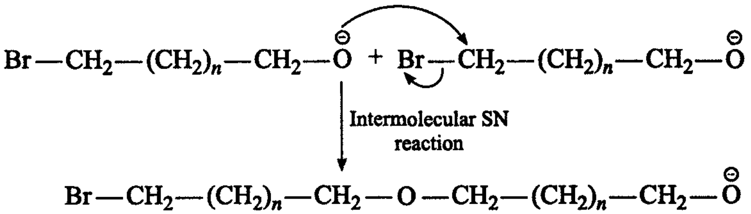
7.6.7 Inter- and Intramolecular Nucleophilic Substitution Reactions

Bifunctional compound that contains both a nucleophile and a leaving group gives either intermolecular or intramolecular nucleophilic substitution reaction.

(A) Intermolecular Nucleophilic Substitution Reactions :

(1) In intermolecular (inter means between) nucleophilic substitution reactions, the nucleophile of one molecule displaces the leaving group of a second molecule of the compound.

(2) Higher concentration of reactant favours intermolecular nucleophilic substitution reaction.



$$Br-CH_2-(CH_2)_n-CH_2-\overset{\ominus}{O} + Br-CH_2-(CH_2)_n-CH_2-\overset{\ominus}{O} \xrightarrow{\text{Intermolecular SN reaction}} Br-CH_2-(CH_2)_n-CH_2-O-CH_2-(CH_2)_n-CH_2-\overset{\ominus}{O}$$

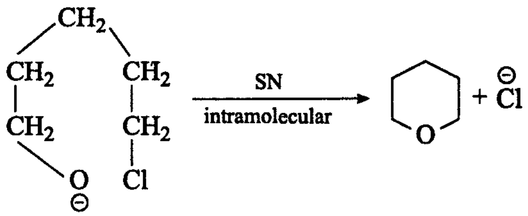
(B) Intramolecular Nucleophilic Substitution Reactions :

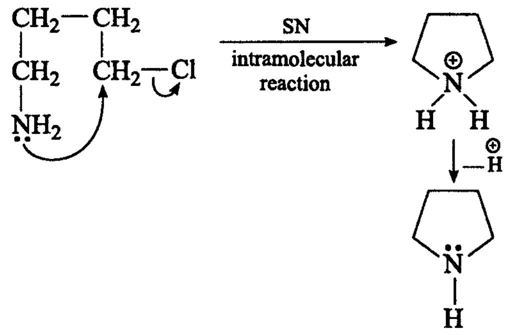
(1) An intramolecular nucleophilic substitution takes place within the molecule. (Intra means within or single)

(2) Low concentration of the reactant favours intramolecular reaction.

(3) Intramolecular reaction gives cyclic product. If intramolecular reaction would form a five or six membered ring, it would be highly favoured over the intermolecular reaction because of the stability.

(4) Intramolecular reactions are less favourable for other size of the ring (*i.e.*, three, four, seven, etc.)





In Chapter 5, we have already discussed elimination reactions in detail. Here (Section 7.6) we have discussed nucleophilic substitution reactions in detail. Now let us have a comparison among these reactions.

7.6.8 Comparison of Factors Governing Substitution and Elimination Reactions

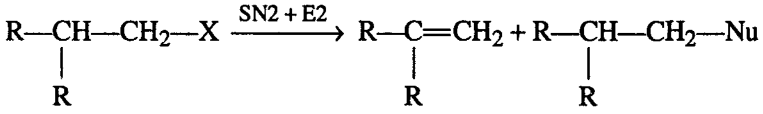
SN1, SN2, E1 and E2 are competing reactions. A single alkyl halide could be undergoing substitution, elimination and rearrangements all in the same reaction flask. If this happens, a mixture of a large number of products can result. However, this can be controlled to a certain extent by a proper choice of the reagents and reaction conditions. The factors which are responsible for this choice are :

(A) The structure of alkyl halides :

(i) Methyl and primary alkyl halides that are not branched at C_2 tend to undergo SN2 reactions. They do not form carbocation and thus cannot undergo SN1 or E1 reactions. Primary alkyl halides undergo E2 reactions slowly if at all.

$$R-CH_2-CH_2-X + \overset{\ominus}{Nu} \xrightarrow{SN2} R-CH_2-CH_2-Nu + \overset{\ominus}{X}$$

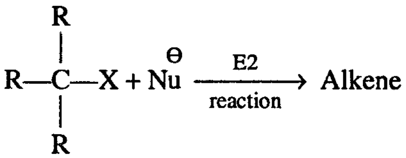
Primary alkyl halides that are branched at C—2 give more elimination because the SN process is retarded.



$$\underset{\displaystyle R}{R-\overset{}{C}H}-CH_2-X \xrightarrow{SN2 + E2} \underset{\displaystyle R}{R-C}=CH_2 + \underset{\displaystyle R}{R-CH}-CH_2-Nu$$

(ii) **Secondary alkyl halides :** These can undergo reaction by any path, but SN2 and E2 are more common than SN1 or E1. The reactions of secondary alkylhalides are more subject to control by the nature of attacking reagent and solvent.

(iii) **Tertiary alkyl halides :** These undergo primarily E2 reactions with a strong base $(\overset{\ominus}{O}H, R\overset{\ominus}{O}, \overset{\ominus}{N}H_2)$ but undergo the SN1 reaction and some E1 reaction with a very weak base (HOH, ROH)



$$R-\underset{\displaystyle R}{\overset{\displaystyle R}{C}}-X + \overset{\ominus}{Nu} \xrightarrow[\text{reaction}]{E2} \text{Alkene}$$

$$\overset{\ominus}{Nu} = \overset{\ominus}{O}H, R\overset{\ominus}{O}, \overset{\ominus}{C}N, NH_3$$

(B) Concentration of the nucleophile or base : A high concentration of nucleophile or base favours SN2 or E2 reaction respectively and a low concentration favours SN1 or E1.

High concentration of nucleophile or base : SN2 or E2; low concentration of nucleophile or base : SN1 or E1

(C) Temperature : An increase in temperature increases the rates of all substitution and elimination reactions. However, an increase in temperature usually leads to a greater increase in elimination products.

7.6.9 Comparison between SN1 and E1 reactions

Points		SN1	E1
1	Step	Two	Two
2.	Reagent	Solvents and weakly basic reagents of low concentration	Weak base
3.	Solvent	Polar protic solvent	Polar protic solvent
4.	Structure and reactivity nature of the alkyl group	3° > 2° > 1°	3° > 2° > 1°
5.	Kinetics	First order	First order
6.	Stereochemistry	Racemisation and partial inversion occur	Non-stereospecific

7.6.10 Comparison between SN2 and E2 reactions

		SN2	E2
1.	Step	One	One
2.	Reagent	Strong nucleophile	Strong base
3.	Solvent	Polar aprotic solvent	Polar aprotic solvent
4.	Structure and reactivity nature of the alkyl group	1° > 2° > 3°	3° > 2° > 1°
5.	Kinetics	Rate = K_2 [R—X][$\overset{\ominus}{\text{Nu}}$]	Rate = K_2 [R—X][B]
6.	Stereospecificity	Stereospecific inversion of configuration	Stereospecific (i) usually anti elimination takes place. (ii) In pyrolytic elimination, the elimination is syn.

7.6.11 Some Nucleophilic Substitution Reactions of Alkyl Halides

(1) Reaction with Moist Silver Oxide : Alkyl halides on treatment with a suspension of Ag_2O in moist ether produce Alcohols.

$$Ag_2O + H_2O \longrightarrow 2AgOH$$

$$R\text{—Br} + AgOH \longrightarrow R\text{—OH} + AgBr$$

(2) Reaction with Sodium Alkoxides : Alkyl halides on reaction with sodium alkoxides give ethers.

$$R'\text{—OH} + Na \longrightarrow R'\text{—}\overset{\ominus}{O}\overset{\oplus}{Na} + \frac{1}{2}H_2\uparrow$$

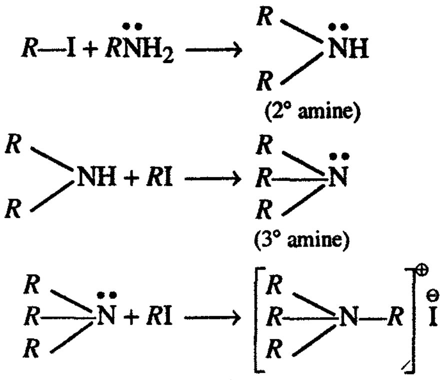
$$R\text{—}X + R'\text{—}\overset{\ominus}{O}\overset{\oplus}{Na} \longrightarrow R\text{—O—}R' + NaX$$

$$C_2H_5Br + C_2H_5ONa \xrightarrow{SN2} \underset{\text{Diethyl ether}}{C_2H_5\text{—O—}C_2H_5} + NaBr$$

This method of making ethers is called **Williamson Ether Synthesis.**

(3) Reaction with Ammonia or Amines : Alkyl halides when heated with alcoholic ammonia under pressure, form amines.

$$R\text{—I} + \ddot{N}H_3 \longrightarrow \underset{\text{Primary amine (1° amine)}}{R\text{—}NH_2} + HI$$



Quaternary ammonium salt

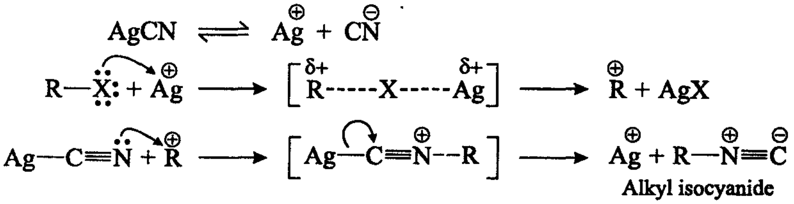
(4) Reaction with alc. KCN and AgCN : Alkyl halides react with KCN in the presence of alcohol to form alkyl cyanides or nitriles.

$$R\text{—Br} + \text{KCN} \xrightarrow{\text{SN2}} R\text{CN} + \text{KBr}$$
$$C_2H_5\text{—Br} + \text{KCN} \longrightarrow C_2H_5CN + \text{KBr}$$

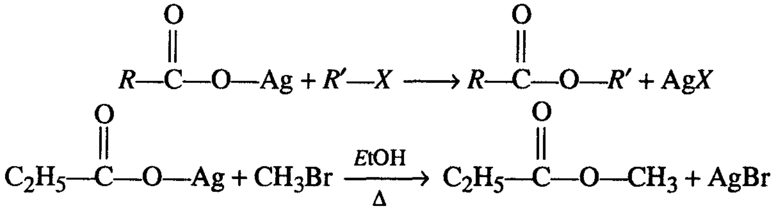
On the other hand, when alkyl halides are treated with AgCN in the presence of alcohol as solvent, alkyl isocyanides or carbylamines are formed.

$$R\text{—}X + \text{AgCN} \longrightarrow R\text{—}\overset{\oplus}{N}\equiv\overset{\ominus}{C} + \text{Ag}X$$
$$C_2H_5Br + \text{AgCN} \longrightarrow \underset{\text{Ethyl isocyanide}}{C_2H_5NC} + \text{AgBr}$$

When silver cyanide is used in place of KCN the major product is alkyl isocynide. Silver cyanide, though covalent in nature, contains traces of $\overset{\oplus}{\text{Ag}}$ which attacks at the halogen atom generating a carbocation. This carbocation reacts with silver cyanide forming the isocyanide.



(5) Reaction with Silver Salt of Fatty Acids : When alkyl halides are heated with alcoholic solution of the silver salts of carboxylic acids, esters are formed.



$$R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—O—Ag} + R'\text{—}X \longrightarrow R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—O—}R' + \text{Ag}X$$
$$C_2H_5\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—O—Ag} + CH_3Br \xrightarrow[\Delta]{EtOH} C_2H_5\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—O—}CH_3 + \text{AgBr}$$

(6) Reaction with Potassium Hydrogen Sulphide : Alkyl halides react with alcoholic KSH to form thiols.

$$R\text{—}X + \text{KSH} \xrightarrow[\Delta]{EtOH} R\text{—SH} + \text{K}X$$

$$C_2H_5Br + \text{KSH} \xrightarrow[\Delta]{EtOH} C_2H_5SH + \text{KBr}$$

(7) Reaction with Alkali Metal Sulphides : Alkyl halides react with K_2S to form dialkyl sulphides.

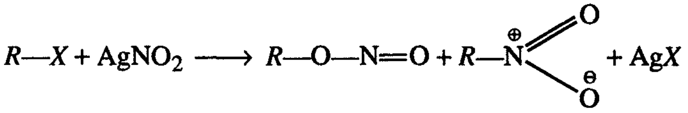
$$2R\text{—}X + K_2S \longrightarrow R\text{—S—}R + 2\text{K}X$$
$$2C_2H_5I + H_2S \longrightarrow C_2H_5\text{—S—}C_2H_5 + 2\text{KI}$$

(8) Reaction with Potassium Nitrite and Silver Nitrite : When alkyl halides are heated with KNO_2 in the presence of alcohol, alkyl nitrites are formed.

$$R\text{—}X + KNO_2 \xrightarrow[\Delta]{EtOH} R\text{—O—N=O} + \text{K}X$$

$$C_2H_5Br + KNO_2 \xrightarrow[\Delta]{EtOH} C_2H_5\text{—O—N=O} + \text{KBr}$$

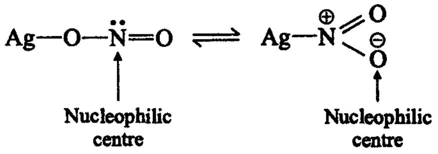
On the other hand, when alkyl halides are treated with alcoholic $AgNO_2$, mixture of nitroalkane and alkyl nitrites are formed.



$$R—X + AgNO_2 \longrightarrow R—O—N=O + R—\overset{\oplus}{N}(=O)—\overset{\ominus}{O} + AgX$$

$$C_2H_5I + AgNO_2 \longrightarrow \underset{\text{Ethyl nitrite}}{C_2H_5—O—N=O} + \underset{\text{Niroethane}}{C_2H_5NO_2} + AgI$$

Treatment with silver nitrite gives mixture of alkyl nitrite and nitroalkane because silver nitrite exists in two forms.



(9) Reaction with Metallic Alkynides : Primary alkyl halides react with sodium or potassium alkylides in inert solvent to form higher alkynes.

$$R—X + \overset{\oplus}{Na}\overset{\ominus}{C}\equiv CH \longrightarrow R—C\equiv CH + NaX$$

$$R—X + R'—C\equiv \overset{\ominus}{C}\overset{\oplus}{Na} \longrightarrow R—C\equiv C—R' + NaX$$

7.7 OTHER REACTIONS OF ALKYL HALIDES

7.7.1 Oxidation Reaction

(i) Only primary and secondary alkyl halides undergo oxidation. Tertiary alkyl halide does not undergo oxidation.

(ii) Primary alkyl halides give aldehyde where as secondary alkyl halides give ketone in this reaction.

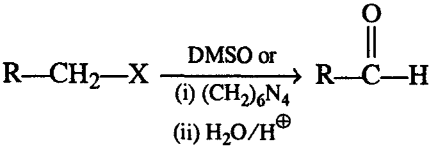
(iii) Oxidising agent is either :

(a) Dimethyl sulphoxide, or

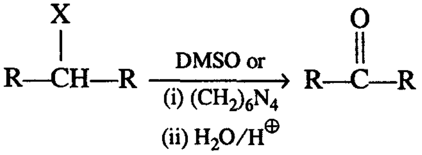
(b) Reaction with $(CH_2)_6N_4$ followed by hydrolysis.

(iv) Reactivity for oxidation reaction depends on the number of hydrogens present on *alpha* carbon of alkyl halides.

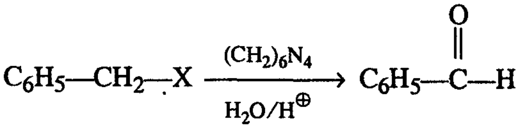
Reactivity ∝ number of α-hydrogens



$$R—CH_2—X \xrightarrow[\substack{\text{(i) } (CH_2)_6N_4 \\ \text{(ii) } H_2O/H^{\oplus}}]{\text{DMSO or}} R—\overset{\overset{O}{\|}}{C}—H$$



$$R—\overset{\overset{X}{|}}{C}H—R \xrightarrow[\substack{\text{(i) } (CH_2)_6N_4 \\ \text{(ii) } H_2O/H^{\oplus}}]{\text{DMSO or}} R—\overset{\overset{O}{\|}}{C}—R$$



$$C_6H_5—CH_2—X \xrightarrow[H_2O/H^{\oplus}]{(CH_2)_6N_4} C_6H_5—\overset{\overset{O}{\|}}{C}—H$$

Note : (1) Oxidation of Benzyl halides by $(CH_2)_6N_4$ is known as **Sommelet aldehyde synthesis**.

Note : Oxidation of alkyl halides with DMSO is known as **Swern** oxidation.

7.7.2 Reduction

Alkyl halides on reduction give alkane

$$R{-}X \xrightarrow[\text{(ii) } Bu_3SnH]{\text{(i) } LiAlH_4} R{-}H$$

7.7.3 Coupling Reaction

(A) Wurtz reaction : This reaction is coupling reaction given by halides in which halogen is present on sp^3 hybrid carbon. Reaction takes place in the presence of Na, Zn, Ag, Fe and activated copper. For coupling reaction, two molecules of halides are needed; both may be same or different.

(i) If both are same, then only one hydrocarbon having even number of carbons is obtained.

$$R{-}X + R{-}X \xrightarrow{\text{Na/dry ether}} R{-}R + 2NaX$$

$$CH_3{-}Br + CH_3{-}Br \xrightarrow{\text{Na/dry ether}} CH_3{-}CH_3 + 2NaBr$$

(ii) If reaction is carried out between two different halides, then three products are formed.

$$R{-}X + R'{-}X \xrightarrow{\text{Na/dry ether}} R{-}R + R'{-}R' + R{-}R'$$

If both halides have either even number of C's or odd number of C's then product always has even number of C's.

$$CH_3{-}CH_2{-}Br + CH_3{-}CH_2{-}CH_2{-}CH_2{-}Br \xrightarrow{\text{Na/dry ether}} n\text{-Butane} + n\text{-octane} + n\text{-hexane}$$

If one halide has even number of carbons and the other has odd number of carbons, then two products have even and one product has odd number of carbons.

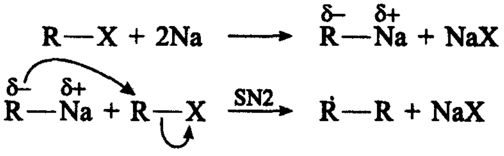
$$CH_3{-}Br + CH_3{-}CH_2{-}Br \xrightarrow{\text{Na/dry ether}} \underset{2C}{\text{Ethane}} + \underset{4C}{\text{Butane}} + \underset{3C}{\text{Propane}}$$

(iii) This reaction is not given by the 3°-alkyl halides.

Two mechanisms have been proposed for this reaction.

First mechanism : In this mechanism, formation of product takes place by formation of an organometallic compound of sodium. This metallic compound has some ionic character, hence carbon bonded to Na behaves as nucleophile and gives SN2 reaction. *Ter* alkyl halides do not give this reaction which supports the mechanism.

Second mechanism : In this mechanism product formation takes place by formation of free radical as reaction intermediate.



$$R{-}X + 2Na \longrightarrow \overset{\delta-}{R}{-}\overset{\delta+}{Na} + NaX$$

$$\overset{\delta-}{R}{-}\overset{\delta+}{Na} + R{-}X \xrightarrow{SN2} R{-}R + NaX$$

$$R{-}X + \dot{Na} \longrightarrow \dot{R} + NaX$$

$$\dot{R} + \dot{R} \longrightarrow R{-}R$$

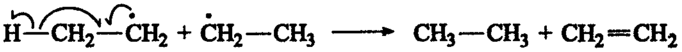
Wurtz reaction gives disproportionation product. This confirms that product formation takes place by formation of free radical as reaction intermediate.

Disproportionation reaction :

$$CH_3—CH_2—X \xrightarrow{\text{Na/dry ether}} CH_3—CH_2—CH_2—CH_3 + CH_2{=}CH_2 + CH_3—CH_3$$

Disproportionation reaction takes place as follows :

(B) Wurtz-Fittig reaction : This reaction is a coupling reaction which takes place between aryl halide and alkyl halide in the presence of sodium metal and dry ether. Mechanism of the reaction is same as in the case of Wurtz reaction.



$$H—CH_2—\dot{C}H_2 + \dot{C}H_2—CH_3 \longrightarrow CH_3—CH_3 + CH_2{=}CH_2$$

$$Ar—X + R—X \xrightarrow{\text{Na/dry ether}} Ar—R + Ar—Ar + R—R$$

The main product of the reaction is always cross product.

$$\underset{}{C_6H_5—I + CH_3—CH_2—I} \xrightarrow{\text{Na/dry ether}} \underset{\text{Ethylbenzene}}{C_6H_5—CH_2—CH_3}$$

(C) Frankland reaction : This reaction takes place in the presence of Zn/C_2H_5OH. This reaction is given by 1°, 2° and 3° alkyl halides.

$$R—X + R—X \xrightarrow[C_2H_5OH/\Delta]{Zn} R—R + ZnX_2$$

This reaction also takes place in the presence of Ag and Mg.

7.7.4 Reaction with Metals

Alkyl halides react with metal to form organometallic compounds.

(i) $$R—X + Mg \longrightarrow \underset{\substack{\text{Alkylmagnesium halide} \\ \text{(Grignard reagent)}}}{R—Mg—X}$$

(ii) $$4R—X + Na—Pb \text{ (Sodium-lead alloy)} \longrightarrow \underset{\text{Tetraalkyllead}}{R_4Pb}$$

(iii) $$2R—X + Zn \longrightarrow \underset{\text{Dialkylzinc}}{R—Zn—R}$$

(iv) $$R—X + 2Li \longrightarrow \underset{\text{Alkyllithium}}{R—Li} + LiX$$

7.8 DIHALOALKANES

Dihalides are classified as :

(A) *Gem* dihalides (B) *Vicinal* dihalides and (C) α, ω-Dihalides.

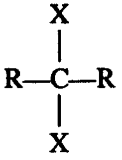
7.8.1 *Gem* dihalides

Dihalides having two halo groups on the same carbon atom are known as *gem* dihalide. These are of two types :

(a) Terminal *gem* dihalides : Dihalides in which both halo groups are present on terminal carbon of the molecule is known as terminal *gem* dihalides, *e.g.*,

$$R—CH_2—CHX_2$$

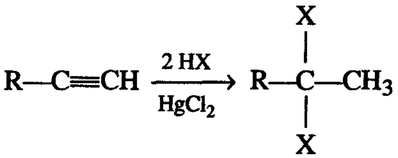
(b) Non-terminal gem dihalides in which both halo groups are present on non-terminal carbon, *e.g.*,



$$R—\overset{X}{\underset{X}{C}}—R$$

Preparation : *Gem* dihalides are prepared from alkynes and carbonyl compounds.

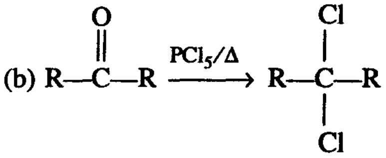
(i) From alkynes : Alkynes react with hydrogen halides in the presence of $HgCl_2$ to give *gem* dihalides.



$$R{-}C{\equiv}CH \xrightarrow[HgCl_2]{2\,HX} R{-}\overset{X}{\underset{X}{C}}{-}CH_3$$

(ii) From carbonyl compounds : Aldehydes and ketones react with PCl_5 to give *gem* dichlorides.

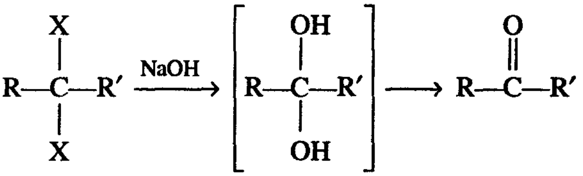
(a) $R{-}CHO \xrightarrow{PCl_5/\Delta} R{-}CHCl_2$



(b) $R{-}\overset{\overset{O}{\|}}{C}{-}R \xrightarrow{PCl_5/\Delta} R{-}\overset{Cl}{\underset{Cl}{C}}{-}R$

Properties : *Gem* dihalide gives all those reactions which are given by monohalides. Some important reactions are :

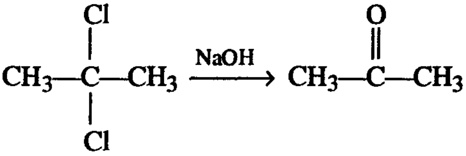
(1) Hydrolysis : Terminal *gem* dihalide gives aldehyde whereas non-terminal gives ketone on hydrolysis.



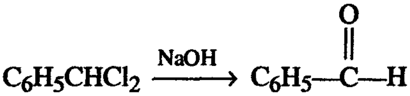
$$R{-}\overset{X}{\underset{X}{C}}{-}R' \xrightarrow{NaOH} \left[R{-}\overset{OH}{\underset{OH}{C}}{-}R'\right] \longrightarrow R{-}\overset{\overset{O}{\|}}{C}{-}R'$$

Thus in this reaction —CX_2— group converts into —CO— group.

$$CH_3{-}CHCl_2 \xrightarrow{NaOH} CH_3{-}CHO$$

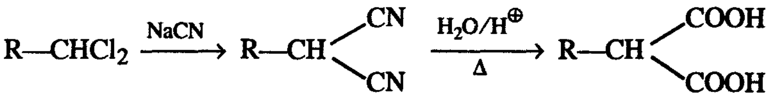


$$CH_3{-}\overset{Cl}{\underset{Cl}{C}}{-}CH_3 \xrightarrow{NaOH} CH_3{-}\overset{\overset{O}{\|}}{C}{-}CH_3$$

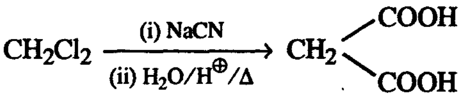


$$C_6H_5CHCl_2 \xrightarrow{NaOH} C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}H$$

(2) Reaction with NaCN : NaCN reacts with *gem* dihalide to give *gem* dicyano compound which is used for the preparation of 1,3-dicarboxylic acids.



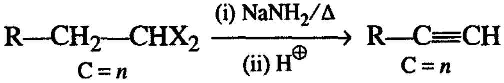
1,3-dibasic acid



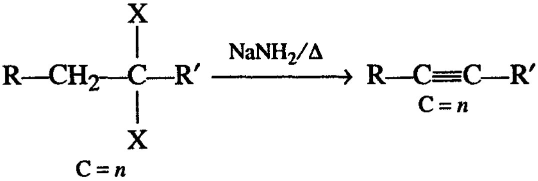
Malonic acid

(3) Dehalogenation reaction :

(a) *Gem* dihalide having at least two β-hydrogens undergoes dehalogenation in the presence of strong base. Product of the reaction is alkyne.



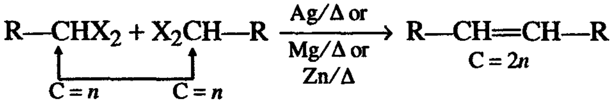
$$\underset{C=n}{R{-}CH_2{-}CHX_2} \xrightarrow[\text{(ii) } H^{\oplus}]{\text{(i) } NaNH_2/\Delta} \underset{C=n}{R{-}C{\equiv}CH}$$



$$\underset{C=n}{R{-}CH_2{-}\overset{\overset{\displaystyle X}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}{-}R'} \xrightarrow{NaNH_2/\Delta} \underset{C=n}{R{-}C{\equiv}C{-}R'}$$

Note : In this reaction number of carbons in reactant and product is same.

(b) *Gem* dihalide also undergoes dehalogenation *via* coupling reaction in the presence of Zn, Ag or Mg.



$$\underset{C=n}{R{-}CHX_2} + \underset{C=n}{X_2CH{-}R} \xrightarrow[\substack{Mg/\Delta \text{ or} \\ Zn/\Delta}]{Ag/\Delta \text{ or}} \underset{C=2n}{R{-}CH{=}CH{-}R}$$

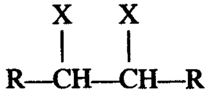
In this reaction number of carbons in product is double to the number of carbons in reactant.

(4) α-Elimination reaction : Terminal *gem* dihalide undergoes α-elimination reaction with strong base. This reaction gives monohalo carbene as reaction intermediate.

$$CH_2X_2 \xrightarrow{\text{alc. KOH}/\Delta} \overset{\bullet\bullet}{C}HX + \overset{\ominus}{X} + HOH$$

7.8.2 *Vicinal* dihalides

Vicinal dihalide contains two halogen atoms on adjacent, *i.e.*, *vicinal* positions.



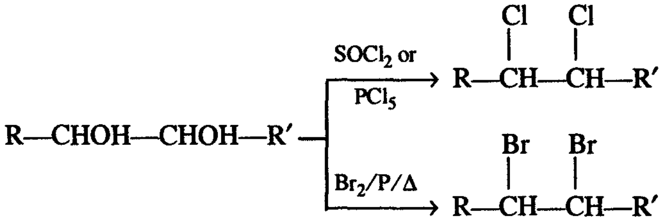
$$R{-}\overset{\overset{\displaystyle X}{|}}{C}H{-}\overset{\overset{\displaystyle X}{|}}{C}H{-}R$$

Preparation : *Vicinal* dihalides are prepared from alkenes and *vic* diols.

(1) **From alkenes :** Alkenes react with X_2 to give *vic* dihalides.

$$R{-}CH{=}CH{-}R' \xrightarrow{X_2/CCl_4} R{-}CHX{-}CHX{-}R'$$

(2) **From *vic* diols :** *Vic* diols can be converted into *vic* dichlorides by the use of PCl_5, PCl_3 or $SOCl_2$. *Vic* dibromides can be prepared by the use of PBr_3 or P/Br_2. *Vic* diodo compounds cannot prepared because they are unstable and convert into alkenes.

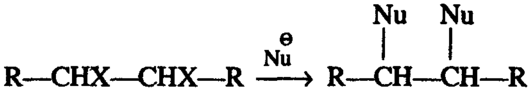


$$R{-}CHOH{-}CHOH{-}R' \xrightarrow[PCl_5]{SOCl_2 \text{ or}} R{-}\overset{\overset{\displaystyle Cl}{|}}{C}H{-}\overset{\overset{\displaystyle Cl}{|}}{C}H{-}R'$$

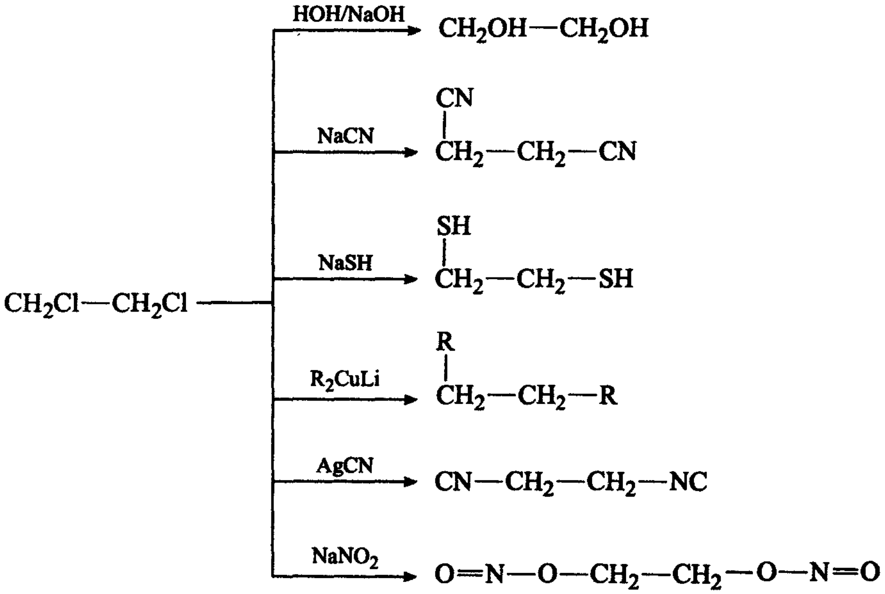
$$R{-}CHOH{-}CHOH{-}R' \xrightarrow{Br_2/P/\Delta} R{-}\overset{\overset{\displaystyle Br}{|}}{C}H{-}\overset{\overset{\displaystyle Br}{|}}{C}H{-}R'$$

Chemical reactions : Chemical reactions of *vic* dihalide are identical to the reactions given by monohalides.

Nucleophilic Substitution Reactions : Nucleophilic substitution reactions of *vicinal* dihalides are identical to mono halides :



$$R\text{—}CHX\text{—}CHX\text{—}R \xrightarrow{\overset{\ominus}{Nu}} R\text{—}\underset{}{\overset{Nu}{\overset{|}{C}H}}\text{—}\overset{Nu}{\overset{|}{C}H}\text{—}R$$

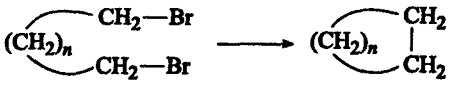


Dehalogenation Reaction : *Vic* dihalides undergo dehalogenation reaction with Zn, Ag or Mg.

$$R\text{—}CHX\text{—}CHX\text{—}R \xrightarrow{Zn/C_2H_5OH} R\text{—}CH\text{=}CH\text{—}R$$

7.8.3 α, ω-Dihalides

(i) One of the most important reactions of α, ω-dihalide is intramolecular dehalogenation in the presence of Na/dry ether or Zn/C_2H_5OH.



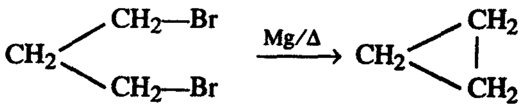
In this reaction $n = 1$ to 4

The reaction is known as **Freund's reaction.**

(ii) α, ω dihalides form Grignard reagents with magnesium in the presence of dry ether.

$$\underset{n = \geq 2}{Br\text{—}CH_2\text{—}(CH_2)_n\text{—}CH_2\text{—}Br} \xrightarrow[\text{dry ether}]{Mg} Br\text{—}Mg\text{—}CH_2\text{—}(CH_2)_n\text{—}CH_2\text{—}MgBr$$

1, 3-Dihalides give cyclopropane instead of Grignard reagent.

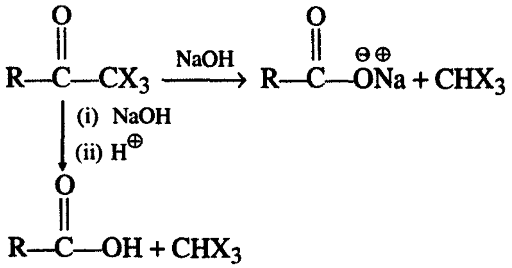


7.9 POLYHALOALKANES

7.9.1 Trihaloalkanes : Haloform : CHX_3

Preparation : (1) From α, α, α-trihalocarbonyl compounds :

α, α, α-Trihalocarbonyl compounds give nucleophilic substitution reaction with $\overset{\ominus}{O}H$ [NaOH, KOH, $Ca(OH)_2$, Na_2CO_3, K_2CO_3] to give haloform and salt of carboxylic acid.

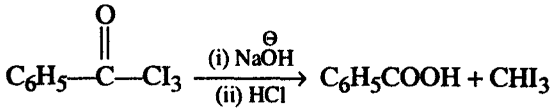


$$R-\overset{\overset{O}{\|}}{C}-CX_3 \xrightarrow{NaOH} R-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{O}\overset{\oplus}{Na} + CHX_3$$

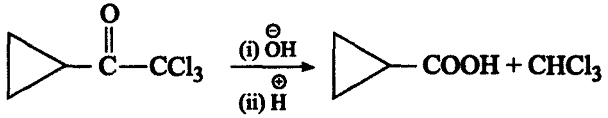
$$R-\overset{\overset{O}{\|}}{C}-CX_3 \xrightarrow[\text{(ii) } H^{\oplus}]{\text{(i) NaOH}} R-\overset{\overset{O}{\|}}{C}-OH + CHX_3$$

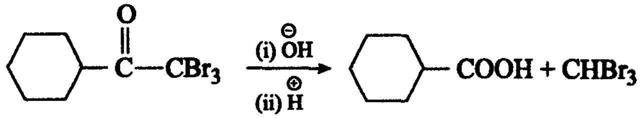
In this reaction CX_3 group present on carbonyl group converts into haloform.

Some examples are :

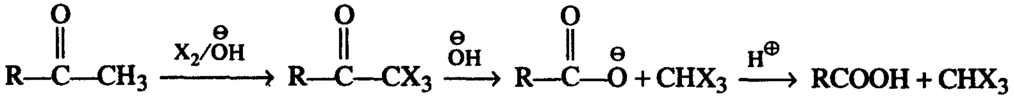


$$C_6H_5-\overset{\overset{O}{\|}}{C}-CI_3 \xrightarrow[\text{(ii) HCl}]{\text{(i) Na}\overset{\ominus}{O}H} C_6H_5COOH + CHI_3$$



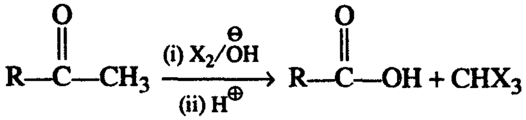


(2) From carbonyl compounds having at least one α—CH_3 group : Carbonyl compound having at least one α—CH_3 group reacts with $X_2/\overset{\ominus}{O}H$ or with hypohalites to give haloform and salt of carboxylic acid.



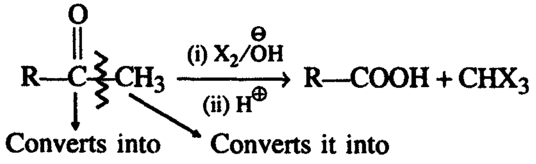
$$R-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{X_2/\overset{\ominus}{O}H} R-\overset{\overset{O}{\|}}{C}-CX_3 \xrightarrow{\overset{\ominus}{O}H} R-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{O} + CHX_3 \xrightarrow{H^{\oplus}} RCOOH + CHX_3$$

Thus overall reaction is written as follows :



$$R-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\text{(ii) } H^{\oplus}]{\text{(i) } X_2/\overset{\ominus}{O}H} R-\overset{\overset{O}{\|}}{C}-OH + CHX_3$$

Product of the reaction can be obtained as follows :

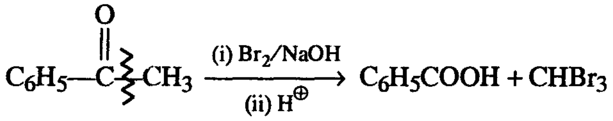


$$R-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\text{(ii) } H^{\oplus}]{\text{(i) } X_2/\overset{\ominus}{O}H} R-COOH + CHX_3$$

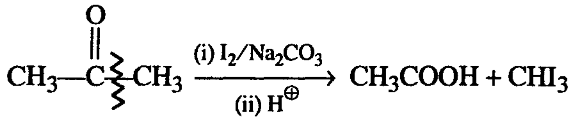
Converts into —COOH

Converts it into CHX_3

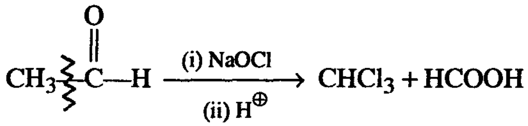
For examples :



$$C_6H_5-\overset{\overset{O}{\|}}{C}\wr CH_3 \xrightarrow[\text{(ii) }H^{\oplus}]{\text{(i) }Br_2/NaOH} C_6H_5COOH + CHBr_3$$

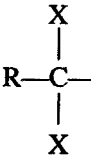


$$CH_3-\overset{\overset{O}{\|}}{C}\wr CH_3 \xrightarrow[\text{(ii) }H^{\oplus}]{\text{(i) }I_2/Na_2CO_3} CH_3COOH + CHI_3$$

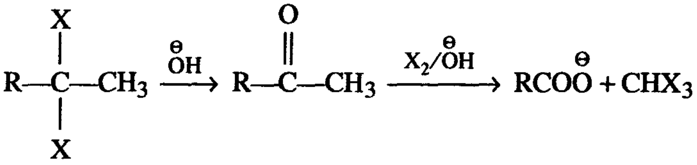


$$CH_3\wr\overset{\overset{O}{\|}}{C}-H \xrightarrow[\text{(ii) }H^{\oplus}]{\text{(i) NaOCl}} CHCl_3 + HCOOH$$

This reaction is known as **haloform reaction** and it is extension of the first reaction.



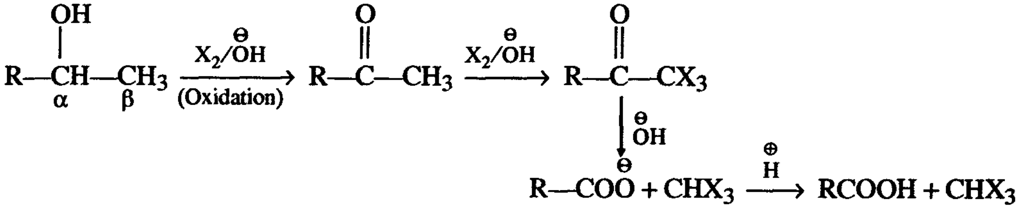
Note : *Gem* dihalides having structure, $R-\underset{X}{\underset{|}{\overset{X}{\overset{|}{C}}}}-CH_3$, also given haloform reaction. The reaction takes place as follows :



$$R-\underset{X}{\underset{|}{\overset{X}{\overset{|}{C}}}}-CH_3 \xrightarrow{\overset{\ominus}{O}H} R-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{X_2/\overset{\ominus}{O}H} RCO\overset{\ominus}{O} + CHX_3$$

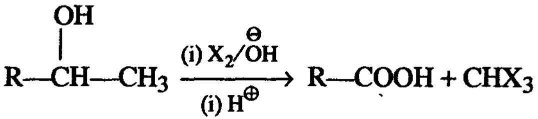
This reaction is extension of second reaction.

(3) From primary and secondary alcohols having at least one β—CH_3 group : Primary and secondary alcohols having at least one β—CH_3 group react with $X_2/\overset{\ominus}{O}H$ or with hypohalites to give haloform and salt of carboxylic acids.



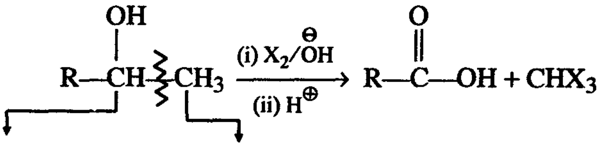
$$\begin{aligned}&\underset{\alpha}{R-\overset{\overset{OH}{|}}{CH}}-\underset{\beta}{CH_3} \xrightarrow[\text{(Oxidation)}]{X_2/\overset{\ominus}{O}H} R-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{X_2/\overset{\ominus}{O}H} R-\overset{\overset{O}{\|}}{C}-CX_3\\ &\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\Big\downarrow{\scriptstyle\overset{\ominus}{O}H}\\ &\qquad\qquad\qquad\qquad\qquad\qquad R-CO\overset{\ominus}{O} + CHX_3 \xrightarrow{\overset{\oplus}{H}} RCOOH + CHX_3\end{aligned}$$

Thus overall reaction can be written as :



$$R-\overset{\overset{OH}{|}}{CH}-CH_3 \xrightarrow[\text{(i) }H^{\oplus}]{\text{(i) }X_2/\overset{\ominus}{O}H} R-COOH + CHX_3$$

Product of the reaction can be obtained as follows :

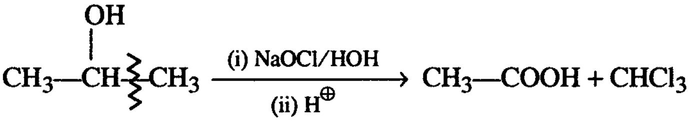


$$\underbrace{R-\overset{\overset{OH}{|}}{CH}}\wr\underbrace{CH_3} \xrightarrow[\text{(ii) }H^{\oplus}]{\text{(i) }X_2/\overset{\ominus}{O}H} R-\overset{\overset{O}{\|}}{C}-OH + CHX_3$$

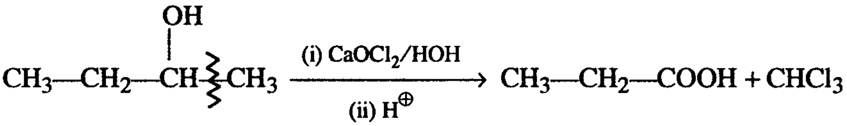
Converts this functional groups into —COOH

Converts this group into CHX_3

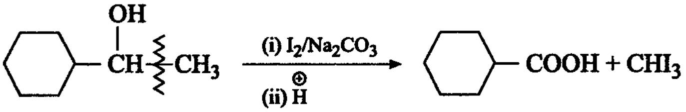
Some examples are :

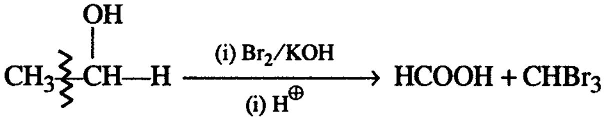


$$CH_3-\overset{OH}{\overset{|}{CH}}-CH_3 \xrightarrow[(ii)\ H^{\oplus}]{(i)\ NaOCl/HOH} CH_3-COOH + CHCl_3$$



$$CH_3-CH_2-\overset{OH}{\overset{|}{CH}}-CH_3 \xrightarrow[(ii)\ H^{\oplus}]{(i)\ CaOCl_2/HOH} CH_3-CH_2-COOH + CHCl_3$$

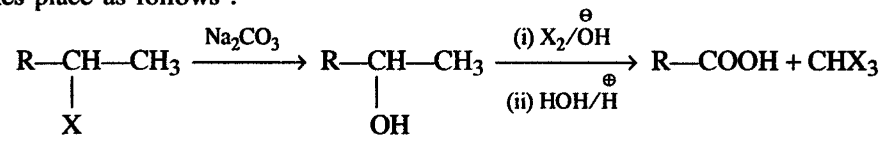




$$CH_3-\overset{OH}{\overset{|}{CH}}-H \xrightarrow[(i)\ H^{\oplus}]{(i)\ Br_2/KOH} HCOOH + CHBr_3$$

This reaction is also known as **Haloform reaction** and this reaction is extension of the second reaction.

Note : Compound having structure, $R-\underset{X}{\underset{|}{CH}}-CH_3$, also gives haloform with X_2/Na_2CO_3. The reaction takes place as follows :

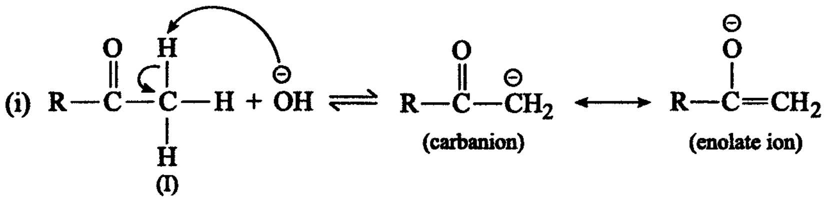


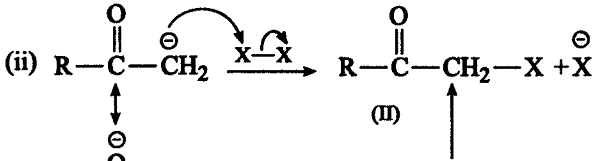
$$R-\underset{X}{\underset{|}{CH}}-CH_3 \xrightarrow{Na_2CO_3} R-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow[(ii)\ HOH/\overset{\oplus}{H}]{(i)\ X_2/\overset{\ominus}{OH}} R-COOH + CHX_3$$

This reaction is extension of third reaction.

Mechanism of Haloform Reaction :

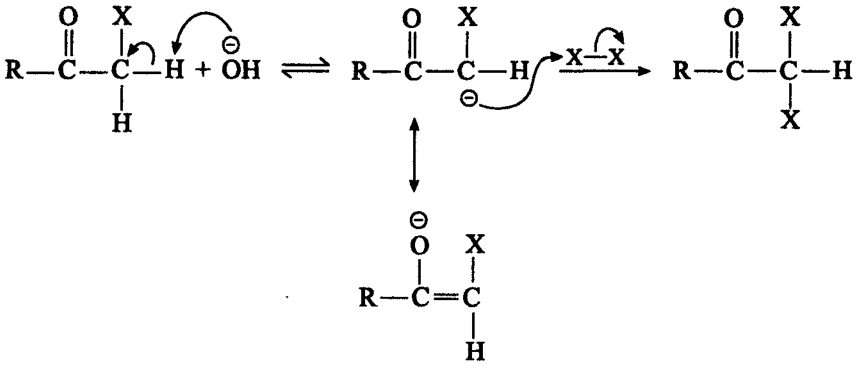
Step I. α-Hydrogen of carbonyl compound is acidic in character. Such compounds undergo α-halogenation with $X_2/\overset{\ominus}{O}H$ (*i.e.*, $X^{\oplus}$ in the presence of base). This halogenation reaction is an example of aliphatic electrophilic substitution reaction.



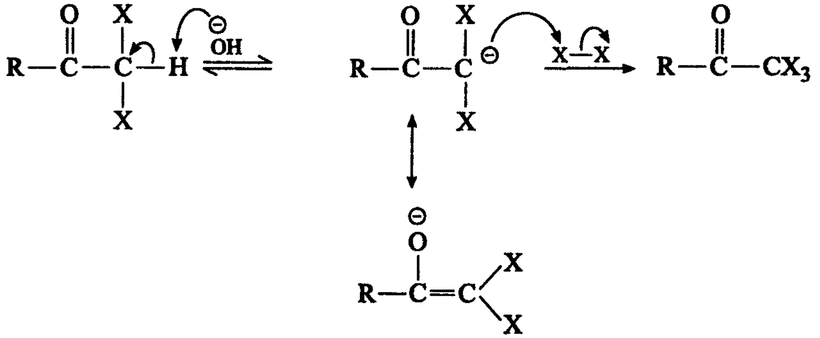


Acidity of α-hydrogen is more than the compound (I) due to the -*I* group (X)

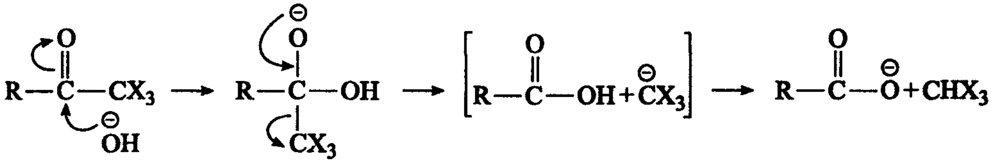
(iii)



(iv)



Step II. α, α, α-Trihalocarbonyl compound obtained in the first step gives addition followed by elimination with $\overset{\ominus}{O}H$.



Properties : Acidic character of haloform :

(i) α-Carbon of haloform is electron deficient due to the presence of three —I groups, therefore hydrogen present on α-carbon will be acidic in character and in fact haloform is acidic in character.

(ii) Acidity ∝ —I power of the group, *i.e.*,

$$\xrightarrow[\text{Acidity would be in decreasing order because —I power is in decreasing order. But that is not the case.}]{CHF_3 > CHCl_3 > CHBr_3 > CHI_3}$$

(iii) Acidity order is as follows :

$$\xrightarrow[\text{Acidity in decreasing order.}]{CHCl_3 > CHF_3 > CHBr_3 > CHI_3}$$

(a) Acidity of $CHBr_3$ and CHI_3 can be explained by —I power of Br and I.

(b) Acidity of CHF_3 and $CHCl_3$ can be explained as follows :

$$CHF_3 \longrightarrow \overset{\oplus}{H} + \underset{(I)}{\overset{\ominus}{C}F_3}$$

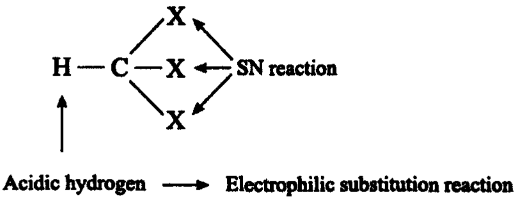
anion (I) is stabilised only by —I effect

$$CHCl_3 \longrightarrow \overset{\oplus}{H} + \underset{(II)}{\overset{\ominus}{C}Cl_3}$$

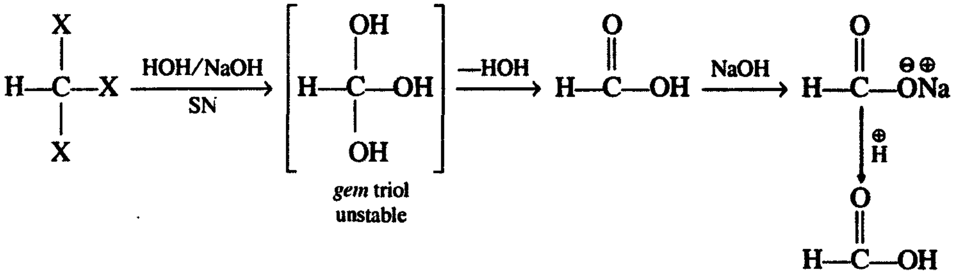
anion (II) is stabilised by (i) —I effect of Cl and

(ii) delocalisation of negative charge by vacant *d*-orbitals on Cl which are not present on F. Hence II is more stable than I. Thus chloroform is more acidic than fluoroform.

Chemical reactions :



(1) Hydrolysis : Chloroform on hydrolysis gives salt of formic acid which on acidification gives HCOOH.



Note : In this reaction —CX_3 group converts into —COOH group.

$$C_6H_5\text{—}\boxed{CCl_3} \xrightarrow[\text{(ii) } H^{\oplus}]{\text{(i) NaOH/HOH}} C_6H_5\text{—}\boxed{COOH}$$

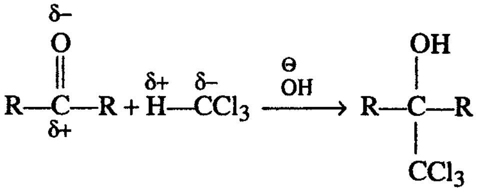
$$CH_3\text{—}\boxed{CCl_3} \xrightarrow[\text{(ii) } H^{\oplus}]{\text{(i) NaOH/HOH}} CH_3\text{—}\boxed{COOH}$$

(2) Nitration : It gives nitration with conc. HNO_3.

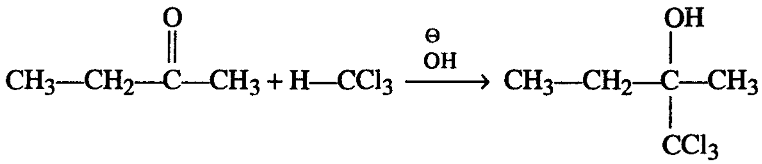
$$\overset{\delta+}{H}\text{—}\overset{\delta-}{CCl_3} + \text{Conc. } \underset{\overset{\Downarrow}{\overset{\oplus}{NO_2}}}{HO\text{—}NO_2} \xrightarrow{\Delta} NO_2\text{—}CCl_3 + HOH$$

Trichloronitromethane (Chloropicrin) used as insecticide and as tear gas (war gas)

(3) Addition reaction with ketones : It gives addition reaction with ketones in the presence of $\overset{\ominus}{OH}$ as catalyst.

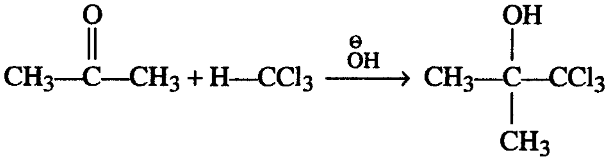


$$R\text{—}\underset{\delta+}{\overset{\overset{\delta-}{O}}{\overset{\|}{C}}}\text{—}R + \overset{\delta+}{H}\text{—}\overset{\delta-}{CCl_3} \xrightarrow{\overset{\ominus}{OH}} R\text{—}\underset{\underset{CCl_3}{|}}{\overset{\overset{OH}{|}}{C}}\text{—}R$$



$$CH_3{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 + H{-}CCl_3 \xrightarrow{\overset{\ominus}{OH}} CH_3{-}CH_2{-}\underset{\underset{\displaystyle CCl_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}{-}CH_3$$

One of the most important reactions of this category is reaction between acetone and chloroform.



$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 + H{-}CCl_3 \xrightarrow{\overset{\ominus}{OH}} CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}{-}CCl_3$$

1, 1, 1-Trichloro-2-methyl-
2-propanol, known
as chloretone, which
is used as hypnotic

(4) Free radical halogenation : It gives free radical halogenation due to the presence of hydrogen.

$$CHCl_3 + Cl_2 \xrightarrow{h\nu} CCl_4$$

Carbon tetrachloride

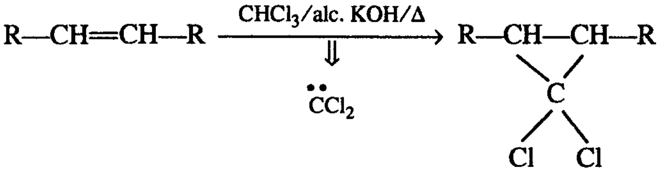
(5) α-Elimination reaction : Chloroform undergoes α-elimination reaction to give dichlorocarbene which is a reaction intermediate.

$$CHCl_3 \xrightarrow{\text{alc. KOH}/\Delta} \ddot{C}Cl_2 + \overset{\ominus}{Cl} + HOH$$

(a) Dichlorocarbene obtained in this reaction is always singlet.

(b) Dichlorocarbene as reaction intermediate gives following three reaction :

(i) Addition reaction with alkenes :



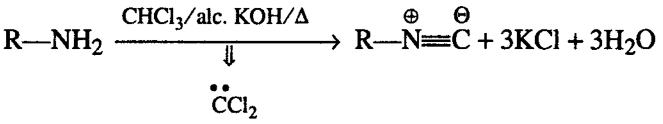
1, 1-Dichloro-2, 3-dialkylcyclopropane

(ii) Reaction with primary amines :

(Carbylamine reaction or Isocyanide reaction)

Alcoholic solution of primary amines (aliphatic as well as aromatic amines) react with chloroform in the presence of potassium hydroxide solution to yield isocyanide or carbylamine. This reaction is known as carbylamine reaction.

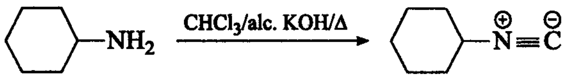
The formation of isocyanides is readily noted by their characteristic nauseating order. Due to this reason, this reaction has been used as a qualitative test for primary animes.



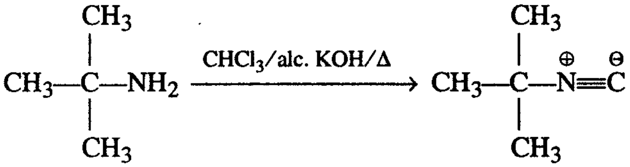
$$R{-}NH_2 \xrightarrow[\underset{\ddot{C}Cl_2}{\Downarrow}]{CHCl_3/\text{alc. KOH}/\Delta} R{-}\overset{\oplus}{N}{\equiv}\overset{\ominus}{C} + 3KCl + 3H_2O$$

Examples are :

$$CH_3{-}CH_2{-}NH_2 \xrightarrow{CHCl_3/\text{alc. KOH}/\Delta} CH_3{-}CH_2{-}\overset{\oplus}{N}{\equiv}\overset{\ominus}{C}$$



$$\mathrm{C_6H_5{-}NH_2} \xrightarrow{\mathrm{CHCl_3/alc.\ KOH/\Delta}} \mathrm{C_6H_5{-}\overset{\oplus}{N}{\equiv}\overset{\ominus}{C}}$$



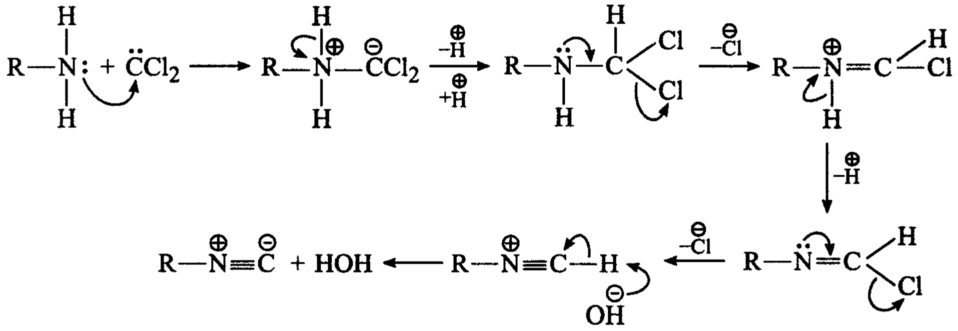
$$\mathrm{CH_3{-}C(CH_3)_2{-}NH_2} \xrightarrow{\mathrm{CHCl_3/alc.\ KOH/\Delta}} \mathrm{CH_3{-}C(CH_3)_2{-}\overset{\oplus}{N}{\equiv}\overset{\ominus}{C}}$$

Mechanism :

Step I. $$\mathrm{CHCl_3} \xrightarrow[\alpha\text{-elimination}]{\overset{\ominus}{O}H/\Delta} \mathrm{\ddot{C}Cl_2}$$

Dichlorocarbene

Step-II.



Note :

(a) In this reaction —NH_2 group converts into isocyanide (—NC) group.

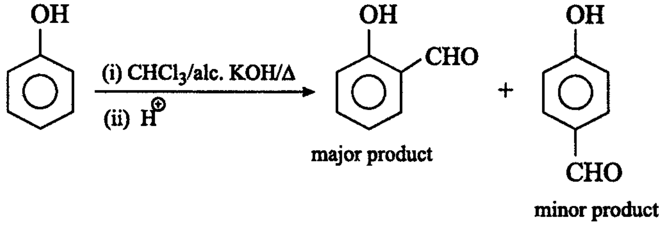
(b) Isocyanide on hydrolysis again converts into primary amine

$$\mathrm{R{-}\overset{\oplus}{N}{\equiv}\overset{\ominus}{C}} \xrightarrow{\mathrm{H_2O/\overset{\ominus}{O}H/\Delta}} \mathrm{R{-}NH_2 + HCOOH}$$

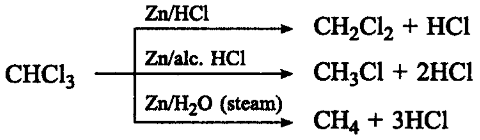
(iii) Reimer-Tiemann reaction : Dichlorocarbene is neutral electrophile. It gives electrophilic substitution reaction with phenol.

The product of the reaction is *o*- and *p*-hydroxybenzaldehyde.

The overall reactions is as follows :



(6) Reduction reaction : In this reaction nature of product depends on nature of reducing agents :

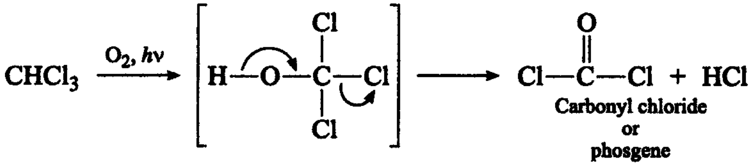


$$\mathrm{CHCl_3} \xrightarrow{\mathrm{Zn/HCl}} \mathrm{CH_2Cl_2 + HCl}$$

$$\mathrm{CHCl_3} \xrightarrow{\mathrm{Zn/alc.\ HCl}} \mathrm{CH_3Cl + 2HCl}$$

$$\mathrm{CHCl_3} \xrightarrow{\mathrm{Zn/H_2O\ (steam)}} \mathrm{CH_4 + 3HCl}$$

(7) Oxidation : On exposure to air and sunlight, chloroform undergoes slow oxidation to form highly poisonous phosgene gas.

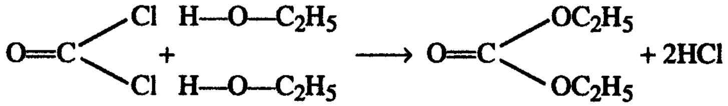


So to keep chloroform pure, to be used as an anaesthetic and base in cough syrup :

(i) It is stored in brown bottles to cut off light.

(ii) The bottles are filled up to the brim to exclude any air (*i.e.*, O_2)

(iii) 0.6 to 1% ethyl alcohol is added. Ethanol acts as negative catalyst for oxidation of chloroform. It converts harmful phosgene (if formed) to harmless diethyl carbonate.

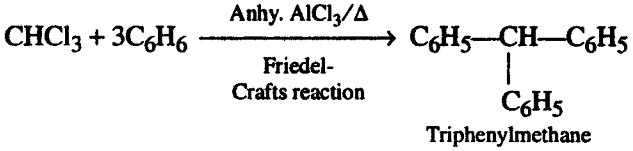


Note : Oxidation of chloroform is tested by the formation of HCl which is the by product of oxidation. The reagent is $AgNO_3$ which gives white precipitate with HCl.

(8) Dehalogenation *via* coupling reaction : Chloroform gives dehalogenation with silver powder / Δ.

$$CHCl_3 + CHCl_3 \xrightarrow{Ag/\Delta} CH{\equiv}CH + 6AgCl$$

(9) Reaction with benzene (Friedel-Crafts reaction) :



$$CHCl_3 + 3C_6H_6 \xrightarrow[\text{Friedel-Crafts reaction}]{\text{Anhy. }AlCl_3/\Delta} \underset{\text{Triphenylmethane}}{C_6H_5-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-C_6H_5}$$

Uses :

(i) As organic solvent.

(ii) As preservative for anatomical specimens.

(iii) In the preparation of chloretone and chloropicrin.

(iv) As a general anaesthetic with ether.

(v) In medicines as base.

7.9.2 Tetrahaloalkanes : Carbon tetrachloride

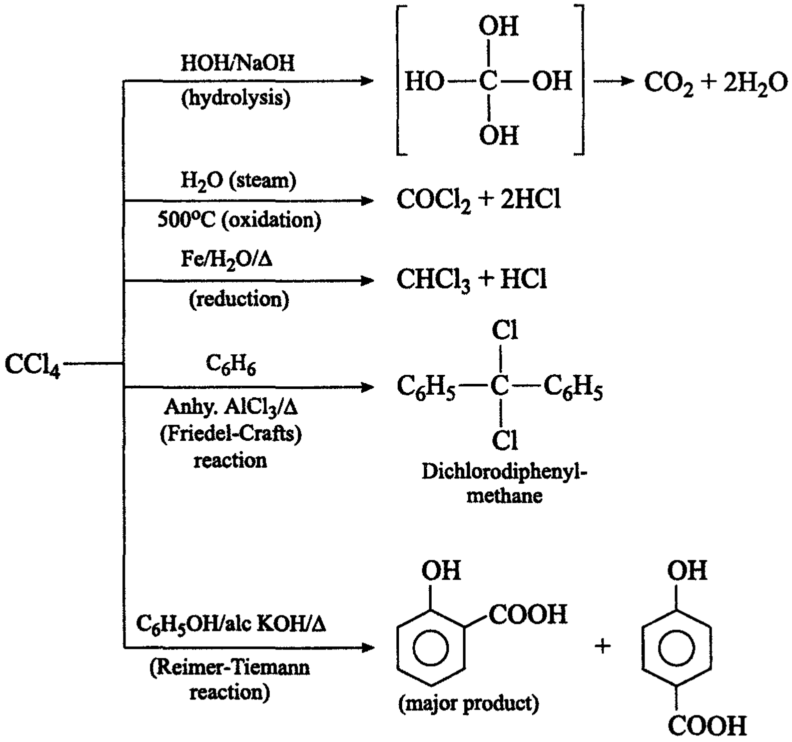
Preparation : Carbon tetrachloride can be prepared as follows :

(i) $$CH_4 \xrightarrow{Cl_2/h\nu} CCl_4 + 4HCl$$

(ii) $$CS_2 \xrightarrow[\Delta]{Cl_2/\text{Anhy. }AlCl_3} CCl_4 + S$$

(iii) $$CHCl_3 \xrightarrow{Cl_2/h\nu} CCl_4 + HCl$$

Properties : Its main properties are as follows :



Note : CCl_4 is stable to red heat, its vapour are highly non-inflammable. Its density is more than water and it is insoluble in water. It is because of these properties that CCl_4 is used as fire extinguisher under the name **pyrene**. However, now a days its use as fire extinguisher is banned because it forms $COCl_2$ with steam. It is used as antihelmentic (antihevle worm) agent.

7.9.3 Chlorofluorocarbons : Freons (CFC's)

Freons are small organic molecules containing carbon, chlorine and fluorine. The most common freons are Freon-11 (CF_3Cl) and Freon-12 (CF_2Cl_2). These two compounds are prepared from CCl_4

$$\underset{\text{(excess)}}{CCl_4 + HF} \xrightarrow{SbF_5} \underset{\text{Freon-11, bp 24°C}}{CFCl_3 + HCl}$$

$$CCl_4 + 2HF \xrightarrow{SbF_5} \underset{\substack{\text{Freon-12} \\ \text{bp −30°C}}}{CCl_2F_2 + 2HCl}$$

Freons are nontoxic, non-inflammable, noncorrosive to the human beings by inhaling them. They are extermely unreactive.

Because of these and other properties at least four major commerial uses of CFC's were developed. Their low boiling points and other heat properties make them excellent refrigerants, far superior to SO_2 and NH_3. Thus CFC's became widely used in freezers and refrigerators as well as in air conditioners. CFC's make excellent blowing agents for rigid foams and for flexible foams. Their low surface tension and low viscosity give them excellent wetting properties which led to thier use as cleaning fluids for printed computer circuits and artificial limbs. They are used as propellants in aerosol spray.

Their stability led to major world problem. CFC's are so stable that when they are released into atmosphere they do not decompose (non-biodegradable) in the lower atmosphere. Instead they eventually rise to the upper atmosphere where they can destroy ozone by free radical mechanism.

$$CF_2Cl_2 \xrightarrow{h\nu} \dot{C}F_2Cl + \dot{C}l\text{; chain initiations}$$

$$\text{or}$$

$$\ddot{C}F_2 + 2\dot{C}l$$

$$\left.\begin{aligned}&\text{(i) } \dot{C}l + O_3 \longrightarrow ClO + O_2\\ &\text{(ii) } ClO + O \longrightarrow \dot{C}l + O_2\end{aligned}\right\}\text{Propagation}$$

Thus chlorine atom obtained from CFC's under UV light damages the ozone layer, needed to protect life on earth from harmful UV rays.

7.10 UNSATURATED HALIDES

7.10.1 Vinyl Halides (Haloethenes)

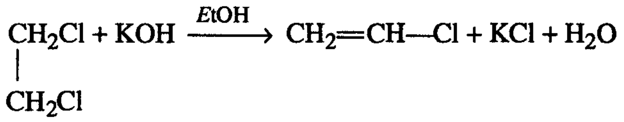
$CH_2{=}CH{-}X$.

Vinyl chloride is the most important of the unsaturated halides. This can be synthesised by a number of methods indicated below :

(i) From acetylene : It is prepared by passing a mixture of $CH{\equiv}CH$ and hydrogen chloride over $HgCl_2$ or $CuCl_2$.

$$CH{\equiv}CH + HCl \xrightarrow{HgCl_2} CH_2{=}CH{-}Cl$$

(ii) From ethylene chloride : On dehydrohalogenation ethylene chloride gives vinyl chloride.



$$\begin{array}{l}CH_2Cl + KOH \xrightarrow{EtOH} CH_2{=}CH{-}Cl + KCl + H_2O\\ |\\ CH_2Cl\end{array}$$

(iii) From ethylene : Ethylene undergoes free radical substitution with chlorine in the presence of sunlight.

$$CH_2{=}CH_2 + Cl_2 \xrightarrow{h\nu} CH_2{=}CHCl + HCl$$

Properties : Vinyl chloride contains two functional groups, double bond and chlorine atom. It shows the usual reactions of the olefinic bond which proceeds in accordance with **Markovnikov rule.**

The halogen atom in vinyl chloride is relatively inert and it does not undergo usual substitution reactions of alkyl halides. For example, it is not hydrolysed by NaOH.

$$CH_2{=}CH{-}Cl + NaOH \longrightarrow CH_2{=}CH{-}OH$$

This unusual behaviour of halogen atom (inert nature) can be explained on the basis of the structure of vinyl chloride.

$$\overset{1}{C}H_2{=}\overset{2}{C}H{-}Cl$$

The carbon atoms 1 and 2 are in sp^2 hybridised state and the double bond is formed by the sideways overlap of unhybridised orbitals. The carbon-chlorine bond is σ bond formed by the overlap of sp^2 hybrid orbital of carbon-2 and p-orbital of chlorine.

However, the chlorine atom has lone pair of electrons in p orbitals which are at right angles to the σ bond and one of the p orbitals of chlorine having a pair of electron is parallel to the p orbitals of carbon atoms. This orbital of chlorine can overlap sideways with the *p* orbital of a carbon—2 as shown in Fig. 7.3a.

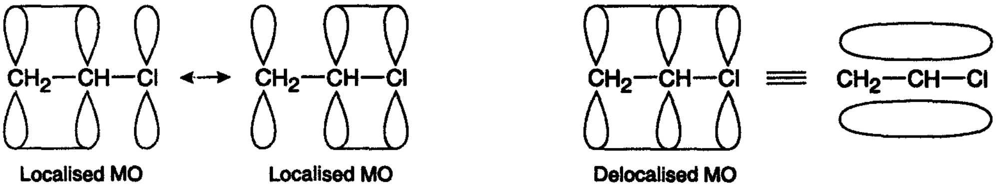


Fig. 7.3(a).

In valence bond structure this can be represented as shown in Fig. 7.3b.

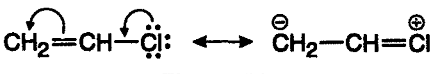


Fig. 7.3(b).

Thus the C—Cl bond in vinyl chloride has a partial double bond character. As a result, the chlorine atom becomes firmly bound to carbon and cannot be replaced easily as in the case of alkyl halides.

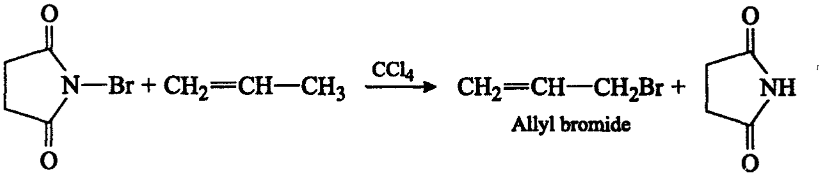
7.10.2 Allyl Halides

$$CH_2{=}CH{-}CH_2X$$

When propene is treated with chlorine at 500°C formation of 3-chloro-1-propene (allyl chloride) takes place and the reaction is known as allylic halogenation.

$$CH_2{=}CH{-}CH_3 + Cl_2 \xrightarrow[500°C]{\Delta} \underset{\text{Allyl chloride}}{CH_2{=}CH{-}CH_2Cl}$$

Propene when treated with NBS (*N*-bromosuccinimide) formation of allyl bromide takes place. NBS introduces bromine at the allylic position but not at other positions. This reaction is known as allylic bromination and is catalysed by light or by some source of free radicals.



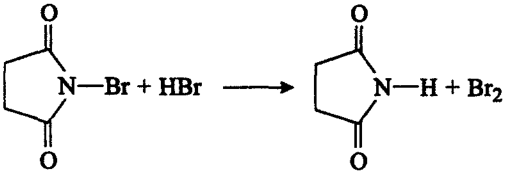
NBS

The selective action of NBS depends partly on its ability to provide a low, but constant concentration of Br_2, which is the halogenating agent. The Br_2 is generated by the reaction of HBr (a product of the halogenation) and NBS. Therefore, as Br_2 is consumed, more is formed.

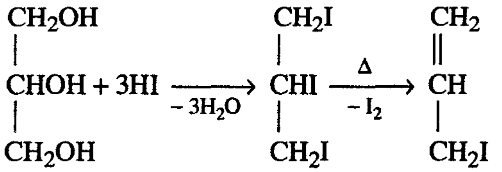
Br_2 consumed :

$$CH_2{=}CH{-}CH_3 + Br_2 \longrightarrow CH_2{=}CH{-}CH_2Br + HBr$$

Br_2 generated :



Allyl iodide is obtained by heating glycerol with hydroiodic acid.

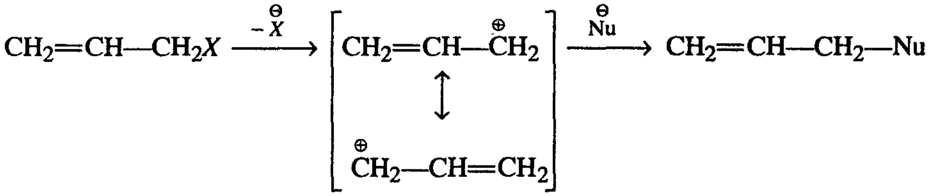


$$\begin{array}{c}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array} + 3HI \xrightarrow[-3H_2O]{} \begin{array}{c}CH_2I\\|\\CHI\\|\\CH_2I\end{array} \xrightarrow[-I_2]{\Delta} \begin{array}{c}CH_2\\\|\\CH\\|\\CH_2I\end{array}$$

Allyl iodide

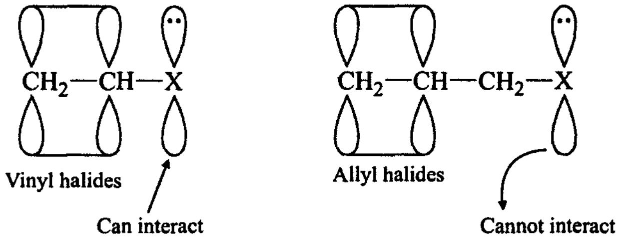
Allyl halides contain a double bond and a halogen atom. It shows the usual addition reactions of the double bond and nucleophilic substitution reaction with nucleophiles.

In allyl halide the *p* orbital of the halogen atom is separated from the π MO of the double bond by a sp^3 hybrid carbon atom. As a result the halogen atom of allyl halides can easily be replaced by a nucleophile.



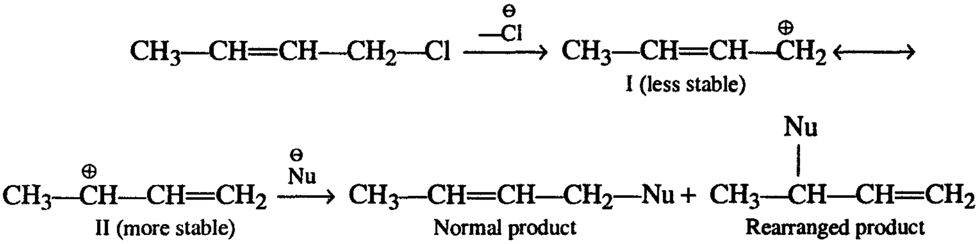
$$CH_2{=}CH{-}CH_2X \xrightarrow{-\overset{\ominus}{X}} \left[\begin{array}{c} CH_2{=}CH{-}\overset{\oplus}{C}H_2 \\ \updownarrow \\ \overset{\oplus}{C}H_2{-}CH{=}CH_2\end{array}\right] \xrightarrow{\overset{\ominus}{Nu}} CH_2{=}CH{-}CH_2{-}Nu$$

Thus in contrast to vinyl halides, allyl halides are very reactive.



Allyl halides give SN1 as well as SN2 reactions.

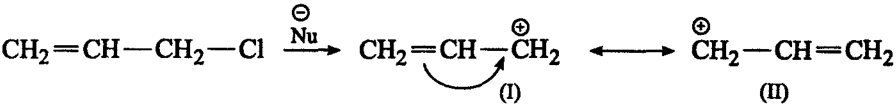
SN1 mechanism



$$CH_3{-}CH{=}CH{-}CH_2{-}Cl \xrightarrow{-\overset{\ominus}{Cl}} \underset{\text{I (less stable)}}{CH_3{-}CH{=}CH{-}\overset{\oplus}{C}H_2} \longleftrightarrow$$

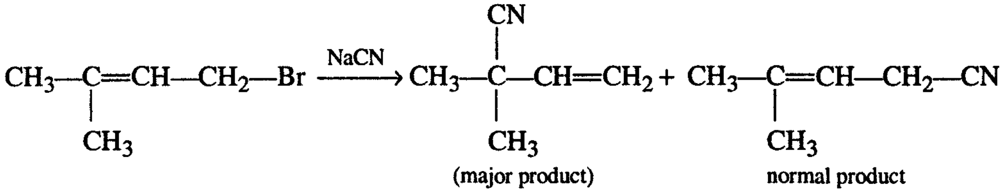
$$\underset{\text{II (more stable)}}{CH_3{-}\overset{\oplus}{C}H{-}CH{=}CH_2} \xrightarrow{\overset{\ominus}{Nu}} \underset{\text{Normal product}}{CH_3{-}CH{=}CH{-}CH_2{-}Nu} + \underset{\text{Rearranged product}}{CH_3{-}\overset{\overset{\displaystyle Nu}{|}}{C}H{-}CH{=}CH_2}$$

Note : Except 3-halopropene all other allyl halides give mixture of two products, normal and rearranged. Rearranged product is the major product. Such SN1 mechanism giving rearranged product is known as SN1′ mechanism.



$$CH_2{=}CH{-}CH_2{-}Cl \xrightarrow{\overset{\ominus}{Nu}} \underset{\text{(I)}}{CH_2{=}CH{-}\overset{\oplus}{C}H_2} \longleftrightarrow \underset{\text{(II)}}{\overset{\oplus}{C}H_2{-}CH{=}CH_2}$$

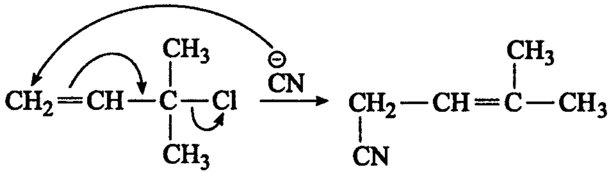
(I) and (II) are same hence it will give only one product.



$$CH_3-\underset{CH_3}{C}=CH-CH_2-Br \xrightarrow{NaCN} CH_3-\underset{CH_3}{\overset{CN}{C}}-CH=CH_2 + CH_3-\underset{CH_3}{C}=CH-CH_2-CN$$

(major product) normal product

SN2 mechanism : It is given in Section 7.6.4. If α-carbon is sterically hindered then it always gives SN2 reaction with rearrangement. In this case the SN2 mechanism is known as SN2′ mechanism.



$$CH_2=CH-\underset{CH_3}{\overset{CH_3}{C}}-Cl \xrightarrow{\overset{\ominus}{CN}} \underset{CN}{CH_2}-CH=\overset{CH_3}{C}-CH_3$$

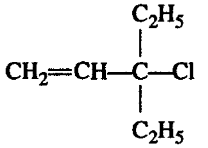
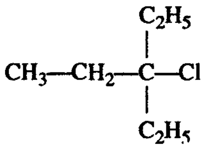
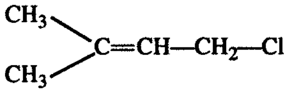
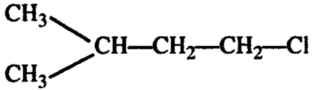
Note : Allyl halides and benzyl halides undergo SN1 and SN2 reactions because their transition state as well as carbocations are stable. SN2 reactions take place in the presence of polar aprotic solvents with concentrated strong nucleophiles. SN1 reactions take place in the presence of polar protic solvents with all types of nucleophiles.

Relative Reactivity of Alkyl Halides *vs* Allyl Halides

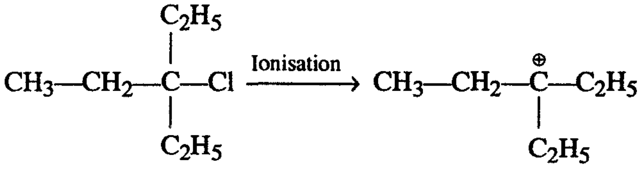
(1) SN1 Reactions : Allylic halides are more reactive in SN1 reactions than their comparably substituted alkyl halides. Some representative cases are shown in the Table 7.2. The tertiary allylic halide is more than 1000 times as reactive as the tertiary alkyl halide.

Table 7.2 ***Comparison of SN1 solvolysis rates of allylic and alkyl halides***

$R-Cl + C_2H_5OH + HOH \longrightarrow ROC_2H_5 + R-OH + HCl$

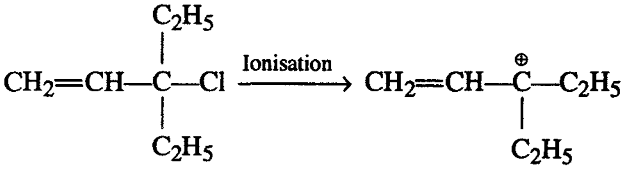
R—Cl	Relative rate
 $CH_2=CH-\underset{C_2H_5}{\overset{C_2H_5}{C}}-Cl$	162
 $CH_3-CH_2-\underset{C_2H_5}{\overset{C_2H_5}{C}}-Cl$	1.00
 $(CH_3)_2C=CH-CH_2-Cl$	38
 $(CH_3)_2CH-CH_2-CH_2-Cl$	0.00002

The greater reactivity of allylic halides is due to resonance stabilisation of the allylic carbocation intermediates that are formed when they react. As we know that more will be stability of reaction intermediate, more is the reactivity of the substrate. For example :



$$CH_3-CH_2-\underset{C_2H_5}{\overset{C_2H_5}{C}}-Cl \xrightarrow{\text{Ionisation}} CH_3-CH_2-\underset{C_2H_5}{\overset{\oplus}{C}}-C_2H_5$$

(A)
Stabilised by inductive and hyperconjugative effects, *i.e.*, by secondary effect.



$$CH_2{=}CH-\underset{C_2H_5}{\overset{C_2H_5}{C}}-Cl \xrightarrow{\text{Ionisation}} CH_2{=}CH-\underset{C_2H_5}{\overset{\oplus}{C}}-C_2H_5$$

(B)
Stabilised by hypercongugative and inductive effects as well as resonance. Hence (B) is more stable than (A).

Thus delocalised allylic carbocations are more stable than similar but localised alkyl cations. This extra stability promotes allylic SN1 reactions.

(2) SN2 Reaction : Allyl halides are also more reactive than the corresponding alkyl halides for SN2 reactions. As an example, allyl bromide reacts with nucleophile by the SN2 mechanism about 40 times faster than *n*-propyl bromide.

This rate enhancement can be explained by allylic delocalisation of electrons in the transition state. The transition state for the SN2 reaction looks like a trigonal carbon atom with a *p*-orbital perpendicular to the three substituents. The electrons of the attacking nucleophile are forming a bond using one lobe of the *p* orbital, and the leaving group's electrons are leaving the other lobe. The incoming nucleophile and the departing leaving group are partially bonded to a 2*p* orbital on the carbon at which substitution occurs.

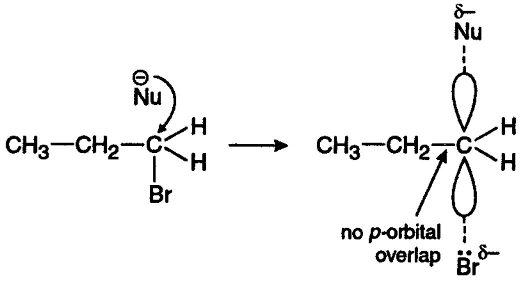


Fig. 7.4. Transition state of *n*-propyl bromide.

When the substrate is allylic, the transition state receives resonance stabilisation through conjugation with the *p* orbitals of the *pi* bond (Fig. 7.5). The electronic structure of this transition state resembles the structure of the allyl carbanion.

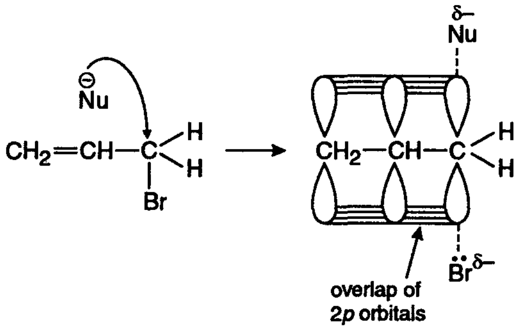


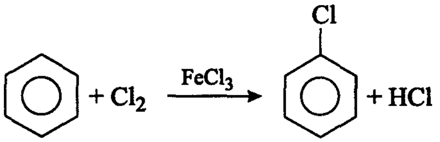
Fig. 7.5. In the transition state for the SN2 reaction of allyl bromide with a nucleophile, the double bond is conjugated with the *p*-orbital that is present on the reacting carbon. The resulting overlap lowers the energy of the transition state and thus increasing the reaction rate.

7.11 ARYL HALIDES

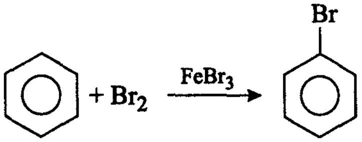
7.11.1 Methods of Preparations

Aryl halides can be synthesised by the following methods :

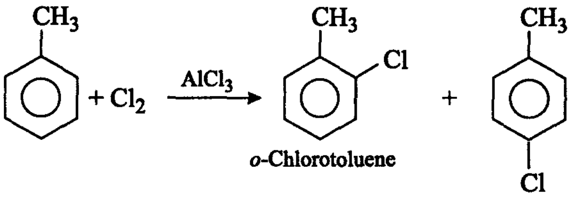
(i) Direct halogenation : Aryl chlorides and bromides are prepared from arenes by electrophilic substitution reaction.



Chlorobenzene



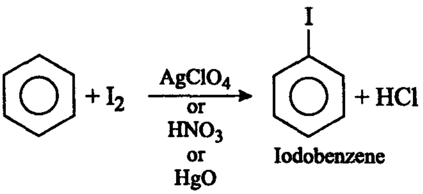
Bromobenzene



o-Chlorotoluene

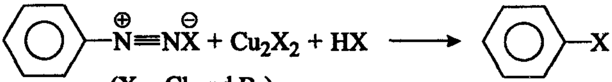
p-Chlorotoluene

Iodine, however, does not react with arenes under above conditions, as HI being a powerful reducing agent, reduces iodoarenes formed, back to arenes. But in the presence of oxidising agent the reaction takes place to give iododerivatives.



Iodobenzene

(ii) From diazonium salts : Aryl halides can be prepared most satisfactorily by the decomposition of aryl diazonium salts.



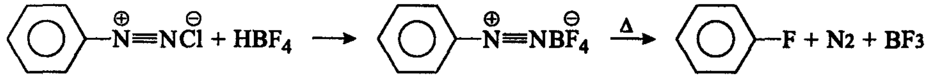
(X = Cl and Br)

This reaction is known as Sandmeyer reaction

Iodocompounds are, however, obtained by the action of KI on diazonium salts.

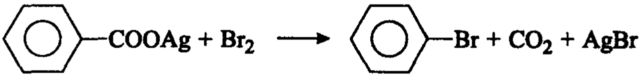
Iodobenzene

Fluorocompounds can be prepared by adding fluoroboric acid in diazonium salt, and decomposing the arenediazonium fluoroborate. This reaction is known as *Shiemann* or *Balz-Shiemann reaction*. This is by far the best method of introducing fluorine into an aromatic ring.



Fluorobenzene

(iii) From silver salt of carboxylic acids : Aryl bromides are obtained by heating the silver salts of aromatic acids with Bromine.



The reaction is known as **Hunsdiecker or Borodine-Hunsdicker reaction.**

7.11.2 Physical Properties of Aryl Halides

Aryl halides are generally colourless liquids or crystalline solids with characteristic odour. They are insoluble in water. This may be attributed to their being incapable of forming hydrogen bonds. Their m.p. and b.p. decrease in the following order :

Ph—I > Ph—Br > Ph—Cl > Ph—F

7.11.3 Chemical Reactions of Aryl Halides

The molecule of aryl halide consists of :

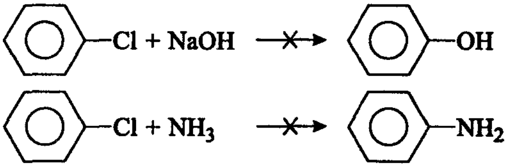
(i) an aromatic nucleus, and

(ii) a halogen atom bonded to the ring

The reactions of aryl halides are, therefore, due to the aromatic ring (electrophilic substitution reactions) and the halogen atom (nucleophilic substitution reaction).

I. Nucleophilic Substitution Reactions

Unlike alkyl halides, aryl halides do not undergo nucleophilic substitution reactions under ordinary conditions.



The reason for this unusual lack of reactivity is that the halogen atom in aryl halides is very firmly held by the benzene nucleus and cannot be easily replaced by nucleophiles.

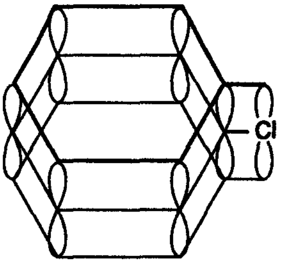


Fig. 7.6(a).

In aryl halides the carbon chlorine bond is σ bond. However, one of the *p* orbitals of chlorine having a pair of electrons is parallel to the delocalised *p* orbitals of the benzene nucleus. This *p*-orbital of chlorine can also overlap with the delocalised *p*-orbitals of benzene nucleus as shown in (Fig. 7.6a).

In valence bond structure this can be represented as below (Fig. 7.6b).

Like vinyl halides, the delocalised π MO gives partial double bond character to C—Cl bond in aryl halides. As a result the halogen atom becomes firmly bound to benzene nucleus and cannot be replaced easily as in the case of alkyl halides.

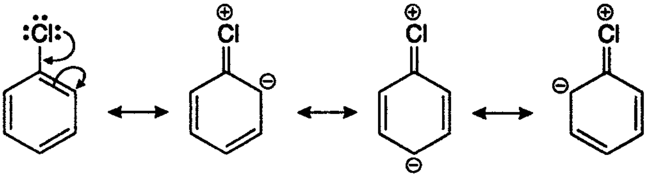
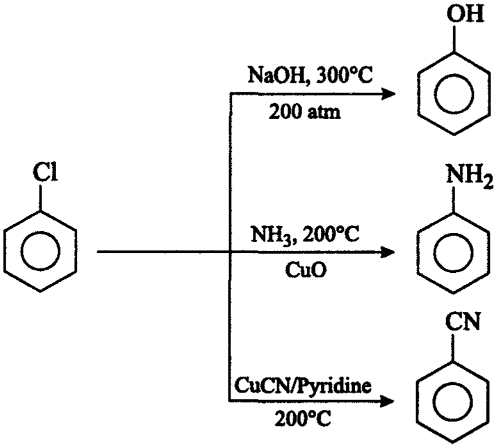


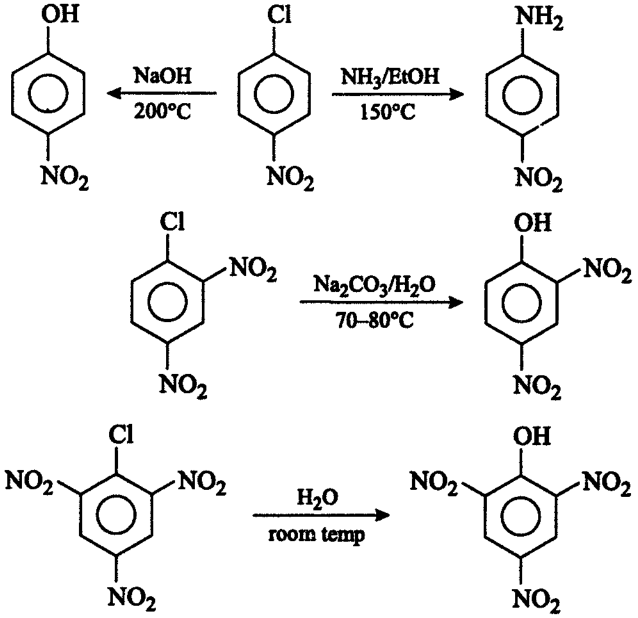
Fig. 7.6(b).

Another reasons for the low activity of aryl halides towards nucleophilic substitution reaction is the presence of six electrons in the delocalised π electron cloud in aromatic ring. This discourages the nucleophile from attacking the ring carbon bearing halogen.

But under drastic conditions, halogen atom can be replaced by a suitable nucleophile.



On the other hand, when a powerful electron-withdrawing group (*m*-director) is present at *ortho* and/or *para* to the halogen atom, replacement of *X* by nucleophilic reagents is facilitated. Thus *m*-directors activate nucleophilic substitution reaction. Some examples are :



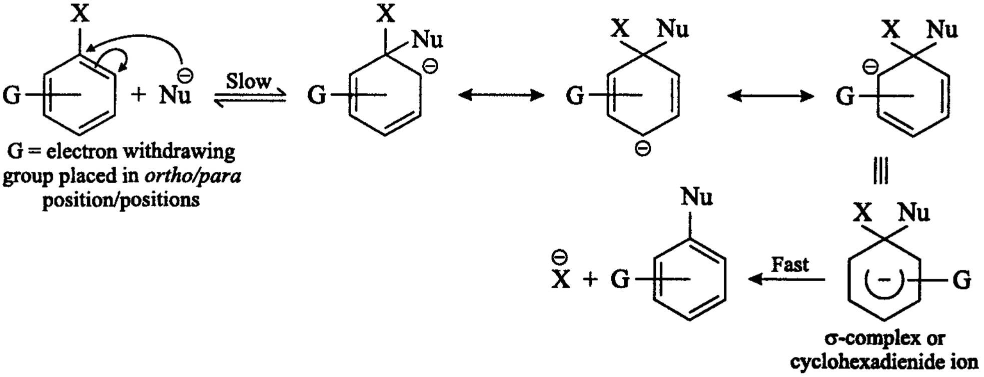
II. Mechanism of Nucleophilic Aromatic Substitutions

Nucleophilic substitutions involving replacement of $\overset{\ominus}{H}$ by a nucleophile in aromatic hydrocarbons do not occur because $\overset{\ominus}{H}$ is one of the strongest nucleophiles. However, if there is suitable leaving group on the ring (halogen atoms or other groups) nucleophilic substitution may take place by one of the following mechanisms :

(1) Bimolecular mechanism or Addition-elemination mechanism : If the benzene ring bears strongly electron withdrawing substituents as well as a good leaving group, nucleophilic substitution reactions take place under mild conditions. Kinetic studies have revealed that the reaction rate depends on the concentration of aromatic substrate and the nucleophile. Thus both the reactants being involved in the rate-determining step.

Rate = K [Aromatic Substrate] × [Nucleophile]

Available evidence suggests that the reaction takes place by addition-elemination process involving attack by nucleophile in the first step, which in many cases is the rate-determining step.



The energy profile diagram is similar to aromatic electrophilic substitution reactions (Fig. 7.7).

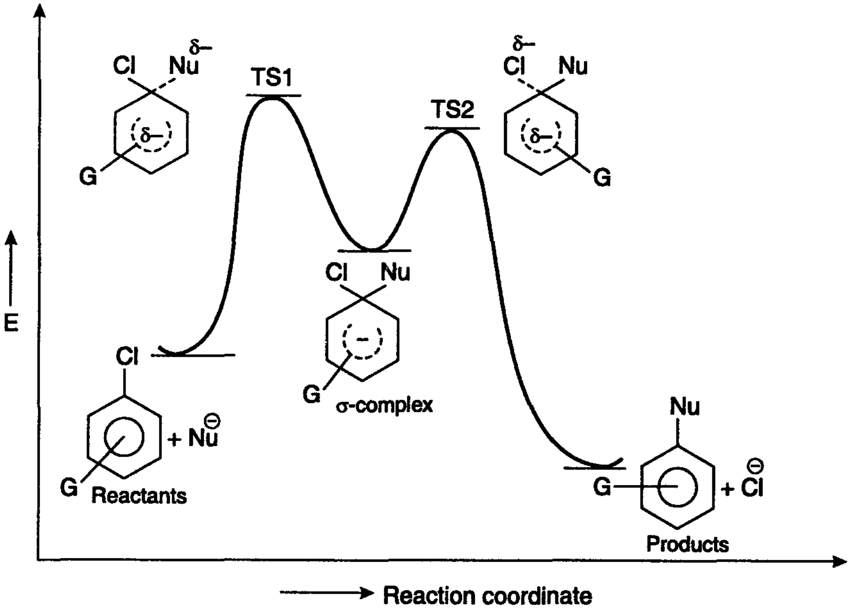
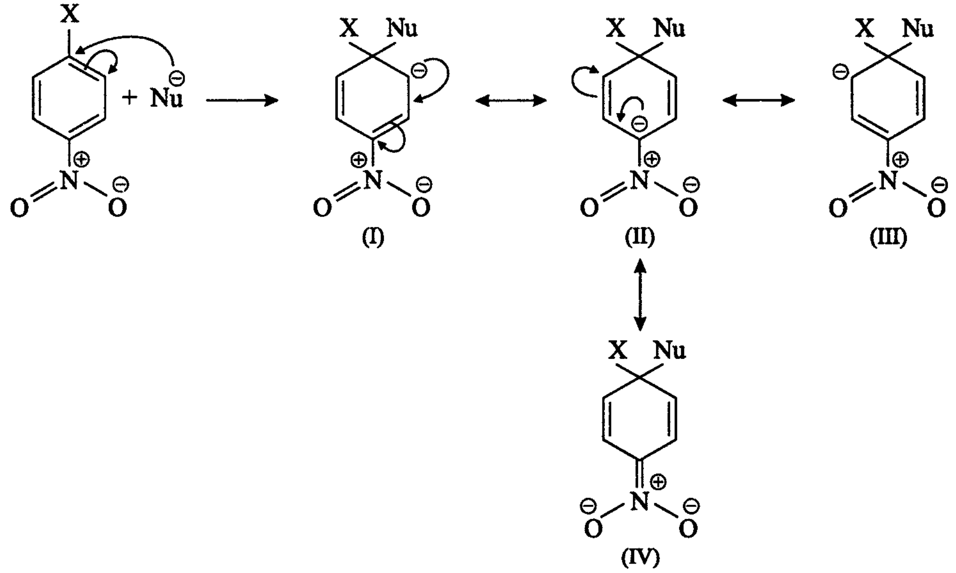


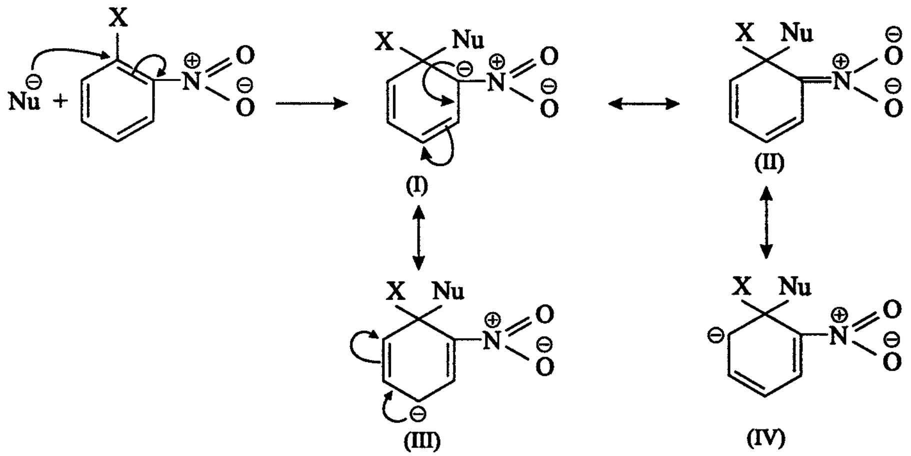
Fig. 7.7. Energy profile diagram of aromatic nucleophilic substitution reaction.

The formation of σ-complex is not possible unless some group capable of accommodating the negative charge is present in the *o*- or *p*-position. Such group stabilises the intermediate carbanion.

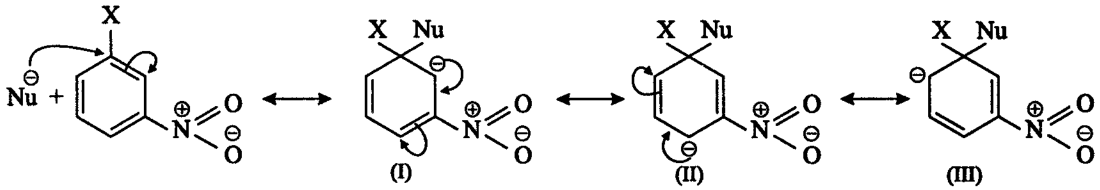
Para



ortho

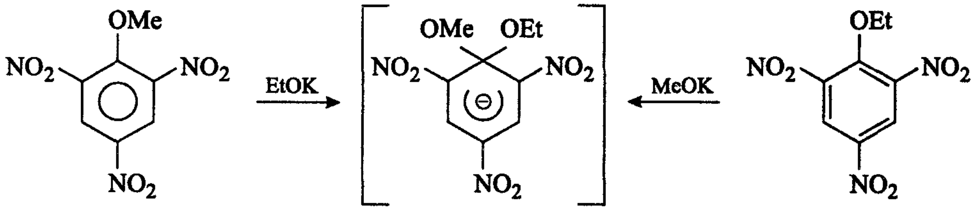


meta



Since the delocalisation of the negative charge via structures (II) to (IV) in the case of *ortho* and *para* derivatives is not possible with *meta* derivatives, they do not undergo such a reactions.

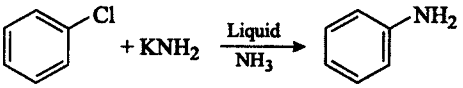
The above mechanism is supported by the fact that Meisenheimer isolated the intermediate σ-complex in the form of a salt in the following reaction :



Meisenheimer complex
or
σ-complex

II. Benzyne (aryne) Mechanism or Elimination-addition Mechanism

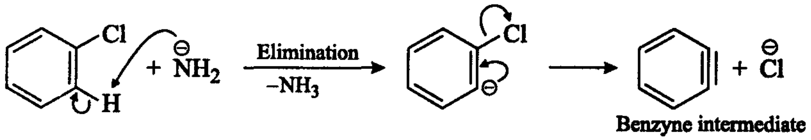
Electron withdrawing groups in *ortho* and *para* positions to the leaving group (*X*) facilitate aromatic nucleophilic substitution reaction. In the absence of such group/groups, substitution can be made to take place by use of very strong base.



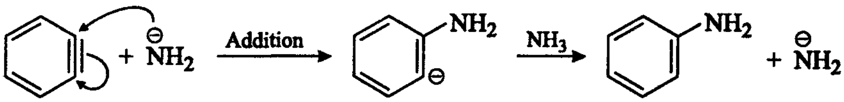
These reactions involve the formation of benzyne (aryne) intermediate and the mechanism is referred to as the **elimination-addition or benzyne** mechanism. The most important requirement for this mechanism to operate is the presence of an *ortho* hydrogen with respect to the leaving group.

The mechanism involves two steps :

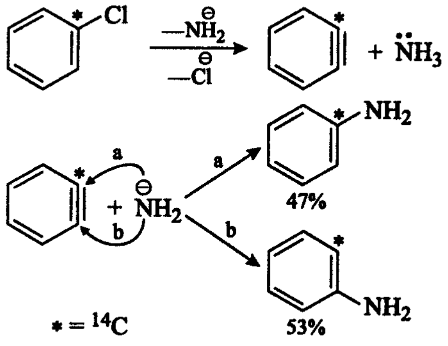
Setp I. Elimination :



Setp II. Addition :

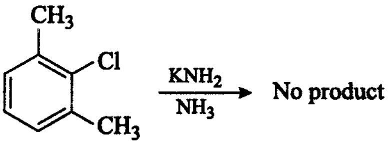


The above mechanism is supported by the fact that when 1—^{14}C-chlorobenzene is treated with KNH_2 in the presence of liquid ammonia at −33°C the reaction mixture gave two products in equal amounts. In half the aniline obtained the amino group was held by ^{14}C and in half it was held by an adjacent carbon.

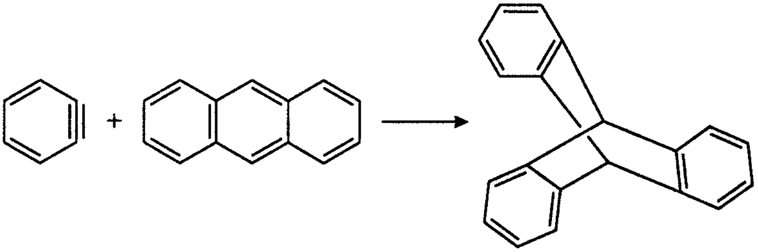


The formation of these two products in almost equal amounts can only be explained by assuming a symmetrical intermediate which can be attacked by $\overset{\ominus}{N}H_2$ at either of the two positions.

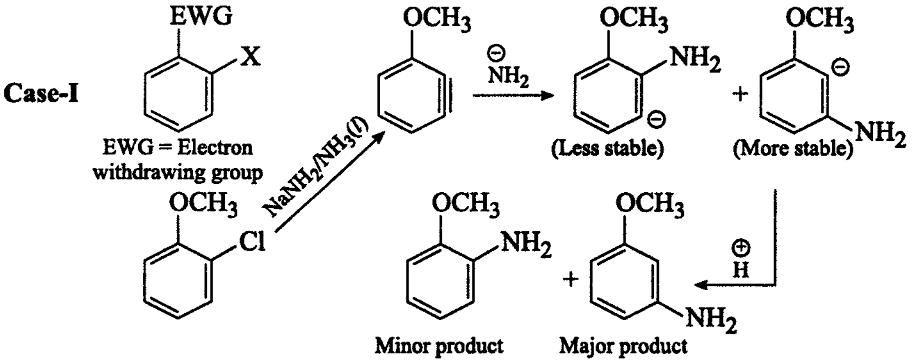
Further confirmation of the benzyne mechanism comes from the observation that compound containing two groups *ortho* to halogen do not react at all. The reason is that when there is no hydrogen to be lost, benzyne cannot be formed.



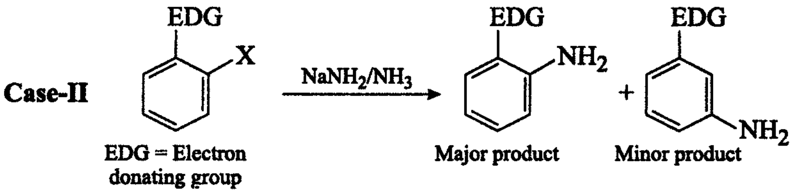
The formaton of **benzyne** as an intermediate has been more directly demonstrated by trapping experiments. For example, the generated benzyne in the presence of anthracene gives Diels-Alder adduct, triptycene in addition to the substitution products.

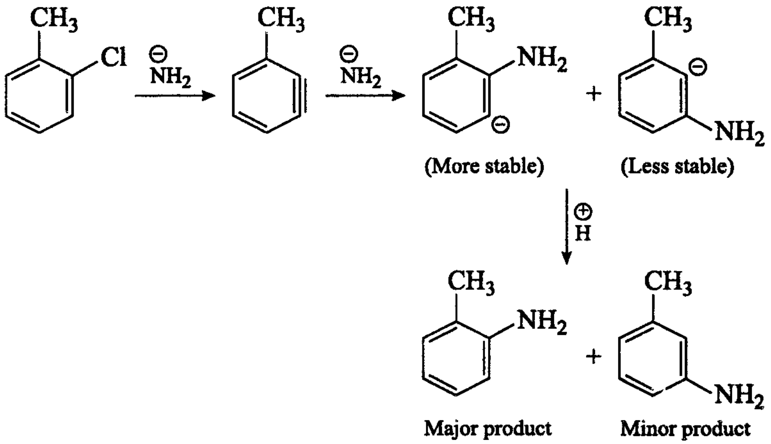

Triptycene

(A) Major Product of the Reaction : If halobenzene is monosubstituted then two or more than two products will be formed. Nature of major product depends on the nature of group *G* and stability of anion. Stability of anion depends on the inductive effect of the group *G* and not on the mesomeric effect of the group *G*.



In this case position of incoming group in major product is far from EWG.



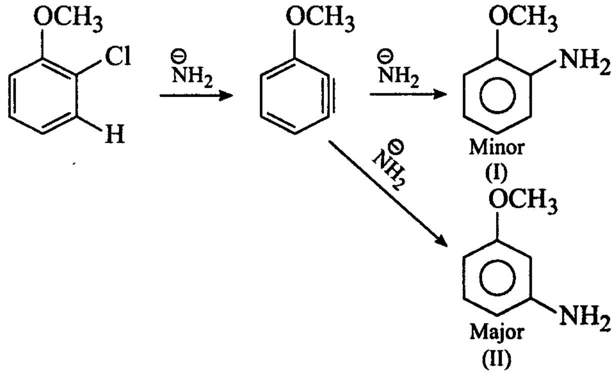


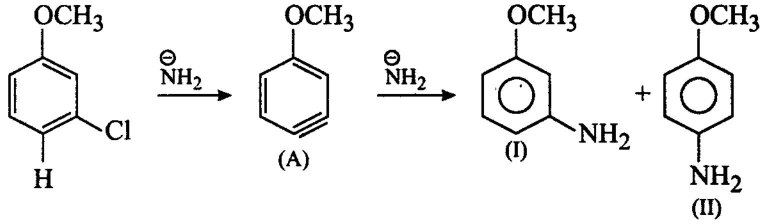
In this case, position of incoming group in major product is near to the EDG.

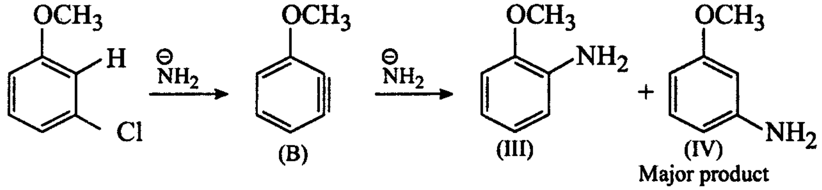
(B) Number of Products in the Monosubstituted Halobenzenes : Number of products depends on the number of hydrogens at *ortho* positions with respect to the halo group. Number of products is given in Table 7.5.

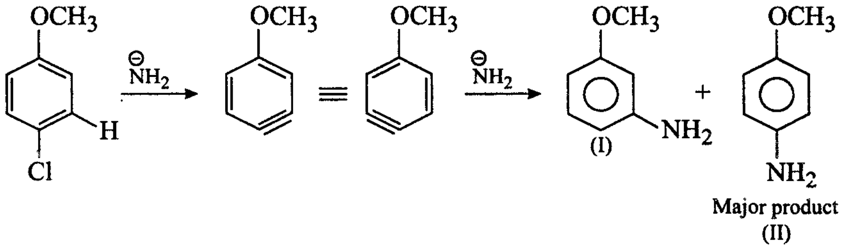
Table 7.5 ***Number of products in monosubstituted halobenzenes***

Compound	*o*-Substituted halobenzene	*m*-Substituted halobenzene	*p*-substituted halobenzene
Number of Products	Two	Three	Two









In the case of *m*-chloroanisole the formation of benzyne (A) is less likely than the benzyne (B), which is formed by the removal of more acidic hydrogen, hence the major product is *m*-aminoanisole (II).

7.11.4 Relative Reactivity of Vinyl Halides *vs* Aryl halides

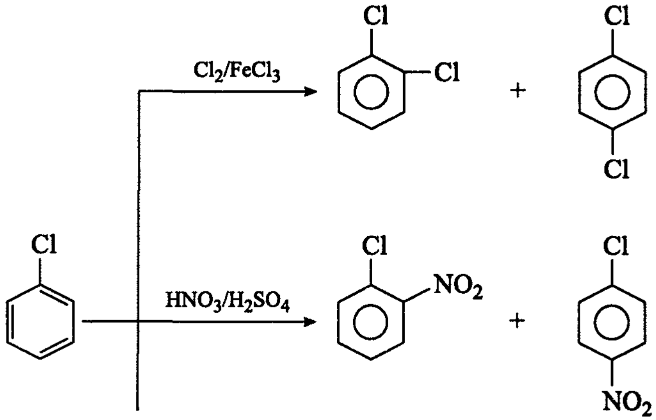
In aryl halides (say chlorobenzene), the carbon-chlorine bond is *sigma* bond. However, one of the *p* orbitals of chlorine having a pair of electrons is parallel to the delocalised *p* orbitals of the benzene nucleus. Thus this *p* orbital of chlorine can also overlap with the delocalised *p* orbitals of benzene nucleus as shown in Figs. 7.6a and 7.6b.

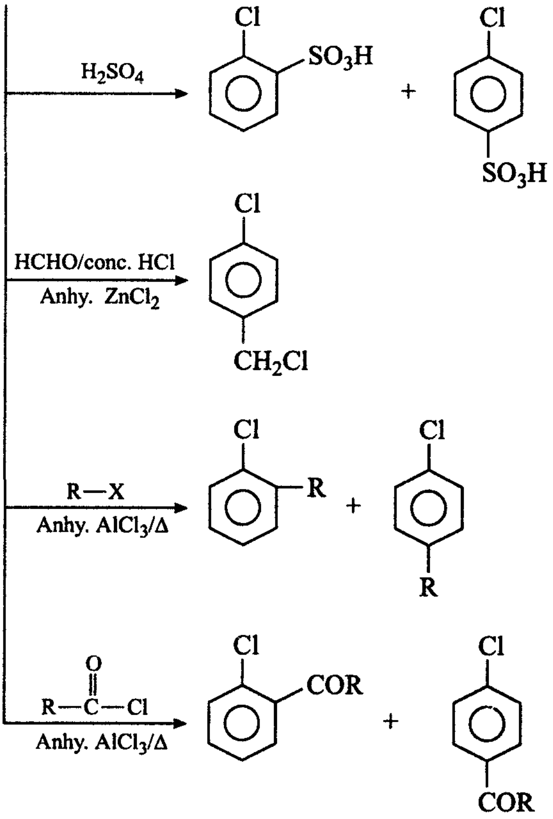
The delocalised *pi* molecular orbitals give partial double bond character to C—Cl bond in aryl halides. The lone pair of *p*-orbital of chlorine is delocalised over six *p* orbitals of the benzene ring. The delocalised π MO gives partial double bond character to C—Cl bond, thus the halogen atom becomes firmly bound to benzene nucleus and cannot be replaced easily.

In vinyl halides also one of the *p*-orbitals of the chlorine having a pair of electrons is parallel to the *p*-orbitals of two carbons only. Thus *p* orbital of chlorine can overlap with the *p* orbital of carbon-1. Thus carbon-chlorine bond in vinyl chloride has also a partial double bond character (Figs. 7.3a and 7.3b). But double bond character in this case is less than that in the chlorobenzene because in chlorobenzene *p* orbital of chlorine overlaps with six orbitals of benzene ring whereas in vinyl chloride it overlaps only with one *p* orbital. Hence Cl of vinyl chloride can be replaced easily than the Cl of chlorobenzene. Therefore, chlorobenzene will be less reactive than vinyl chloride.

7.11.5 Electrophilic Aromatic Substitution Reactions

Because of the presence of benzene ring, aryl halides undergo typical electrophilic substitution reactions though less readily than benzene. The effect of halogen atom is that the incoming group goes to *ortho* and *para* positions with respect to halogen atom. The electrophilic substitution reactions of aryl halides are shown below by taking example of chlorobenzene.





7.11.6 Other Reactions of Aryl Halides

(1) Wurtz-Fittig and Fittig Reactions : When an ethereal solution of an aryl halide is heated with an alkyl halide or aryl halide in the presence of sodium, alkyl benzene or diaryls is formed.

$$C_6H_5Cl + 2Na + CH_3Cl \longrightarrow C_6H_5\text{—}CH_3 \text{ (Wurtz–Fittig reaction)}$$

$$C_6H_5Cl + 2Na + C_6H_5Cl \longrightarrow C_6H_5\text{—}C_6H_5 \text{ (Fittig reaction)}$$

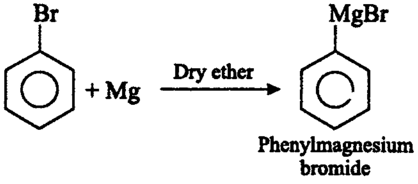
(2) Ullmann Reaction : Iodobenzene on heating with copper powder in a sealed tube affords biphenyl.

$$C_6H_5I + 2Cu + C_6H_5I \longrightarrow C_6H_5\text{—}C_6H_5 + 2CuI$$

Aryl bromide and chloride also participate in this reaction if an electron withdrawing group is present at *ortho* or *para* position to the halogen. The order of reactivity of aryl halides is :

$$Ar\text{—}I > Ar\text{—}Br > Ar\text{—}Cl$$

(3) Formation of Organometallic Compounds : Aryl bromides form Grignard reagent when treated with dry magnesium powder in dry ether.



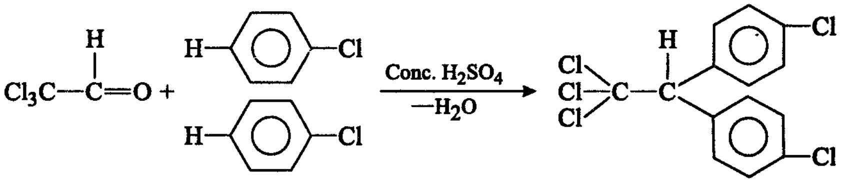
Aryllithium compounds are obtained by treating aryl halide with Lithium metal in dry ether.

$$C_6H_5Br + Li \longrightarrow \underset{\text{Phenyllithium}}{C_6H_5Li} + LiBr$$

Aryllithium compounds are also obtained by the halogen-metal exchange reaction. When aryl halides are treated with BuLi formation of aryllithium takes place.

7.12 DDT

Chlorobenzene is used for the manufacture of the insecticide *p*, *p*′-dichlorodiphenyltrichloroethane (DDT) by condensing it with chloral.

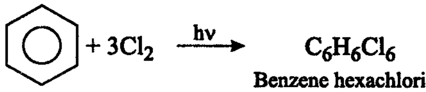


It is a solid mp 109–110°C. DDT is used as insecticide. This insecticide was used successfully to combat typhus epidemics in Europe and malaria epidemics in the south pacific for saving many lives.

Being an inexpensive and easily produced insecticide, the use of DDT became widespread. However, DDT is a stable material and is not metabolised easily and hence persists in the environment. It is transported globally by air currents and return to the earth by rainfall. Since DDT is fat soluble, it is absorbed into the fatty tissue of living organism and becomes concentrated as higher links are reached in a particular food chain. There is evidence that DDT produces cancerous tumours in laboratory rats and mice, hence it could be carcinogenic for humans being.

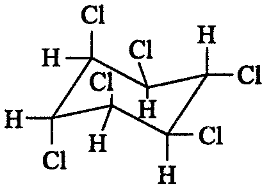
7.13 BENZENE HEXACHLORIDE (BHC)

Benzene hexachloride is obtained when chlorine reacts with benzene in the presence of ultraviolet light.



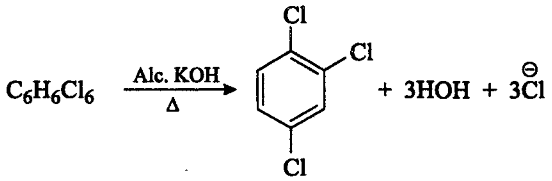
Benzene hexachloride
(1, 2, 3, 4, 5, 6-hexacloro-cyclohexane)

Eight stereoisomers are possible for benzene hexachloride but only seven are known, *e.g.*, α, β, γ, δ etc. The so called γ-isomer (gammexane, Lindane or 666) has insecticidal properties and constitutes 18% of the mixture. Gammexane is a very powerful insectiside. It is more powerful than the DDT.



γ-benzene hexachloride

Reaction of benzene hexachloride with hot alcoholic potassium hydroxide gives 1, 2, 4-trichlorobenzene.



7.14 SIDE-CHAIN HALOGEN DERIVATIVES : BENZYL CHLORIDE, BENZAL CHLORIDE AND BENZOTRICHLORIDE

Side-chain substitution is favoured by high temperature, and the absence of halogen carrier, *e.g.*, when toluene is chlorinated at its boiling point, it gives benzyl, benzal and benzotrichloride depending on the amounts of the reactants.

$$\text{Cl—Cl} \xrightarrow{h\upsilon} \dot{\text{Cl}} + \dot{\text{Cl}}$$

$$C_6H_5CH_3 + \dot{\text{Cl}} \longrightarrow C_6H_5\dot{C}H_2 + HCl$$

$$C_6H_5\dot{C}H_2 + \text{Cl—Cl} \longrightarrow C_6H_5CH_2Cl + \dot{\text{Cl}}; \text{ etc.}$$

$$C_6H_5CH_3 \xrightarrow[\text{hv or } \Delta]{Cl_2} \underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} \xrightarrow[\text{hv or } \Delta]{Cl_2} \underset{\text{Benzal or benzylidene chloride}}{C_6H_5CHCl_2}$$

$$\xrightarrow[\text{hv or } \Delta]{Cl_2} \underset{\text{Benzotrichloride}}{C_6H_5CCl_3}$$

7.14.1 Chemical Reactions of Side-chain Halogen Derivatives

The properties of side-chain halogen derivatives are very much different from those of the nuclear halogen derivatives. The side-chain derivatives closely resemble alkyl halides, and show chemical reactions similar to them, *e.g.*, nucleophilic substitution reactions, Wurtz reaction, formation of Griganard reagent, etc. Some of their reactions are given below :

$$C_6H_5CH_2Cl \xrightarrow{\text{aq. KOH}} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}$$

$$C_6H_5CH_2Cl \xrightarrow{\text{aq. KCN}} \underset{\text{Benzyl cyanide}}{C_6H_5CH_2CN}$$

$$C_6H_5CH_2Cl \xrightarrow{NH_3} \underset{\text{Benzylamine}}{C_6H_5CH_2NH_2}$$

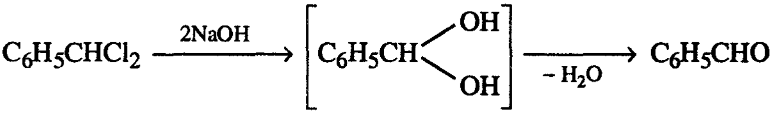
$$C_6H_5CH_2Cl \xrightarrow{CH_3COOAg} \underset{\text{Benzyl acetate}}{C_6H_5CH_2OOCCH_3}$$

$$C_6H_5CH_2Cl \xrightarrow[\text{KMn04/}\overset{\ominus}{\text{O}}\text{H}]{\text{Dil. }HNO_3\text{ or}} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

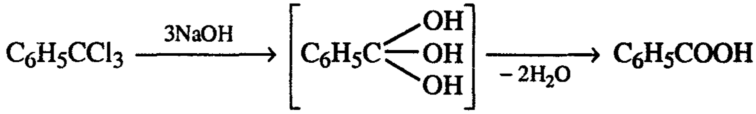
$$C_6H_5CH_2Cl \xrightarrow[\text{Dry ether}]{Mg} \underset{\text{Benzylmagnesium chloride}}{C_6H_5CH_2MgBr}$$

$$C_6H_5CH_2Cl + 2Na + ClCH_2C_6H_5 \xrightarrow{\text{Dry ether}} \underset{\text{Bibenzyl}}{C_6H_5CH_2CH_2C_6H_5}$$

$$C_6H_5CH_2Cl \xrightarrow{\text{Zn—Cu couple}} \underset{\text{Toluene}}{C_6H_5CH_3} + HCl$$



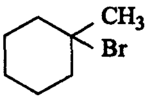
$$C_6H_5CHCl_2 \xrightarrow{2NaOH} \left[C_6H_5CH\begin{matrix} OH \\ OH \end{matrix} \right] \xrightarrow[-H_2O]{} C_6H_5CHO$$



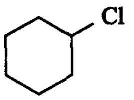
$$C_6H_5CCl_3 \xrightarrow{3NaOH} \left[C_6H_5C\begin{matrix} OH \\ OH \\ OH \end{matrix} \right] \xrightarrow[-2H_2O]{} C_6H_5COOH$$

VERY SHORT ANSWER QUESTIONS

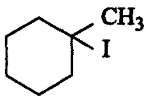
1. Write the structures of all the possible isomers of C_7H_7Cl containing a benzene ring. Indicate the structure with the weakest C—Cl bond.
2. Arrange the following in decreasing order of SN2 reactivity :
   $CH_3CH_2CH_2Cl$, $CH_3CH_2CHClCH_3$, $CH_2{=}CHCHClCH_3$
3. Arrange the following in order of increasing boiling points :
   n-aryl chloride, neoamyl chloride, *tert*-amyl chloride, isoamyl chloride.
4. Predict the decreasing order of reactivity of the following compounds towards SN1 reactions :



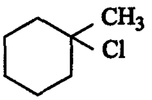
I



II

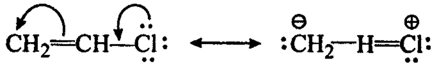


III



IV

5. Arrange the following alkyl halides in order of decreasing SN2 reactivity :
   CH_3Cl, CH_3Br, $(CH_3)_2CHCl$, CH_3CH_2Cl
6. A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single mono chloro derivative C_6H_9Cl in bright sunlight. Identify the hydrocarbon.
7. How will you synthesise vinyl bromide from ethyl alcohol?
8. How will you distinguish between ethyl chloride and vinyl chloride?
9. How will you prepare Freon-12?
10. What effect should the following resonance of vinyl chloride have on its dipole moment?



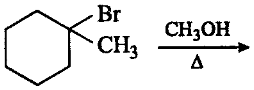
$$CH_2{=}CH{-}\ddot{\underset{\cdot\cdot}{Cl}}: \longleftrightarrow \overset{\ominus}{:CH_2}{-}H{=}\overset{\oplus}{\underset{\cdot\cdot}{Cl}}:$$

11. Which methyl halide has the highest density and why?
12. What happens when $CHCl_3$ is heated with sodium ethoxide?
13. Explain why CHF_3 is less acidic than $CHCl_3$?
14. How will you distinguish between chloroform and carbon tetrachloride?
15. Three isomers A, B and C of molecular formula C_8H_9Br gave the following compounds on oxidation :
    A gives benzoic acid; B gives phthalic acid; C gives *p*-bromobenzoic acid
    A is optically active. Both A and B, but not C, give a white precipitate when warmed with $AgNO_3$ solution. Identify A, B and C.

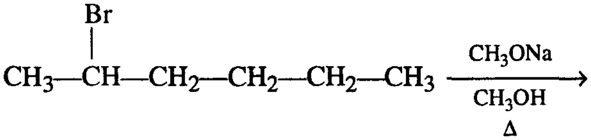
PROBLEMS WITH SOLUTIONS

1. Ethyl chloride gives nucleophilic substitution reaction slowly with water. This reaction is accelarated in the presence of small amount of KI. Explain.
2. The rate of hydrolysis of tertiary butyl bromide in 50% aqueous methanol is thousand times faster than in pure methanol. Explain.
3. Hydrolysis of ethyl chloride can be carried out with aqueous Na_2CO_3 solution but that of chlorobenzene requires aqueous NaOH at 360°C under 320 atm pressure. Account for the much less reactivity of chlorobenzene than of ethyl chloride.
4. Explain why aryl halides and vinyl halides do not give insoluble precipitate of silver halides when these are treated with alcoholic silver nitrate solution.
5. What is difference between nucleophilicity and basicity ?
6. Hydrolysis of 2-bromo-3-methylbutane gives only 2-methyl-2-butanol. Explain.
7. Account for the rapid rate of hydrolysis of $CH_3-CH_2-O-CH_2-Cl$ although the substrate is 1° halide.
8. Predict the products and mechanisms of the following reactions :

(a)



(b)

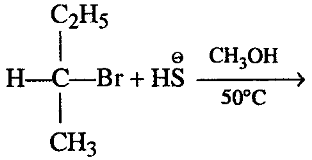


$$CH_3-\overset{\overset{Br}{|}}{C}H-CH_2-CH_2-CH_2-CH_3 \xrightarrow[CH_3OH \atop \Delta]{CH_3ONa}$$

9. Give the product(s) that you would expect to be formed in each of the following reactions. In each case predict the relative amount of each.

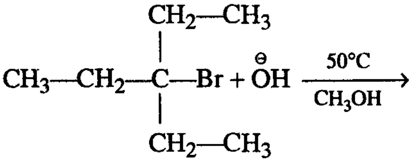
(a) $CH_3-CH_2-CH_2-Br + CH_3\overset{\ominus}{O} \xrightarrow[50°C]{CH_3OH}$ (b) $CH_3-CH_2-CH_2-Br + (CH_3)_3C-\overset{\ominus}{O} \xrightarrow[50°C]{(CH_3)_3COH}$

(c)



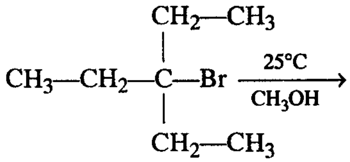
$$H-\underset{CH_3}{\overset{C_2H_5}{C}}-Br + H\overset{\ominus}{S} \xrightarrow[50°C]{CH_3OH}$$

(d)



$$CH_3-CH_2-\underset{CH_2-CH_3}{\overset{CH_2-CH_3}{C}}-Br + \overset{\ominus}{O}H \xrightarrow[CH_3OH]{50°C}$$

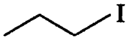
(e)

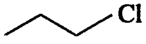


$$CH_3-CH_2-\underset{CH_2-CH_3}{\overset{CH_2-CH_3}{C}}-Br \xrightarrow[CH_3OH]{25°C}$$

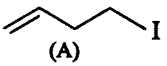
10. When alkyl halide is treated with aqueous alcoholic solution of KCN the major product is alkyl cyanide and a trace amount of alkyl isocyanide is also formed, whereas an alkyl halide on treatment with AgCN gives alkyl isocyanide as the major product along with trace amount of alkyl cyanide. Explain the observed results.

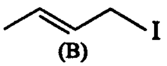
11. Which substrate in each of the following pairs will react more rapidly with hydroxide ion under SN2 reaction conditions :

(a) 

(A)
and 

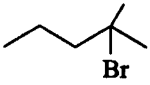
(B)

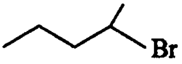
(b) 

(A)
and 

(B)

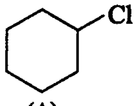
(c) $C_6H_5CH_2Br$ (A) and $C_6H_5CH_2CH_2Br$ (B)

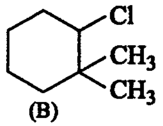
(d) 

(A)
and 

(B)

(e) CH_3Cl (A) and CH_2Cl_2 (B)

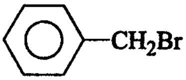
(f) 

(A)
and 

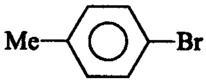
(B)

12. Predict the order of reactivity of the following halides with :
(a) NaI in acetone (b) Aqueous alcoholic $AgNO_3$

CH_3Br (A) CH_3CH_2Br (B)

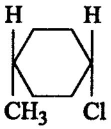


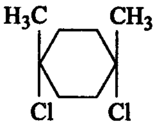
(C)

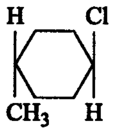


(D)

13. (i) Predict the product(s) of SN2 reaction of the following compounds with hydroxide ions :

(a) 

(b) 

(c) 

(ii) What product(s) would be formed in an SN1 reaction of these compounds ?

14. Which alkyl halide would you expect to react more rapidly by an SN2 mechanism?

(a) $\underset{\text{I}}{CH_3-CH_2-CH_2-I}$ or $\underset{\text{II}}{(CH_3)_2CHI}$

(b) $\underset{\text{III}}{CH_3-CH_2-CH_2-CH_2-Cl}$ or $\underset{\text{IV}}{CH_3-CH_2-CH_2-CH_2-Br}$

(c) $\underset{\text{V}}{(CH_3)_2CH-CH_2Br}$ or $\underset{\text{VI}}{CH_3-CH_2-CH_2-CH_2-Br}$

(d) $\underset{\text{VII}}{(CH_3)_2CHCH_2CH_2Cl}$ or $\underset{\text{VIII}}{CH_3-CH_2-CH(CH_3)CH_2Cl}$

15. Which SN2 reaction of each pair would you expect to take more readily in polar aprotic solvent.

(a) 1. $CH_3-CH_2-CH_2-I + CH_3-\overset{\ominus}{O} \longrightarrow CH_3-CH_2-CH_2-OCH_3$

or

2. $CH_3-CH_2-CH_2-I + CH_3OH \longrightarrow CH_3-CH_2-CH_2-O-CH_3$

(b) 1. $CH_3-CH_2-CH_2-Cl + (C_6H_5)_3N \longrightarrow CH_3-CH_2-CH_2-\overset{\oplus}{N}(C_6H_5)_3\,\overset{\ominus}{Cl}$

or

2. $CH_3-CH_2-CH_2-Cl + (C_6H_5)_3P \longrightarrow CH_3-CH_2-CH_2-\overset{\oplus}{P}(C_6H_5)_3\,\overset{\ominus}{Cl}$

(c) 1. $CH_3-CH_2-Br\ (1{\cdot}0\ M) + CH_3\overset{\ominus}{O}\ (1{\cdot}0\ M) \longrightarrow CH_3-CH_2-O-CH_3 + \overset{\ominus}{Br}$

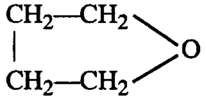
or

2. $CH_3-CH_2-Br\ (1{\cdot}0\ M) + CH_3-\overset{\ominus}{O}\ (2{\cdot}0\ M) \longrightarrow CH_3-CH_2-O-CH_3 + \overset{\ominus}{Br}$

16. Tertiary butyl bromide can give substitution as well as elimination reaction, under what experimental conditions :
    (i) The reaction will be elimination reaction
    (ii) The reaction will be substitution reaction

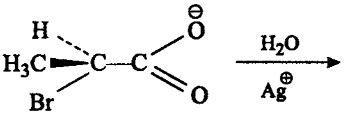
17. The rate of SN2 reaction of neopentyl bromide, with sodium ethoxide proceeds about 10^5 times as slow as the reaction with bromoethane. Explain.

18. Each of the following might have been synthesised by an SN2 reaction. Suggest a combination of substrate and nucleophile which could have led to its production.
    (a) CH_3-O-CH_3
    (b) CH_3-Cl
    (c) $CH_3-CH_2-PH_2$
    (d) $CH_3-O-CH_2-CH_3$
    (e) $CH_2=CH-CH_2-CH_2-CH=CH_2$
    (f)

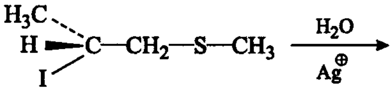


19. Complete the following reactions and indicate the stereochemistry at the chiral carbon.

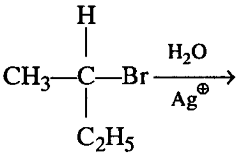
(a)



(b)

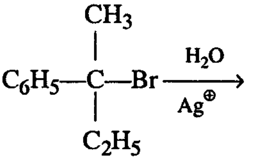


(c)



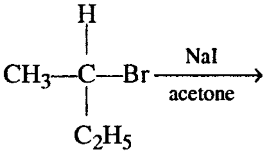
$CH_3-\underset{C_2H_5}{\overset{H}{C}}-Br \xrightarrow[Ag^{\oplus}]{H_2O}$

(d)



$C_6H_5-\underset{C_2H_5}{\overset{CH_3}{C}}-Br \xrightarrow[Ag^{\oplus}]{H_2O}$

(e)

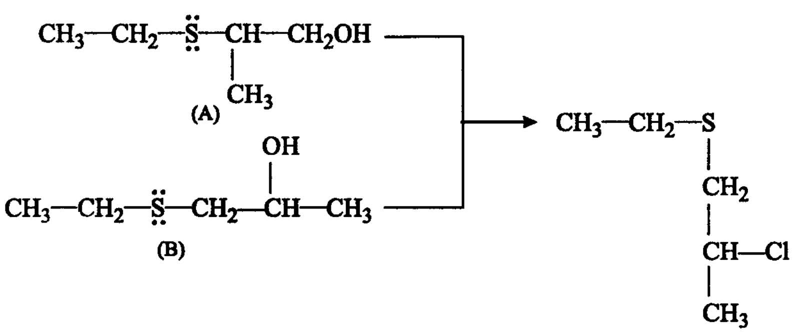


$CH_3-\underset{C_2H_5}{\overset{H}{C}}-Br \xrightarrow[acetone]{NaI}$

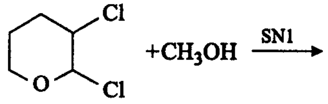
20. *Tert*-butyl chloride undergoes solvolysis in the presence of acetic acid ($\varepsilon = 6$) as well as in formic acid ($\varepsilon = 59$).
    (a) What is the SN1 solvolysis product in each solvent?
    (b) In which solvent is the reaction more rapid and why?

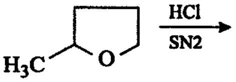
21. When methyl bromide is dissolved in methanol and an equimolar amount of KI is added, the concentration of iodiode ion quickly decreases, and then slowly returns to its original value. Explain.

22. Explain why the following two alchols each react with HCl to give same alkyl chloride.

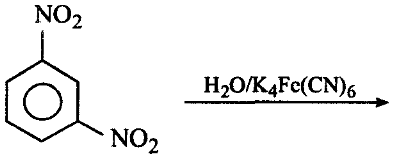


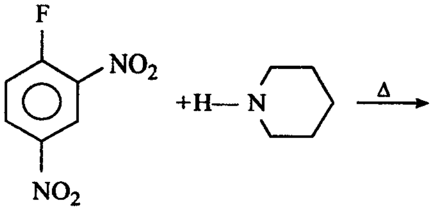
23. Complete the following reactions and indicate major product in each case.

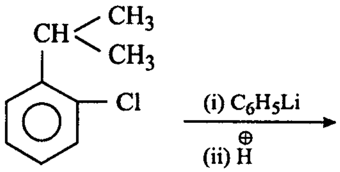
(a) 

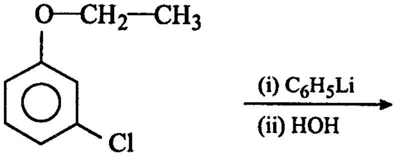
(b) 

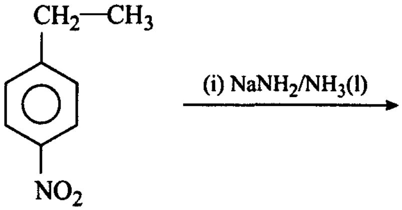
24. Give product/products in each of the following :

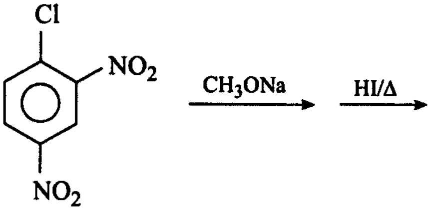
(a) 

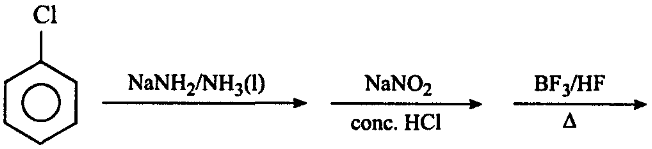
(b) 

(c) 

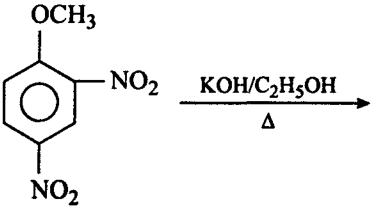
(d) 

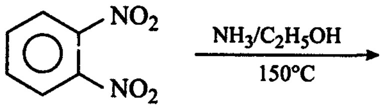
(e) 

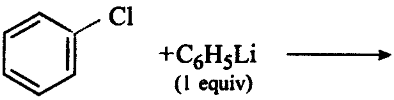
(f) 

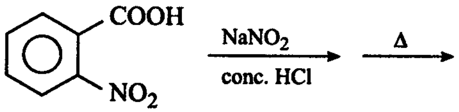
(g) 

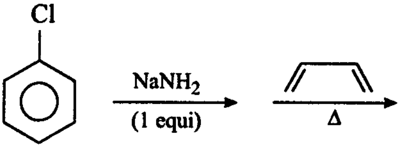
25. Complete the following reactions :

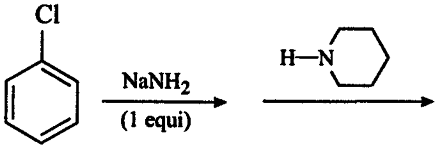
(a) 

(b) 

(c) 

(d) 

(e) 

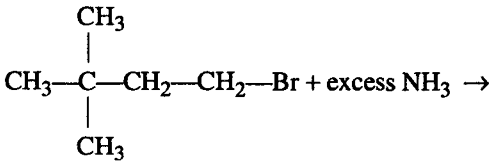
(f) 

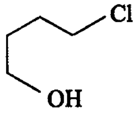
PROBLEMS FOR SELF ASSESSMENT

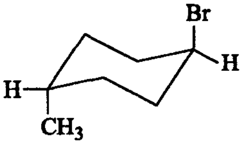
1. Predict the products of the following SN1 reactions :

(a) $CH_3-CH_2-Cl + CH_3-CH_2ONa \xrightarrow{C_2H_5OH}$ (b) $C_6H_5-CH_2-CH_2-Br + NaCN \xrightarrow{Acetone}$

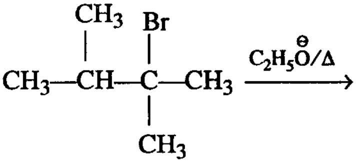
(c) $C_6H_{11}Cl + CH_3SNa \longrightarrow$

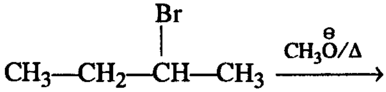
(d) 
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_2-Br + \text{excess } NH_3 \rightarrow$

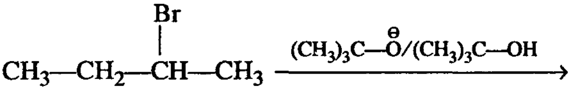
(e)  + NaOH ⟶

(f)  $\xrightarrow[CH_3OH]{NaOH}$

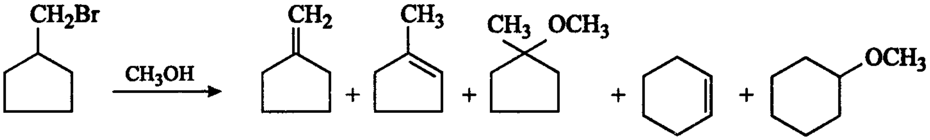
2. Predict the major and minor products of the E2 reactions of each of the following :

(a) 
$CH_3-\overset{CH_3}{CH}-\underset{CH_3}{\overset{Br}{C}}-CH_3 \xrightarrow{C_2H_5\overset{\ominus}{O}/\Delta}$

(b) 
$CH_3-CH_2-\overset{Br}{CH}-CH_3 \xrightarrow{CH_3\overset{\ominus}{O}/\Delta}$

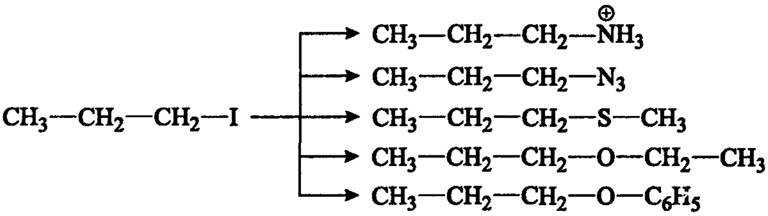
(c) 
$CH_3-CH_2-\overset{Br}{CH}-CH_3 \xrightarrow{(CH_3)_3C-\overset{\ominus}{O}/(CH_3)_3C-OH}$

3. Upon solvolysis the bromomethylcyclopentane in methanol gives the mixture of five products. Give a mechanism to account for the formation of each of these products :



4. Indicate which member of the following pairs of compounds will react faster in (i) the SN1 reaction and (ii) the SN2 reaction. Explain your reasoning :
   (a) 1-Bromobutane and 2-bromobutane
   (b) 1-Chloropentane and cyclopentyl chloride
   (c) 1-Chloropropane and 1-iodopropane
   (d) *tert*-butyl iodide and isopropyl iodide

5. What nucleophile would serve to effect the following conversions of 1-iodopropane :



$CH_3-CH_2-CH_2-I \longrightarrow$

$CH_3-CH_2-CH_2-\overset{\oplus}{N}H_3$

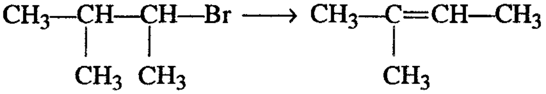
$CH_3-CH_2-CH_2-N_3$

$CH_3-CH_2-CH_2-S-CH_3$

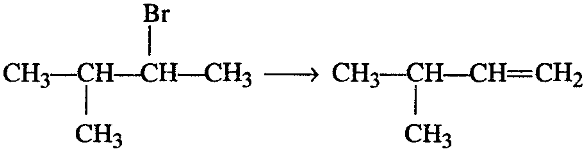
$CH_3-CH_2-CH_2-O-CH_2-CH_3$

$CH_3-CH_2-CH_2-O-C_6H_5$

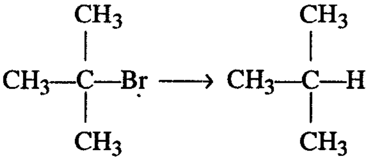
6. Provide reagents that will effect the following changes :

(a) 

$CH_3-\underset{CH_3}{CH}-\underset{CH_3}{CH}-Br \longrightarrow CH_3-\underset{CH_3}{C}=CH-CH_3$

(b) 

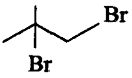
$CH_3-\underset{CH_3}{CH}-\overset{Br}{CH}-CH_3 \longrightarrow CH_3-\underset{CH_3}{CH}-CH=CH_2$

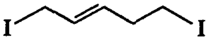
(c) 

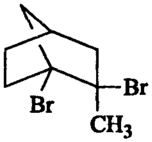
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-H$

7. The SN2 reactions at the allylic carbon are especially facile. For example, allylic compounds are even more reactive than methyl compounds. Explain this rate difference. Why are allyl compounds especially highly reactive?

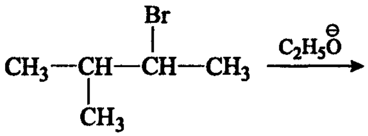
8. Each of the following molecules contains two halogens at different positions in the molecule. In each case, determine which of the two halogens will be the more reactive in the SN1 reaction. Explain.

(a) 

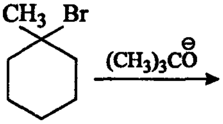
(b) 

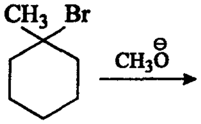
(c) 

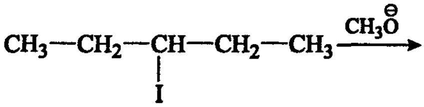
9. Predict the product of the following E2 reactions. If more than one product is expected, indicate which will be the major compound formed.

(a) 

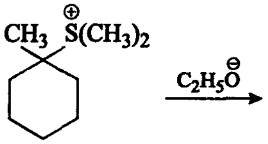
$CH_3-\underset{CH_3}{CH}-\overset{Br}{CH}-CH_3 \xrightarrow{C_2H_5\overset{\ominus}{O}}$

(b) 

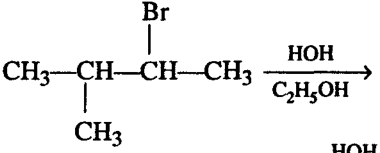
(c) 

(d) 

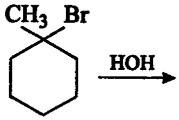
$CH_3-CH_2-\underset{I}{CH}-CH_2-CH_3 \xrightarrow{CH_3\overset{\ominus}{O}}$

(e) 

10. Predict the products of the following E1 reactions. If more than one product is expected, indicate which will be the major compound formed.

(a) 

$CH_3-\underset{CH_3}{CH}-\overset{Br}{CH}-CH_3 \xrightarrow[C_2H_5OH]{HOH}$

(b) 

(c) $CH_3-CH_2-CH_2-CH_2-I \xrightarrow{HOH}$

11. Answer the questions below for SN2 reaction :

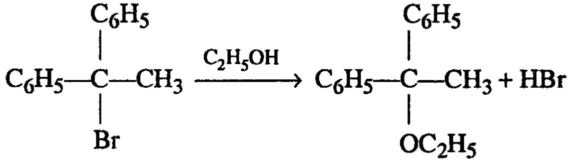
$$CH_3—CH_2—CH_2—CH_2—Br \xrightarrow{NaOH/C_2H_5OH} CH_3—CH_2—CH_2—CH_2—OH + NaBr$$

(a) What is the rate law for the reaction ?

(b) Draw an energy diagram for the reaction.

(c) What will be the effect on the rate of the reaction of doubling the concentration of *n*-butyl bromide ?

12. Answer the questions below for SN1 reaction :



$$(C_6H_5)_2C(CH_3)Br \xrightarrow{C_2H_5OH} (C_6H_5)_2C(CH_3)OC_2H_5 + HBr$$

(a) What is the rate law for the reaction ?

(b) Draw an energy diagram for the reaction.

(c) Will the rate of the reaction change significantly if some water is added to the solvent which is ethanol?

13. When 1-chloro-2-butene reacts in 50% aqueous acetone at 47°C, the product is a mixture of two alcohols. Complete the reaction. Write a detailed mechanism that account for the observed experimental facts.

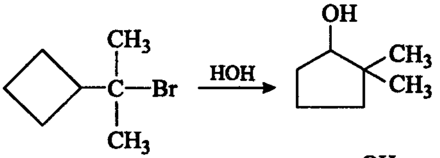
14. 3-Bromo-3-methyl-1-butene forms two substitution products when it is added to a solution of sodium acetate in acetic acid.

(a) Give the structures of the substitution product.

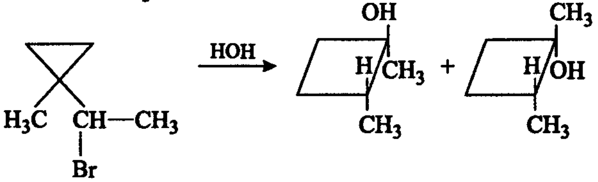
(b) Which is kinetically controlled product and which is thermodynamically controlled product ?

15. Propose a mechanism for each of the following reactions :

(a)



(b)



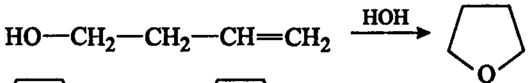
16. Using the given starting material and any necessary organic or inorganic reagents indicate how the desired compound could be synthesised ?

(a) $C_6H_5—CH_2—CH_3 \longrightarrow C_6H_5—CH{=}CH_2$

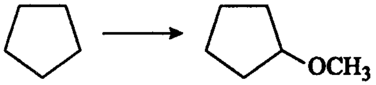
(b) $CH_3—CH_2—CH{=}CH_2 \longrightarrow CH_3—CH_2—CH_2—CH_2—NH_2$

(c) $CH_3—CH_2—CH{=}CH_2 \longrightarrow CH_2{=}CH—CH{=}CH_2$

(d)



(e)



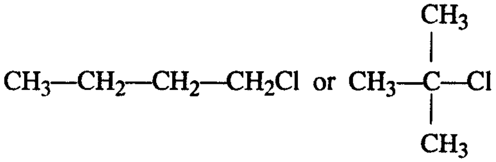
17. Two elimination products are formed from the following E2 reaction :

$$CH_3—CH_2—CHD—CH_2Br \xrightarrow{\overset{\ominus}{OH}} A + B$$

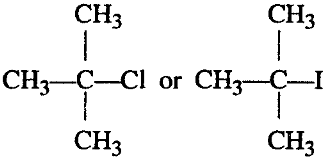
(a) What the elimination products ?

(b) Which is formed in greater yield ? Explain.

18. Select the member of each pair that undergoes SN1 solvolysis in aqueous ethanol more rapidly.

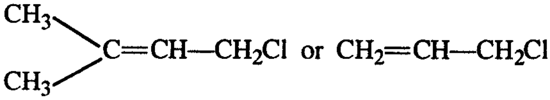
(a) 

$CH_3—CH_2—CH_2—CH_2Cl$ or $CH_3—\underset{CH_3}{\overset{CH_3}{C}}—Cl$

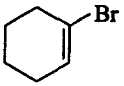
(b) 

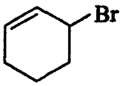
$CH_3—\underset{CH_3}{\overset{CH_3}{C}}—Cl$ or $CH_3—\underset{CH_3}{\overset{CH_3}{C}}—I$

(c) $CH_2{=}CH—CH_2—Cl$ or $CH_3—CH_2—CH_2—Cl$

(d) 

$(CH_3)_2C{=}CH—CH_2Cl$ or $CH_2{=}CH—CH_2Cl$

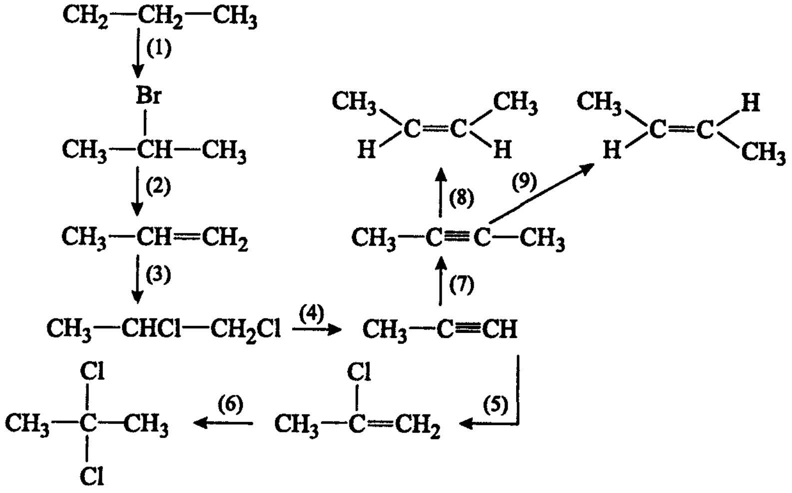
(e) 

or 

19. Account for the following relative rates of solvolysis under experimental conditions favouring SN1 reaction.

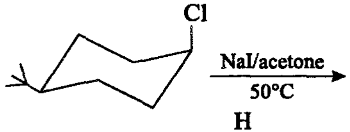
Relative rate of solvolysis	**Structure of substrate**
0.2	$CH_3—O—CH_2—CH_2—Cl$
1	$CH_3—CH_2—CH_2—CH_2—Cl$
10^9	$CH_3—CH_2—O—CH_2—Cl$

20. Show reagents and experimental conditions required to bring about the following transformations :

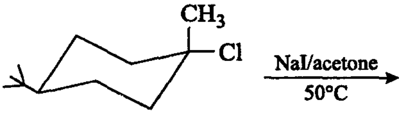


21. What products do you except when *p*-bromoanisole is treated with $KNH_2/NH_3(l)$.
22. Compare the reactivity of vinyl and allylic halides towards nucleophilic substituion reaction.
23. Discuss the various mechanisms of aromatic nucleophilic substitution reactions.
24. Discuss the factors which facilitate the ArSN2 mechanism for aryl halides.
25. Complete the following substitution reactions :

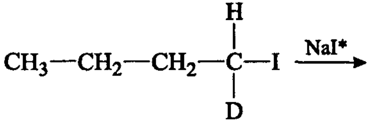
(a)



(b)



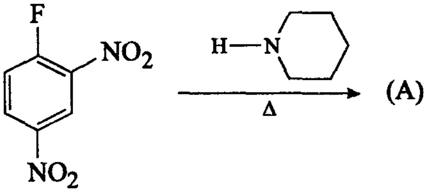
(c)



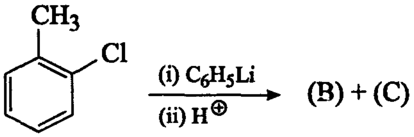
$$CH_3{-}CH_2{-}CH_2{-}\overset{\displaystyle H}{\underset{\displaystyle D}{C}}{-}I \xrightarrow{NaI^*}$$

26. Give product/products in each of the following :

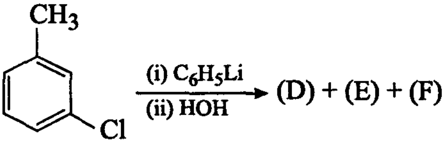
(a)



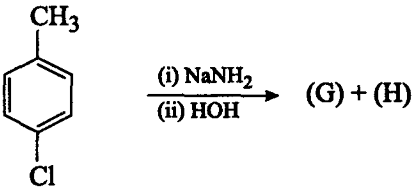
(b)



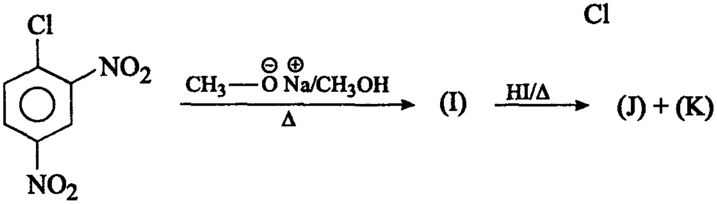
(c)



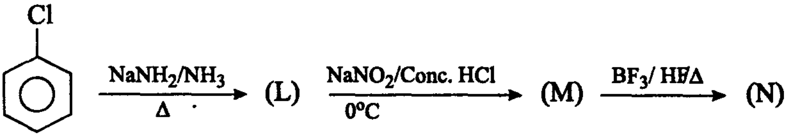
(d)



(e)

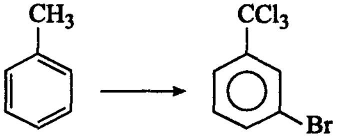


(f)

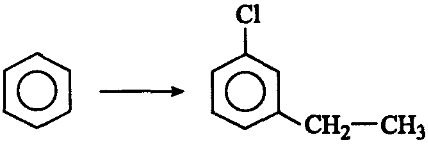


27. Complete the following coversion.

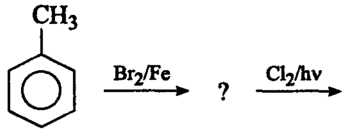
(a)



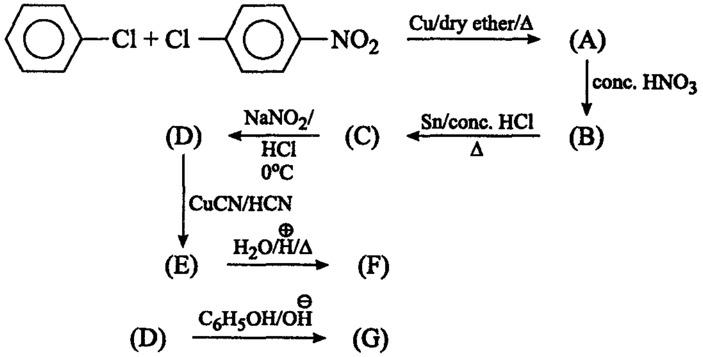
(b)



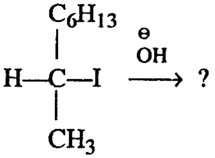
(c)



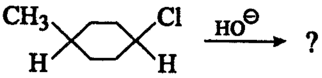
28. Identify (A) to (G) in the given sequence of reactions :



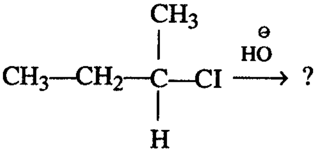
29. Give product/products in each of the following reactions :

(a) 

$$\mathrm{H{-}\underset{CH_3}{\overset{C_6H_{13}}{C}}{-}I} \xrightarrow{\overset{\ominus}{OH}} ?$$

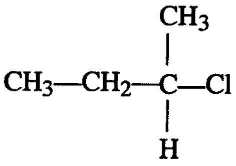
(b) 

cis-1-chloro-3-methylcyclohexane

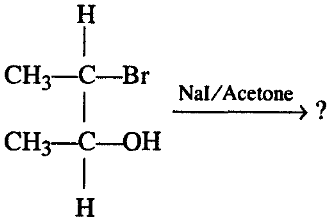
(c) 

$$\mathrm{CH_3{-}CH_2{-}\underset{H}{\overset{CH_3}{C}}{-}Cl} \xrightarrow{\overset{\ominus}{HO}} ?$$

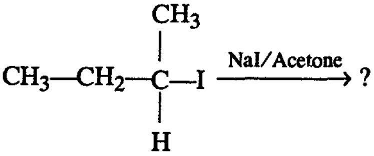
(d) When optically active (+)-2-chlorobutane is treated with NaI/acetone, the product is (−)-2-iodobutane. Write the configuration of the product. Configuration of the reactant is



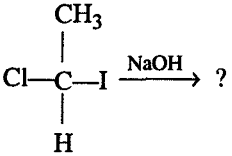
$$\mathrm{CH_3{-}CH_2{-}\underset{H}{\overset{CH_3}{C}}{-}Cl}$$

(e) 

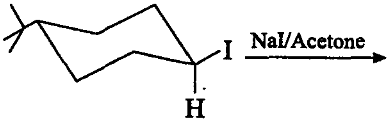
$$\begin{array}{c}\mathrm{H}\\ |\\ \mathrm{CH_3{-}C{-}Br}\\ |\\ \mathrm{CH_3{-}C{-}OH}\\ |\\ \mathrm{H}\end{array} \xrightarrow{\text{NaI/Acetone}} ?$$

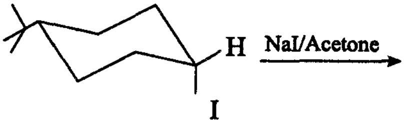
(f) 

$$\mathrm{CH_3{-}CH_2{-}\underset{H}{\overset{CH_3}{C}}{-}I} \xrightarrow{\text{NaI/Acetone}} ?$$

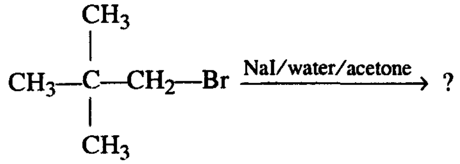
(g) 

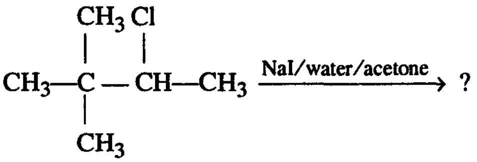
$$\mathrm{Cl{-}\underset{H}{\overset{CH_3}{C}}{-}I} \xrightarrow{\text{NaOH}} ?$$

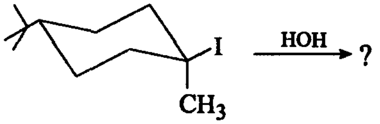
(h) 

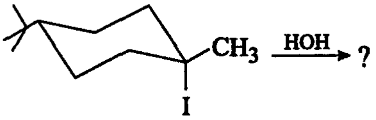
(i) 

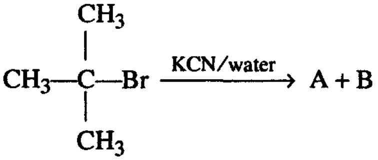
30. Complete the following reactions and give only major product in each case :

(a) 
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-Br \xrightarrow{NaI/water/acetone} ?$

(b) 
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{Cl}{CH}-CH_3 \xrightarrow{NaI/water/acetone} ?$

(c) 

(d) 

(e) 
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br \xrightarrow{KCN/water} A+B$

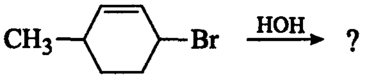
31. Complete the following reactions :

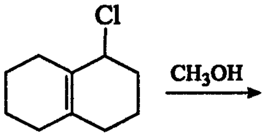
(a) $CH_2{=}CH-CH_2-Cl + HOH \longrightarrow ?$

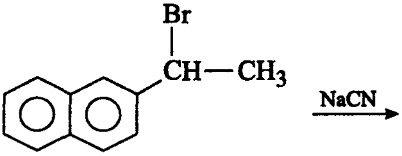
(b) $C_6H_5-CH_2-Cl + HOH \longrightarrow ?$

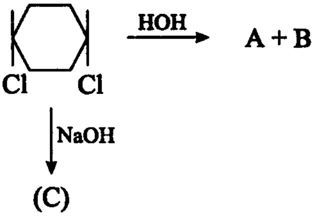
(c) $CH_3-CH{=}CH-CH_2-Cl + HOH \longrightarrow ?$

(d) $CH_2{=}CH-CH_2-Cl \xrightarrow{NaOH}$

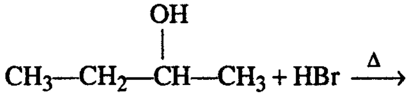
(e) 

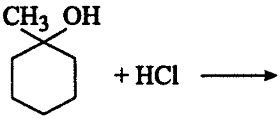
(f) 

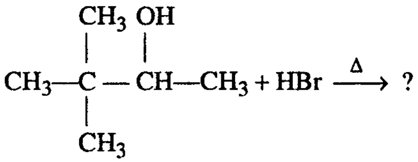
(g) 

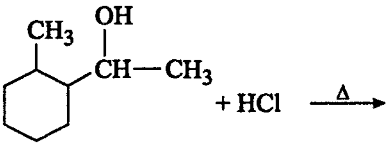
(h) 

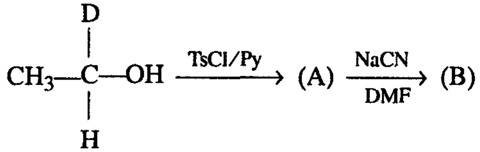
32. Give product/products in each of the following :

(a) 
$CH_3-CH_2-\overset{OH}{CH}-CH_3 + HBr \xrightarrow{\Delta}$

(b) 

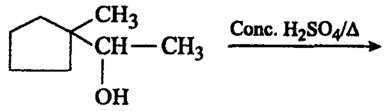
(c) 
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{OH}{CH}-CH_3 + HBr \xrightarrow{\Delta} ?$

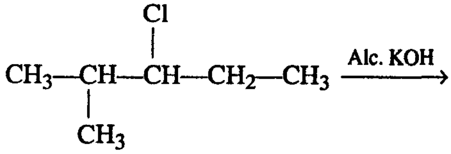
(d) 

(e) 

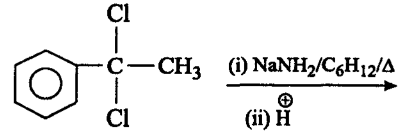
$$\mathrm{CH_3-\overset{\overset{D}{|}}{\underset{\underset{H}{|}}{C}}-OH \xrightarrow{TsCl/Py} (A) \xrightarrow[DMF]{NaCN} (B)}$$

33. Give major product in each of the following reactions :

(a) 

(b) 

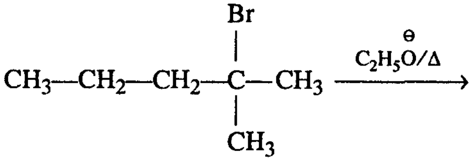
$$\mathrm{CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{Cl}{|}}{CH}-CH_2-CH_3 \xrightarrow{Alc.\ KOH}}$$

(c) 

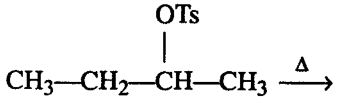
34. Starting with an appropriate alkyl halide and base, outline synthesis that would yield each of the following alkanes as the major product (or only) product.

(a) 1-pentene
(b) 3-methyl-1-butene
(c) 2, 3-dimethyl-1-butene
(d) 4-methylcyclohexene
(e) 1-methylcyclopentene

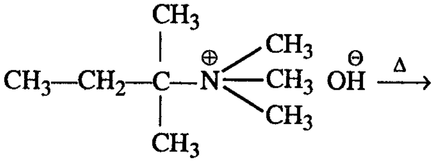
35. Indicate the major alkene produced by each of the following :

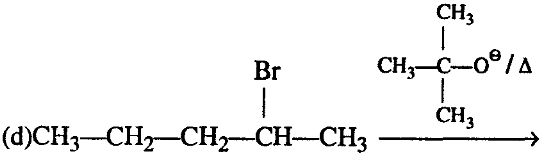
(a) 

$$\mathrm{CH_3-CH_2-CH_2-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 \xrightarrow{C_2H_5\overset{\ominus}{O}/\Delta}}$$

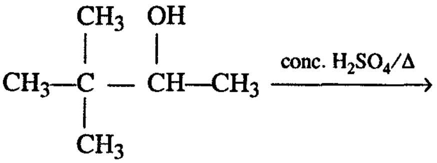
(b) 

$$\mathrm{CH_3-CH_2-\overset{\overset{OTs}{|}}{CH}-CH_3 \xrightarrow{\Delta}}$$

(c) 

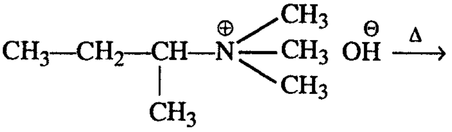
(d) 

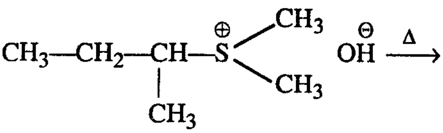
$$\mathrm{CH_3-CH_2-CH_2-\overset{\overset{Br}{|}}{CH}-CH_3 \xrightarrow{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-O^{\ominus}/\Delta}}$$

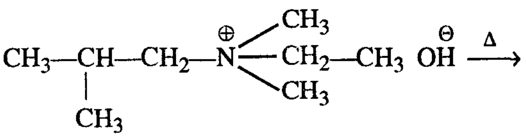
(e) 

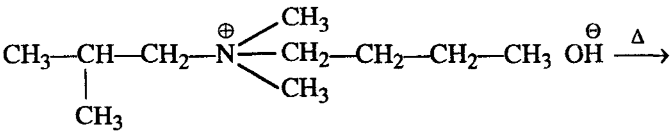
$$\mathrm{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{\overset{OH}{|}}{CH}-CH_3 \xrightarrow{conc.\ H_2SO_4/\Delta}}$$

36. Indicate the products which are expected from the following elimination reactions. If several alkenes will be formed then indicate which will be the major product.

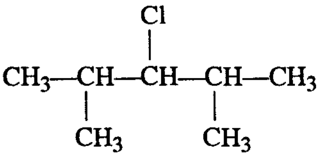
(a) 

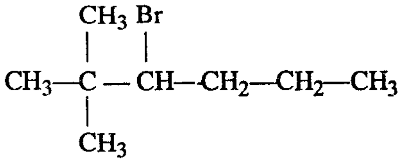
(b) 

(c) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-\overset{\oplus}{N}(CH_3)_2-CH_2-CH_3\ \overset{\ominus}{OH} \xrightarrow{\Delta}$

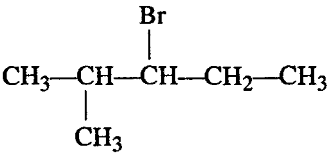
(d) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-\overset{\oplus}{N}(CH_3)_2-CH_2-CH_2-CH_2-CH_3\ \overset{\ominus}{OH} \xrightarrow{\Delta}$

37. Each of the following alkyl halides can undergo rearrangement in SN1 reaction. For each show the initial carbocation, the rearranged carbocation and the major rearranged product.

(a) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{Cl}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

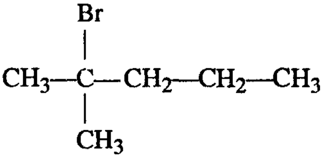
(b) 
$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\overset{Br}{|}}{CH}-CH_2-CH_2-CH_3$

38. Which compound in each of the following pairs undergoes E2 reaction more rapidly?

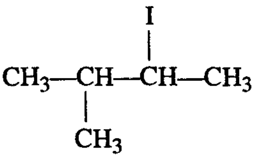
(a) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{Br}{|}}{CH}-CH_2-CH_3$

(i)

or

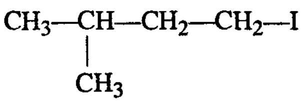

$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}}-CH_2-CH_2-CH_3$

(ii)

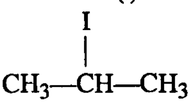
(b) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{I}{|}}{CH}-CH_3$

(i)

or

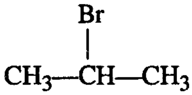

$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-I$

(ii)

(c) 
$CH_3-\overset{\overset{I}{|}}{CH}-CH_3$

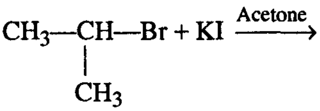
(i)

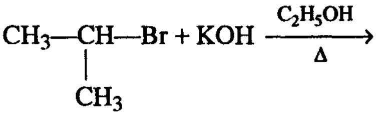
or

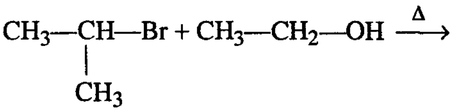

$CH_3-\overset{\overset{Br}{|}}{CH}-CH_3$

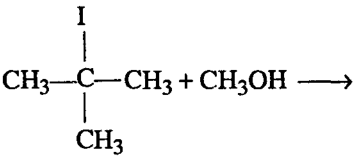
(ii)

39. Complete the following equations showing only major product and predict which reaction mechanism (SN1, SN2, E1, E2) is the most likely :

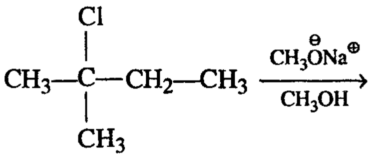
(a) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-Br + KI \xrightarrow{\text{Acetone}}$

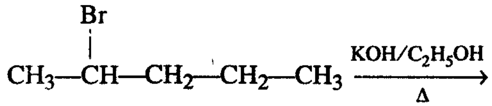
(b) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-Br + KOH \xrightarrow[\Delta]{C_2H_5OH}$

(c) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-Br + CH_3-CH_2-OH \xrightarrow{\Delta}$

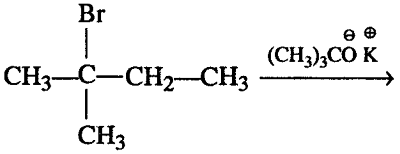
(d) 
$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{I}{|}}{C}}-CH_3 + CH_3OH \longrightarrow$

(e) $C_6H_5\overset{\ominus}{O} + CH_3-I \longrightarrow$

(f) 
$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_2-CH_3 \xrightarrow[CH_3OH]{CH_3\overset{\ominus}{O}Na^{\oplus}}$

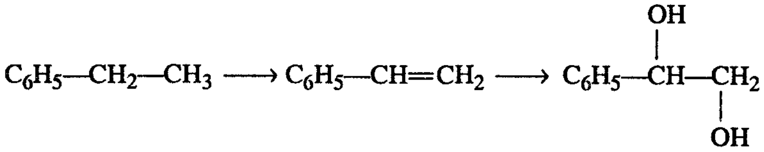
(g) 

$CH_3-\overset{Br}{CH}-CH_2-CH_2-CH_3 \xrightarrow[\Delta]{KOH/C_2H_5OH}$

(h) 

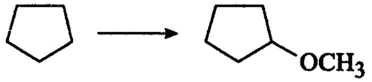
$CH_3-\underset{CH_3}{\overset{Br}{C}}-CH_2-CH_3 \xrightarrow{(CH_3)_3C\overset{\ominus}{O}\overset{\oplus}{K}}$

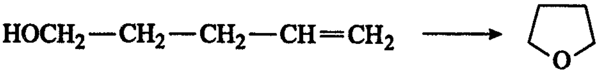
40. Using the given starting material and any necessary organic or inorganic reagents indicate how the desired compounds could be synthesised.

(a) 

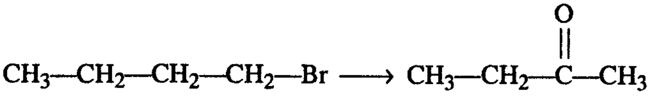
$C_6H_5-CH_2-CH_3 \longrightarrow C_6H_5-CH=CH_2 \longrightarrow C_6H_5-\overset{OH}{CH}-\underset{OH}{CH_2}$

(b) $CH_3-CH_2-CH=CH_2 \longrightarrow CH_2=CH-CH=CH_2$

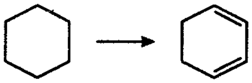
(c) 

(d) 

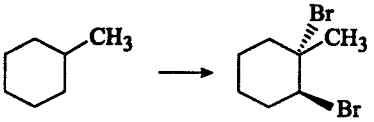
(e) $CH_3-CH_2-CH=CH_2 \longrightarrow CH_3-CH_2-CH_2-CH_2-NH_2$

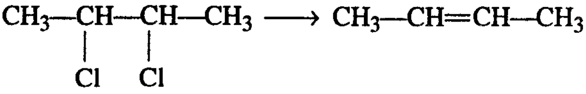
(f) 

$CH_3-CH_2-CH_2-CH_2-Br \longrightarrow CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

(g) 

(h) $CH_3-CH=CH-CH_3 \longrightarrow CH_3-C\equiv C-CH_3$

(I) 

(j) 

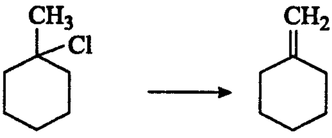
$CH_3-\underset{Cl}{CH}-\underset{Cl}{CH}-CH_3 \longrightarrow CH_3-CH=CH-CH_3$

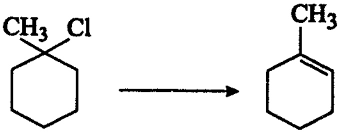
41. Two elimination products are obtained from the following E2 reaction :

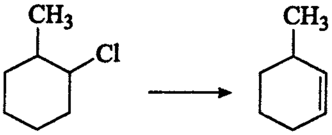
$$CH_3-CH_2-CHD-CH_2Br \xrightarrow[\Delta]{\overset{\ominus}{HO}}$$

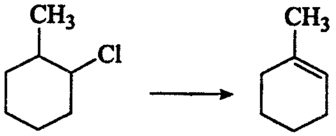
(a) What are the elimination products? (b) Which is formed in greater yield and why?

42. How these conversions can be performed

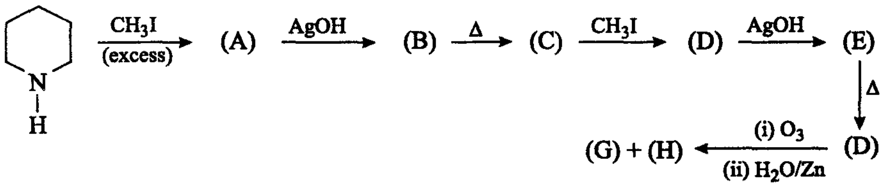
(a) 

(b) 

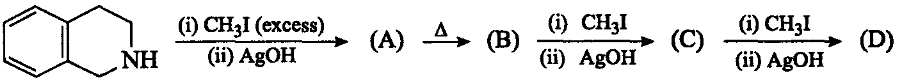
(c) 

(d) 

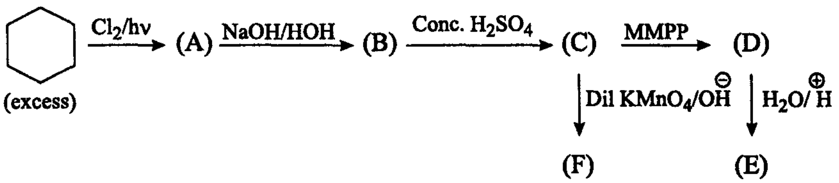
43. Identify A to H in the given reaction sequence :



44. Assign A to (D) in the given reaction sequence :



45. Identify A to F in the following series of reactions :



46. Two isomeric alkyl halides (A) and (B) C_3H_7Cl, on treatment with NaOH/HOH give two isomeric alcohols (C) and (D).

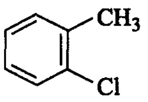
(C) gives yellow precipitate with I_2/NaOH but (D) does not. What will be structure of (A), (B), (C) and (D)?

48. A liquid (A) C_3H_7I was boiled with a solution of KOH in ethyl alcohol and a gas (B) was generated. When gas (B) was passed into concentrated HI, a liquid (C) was formed having MF C_3H_7I, but the boiling point of (A) and (C) was not the same. Identify (A), (B) and (C).

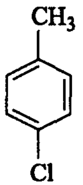
49. Compound (A) C_7H_{14} decolorises Br_2 in CCl_4. (A) on oxymercuration/demercuration gives optically active compound (B). (A) on ozonolysis gives the same compound (C) which is obtained by the oxidation of 3-hexanol with aluminium *ter*-butoxide. Identify (A), (B) and (C).

ANSWER TO VERY SHORT ANSWER QUESTIONS

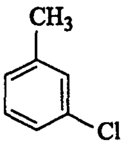
1.



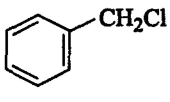
I



II



III



IV

Benzyl chloride (IV) has the weakest C—Cl bond.

2. $CH_2{=}CHCHClCH_3 > CH_3CH_2CH_2CH_2Cl > CH_2CH_2CHClCH_3$
3. Amongst isomeric alkyl halides, boiling points decrease as the branching increases. Thus : *n*-amyl chloride > isoamyl chloride > *tert*-amyl chloride > neoamyl chloride
4. III > I > IV > II
5. $CH_3Br > CH_3Cl > CH_3CH_2Cl > (CH_3)_2CHCl$
6. Cyclopentane

7. $CH_3CH_2OH \xrightarrow[\Delta]{H_2SO_4} CH_2{=}CH_2 \xrightarrow[CCl_4]{Br_2} BrCH_2{-}CH_2Br \xrightarrow{\text{alc. KOH}} \underset{\text{Vinyl bromide}}{BrCH{=}CH_2}$

8. Ethyl chloride reacts with $AgNO_3$ to give white precipitate of AgCl whereas vinyl chloride does not give this test.
$CH_3CH_2Cl + AgNO_3 + C_2H_5OH \longrightarrow AgCl\downarrow + CH_3CH_2OC_2H_5 + HNO_3$

9. $CCl_4 + 2HF \xrightarrow{SbF_5} \underset{\text{Freon-12}}{CCl_2F_2} + 2HCl$

10. It will decrease the dipole moment.

11. CH_3I because of its smallest carbon content and heaviest halogen.

12. $C_2H_5\overset{\ominus}{O} + CHCl_3 \rightleftharpoons :\overset{\ominus}{C}Cl_3 + C_2H_5OH$

$$:\overset{\ominus}{C}Cl_3 \xrightarrow{\text{slow}} \underset{\text{Dichlorocareone}}{:\overset{\bullet\bullet}{C}Cl_2} + \overset{\ominus}{Cl}$$

$$\overset{\bullet\bullet}{C}Cl_2 + 2C_2H_5\overset{\ominus}{O} \longrightarrow \overset{\bullet\bullet}{C}(OC_2H_5)_2 + 2\overset{\ominus}{Cl}$$

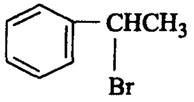
$$\overset{\bullet\bullet}{C}(OC_2H_5)_2 + C_2H_5OH \longrightarrow \underset{\text{Triethyl orthoformate}}{HC(OC_2H_5)_3}$$

13. Due to stronger $-I$ effect of F than Cl, CHF_3 should be more acidic than $CHCl_3$. But actually reverse is true. This is because $\overset{\ominus}{C}Cl_3$ left after the removal of a proton from $CHCl_3$ is more stabilised by resonance due to the presence of *d* orbitals in Cl but $\overset{\ominus}{C}F_3$ left after removal of a proton from CHF_3 is not stabilized by resonance due to the absence of *d* orbitals in F.

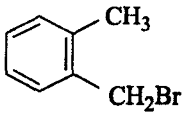
14. Chloroform gives carbylamine test whereas carbon tetrachloride does not give this test.

$$PhNH_2 + CHCl_3 + 3KOH \xrightarrow[\Delta]{\text{alcohol}} \underset{\substack{\text{Phenyl isocyanide}\\ \text{(Offensive odour)}}}{Ph\overset{\oplus}{N}{\equiv}\overset{\ominus}{C}} + 3KCl + 3H_2O$$

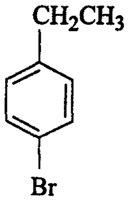
15. A is 1-bromo-1-phenylethane



B is *o*-methylbenzyl bromide



C is *p*-bromoethyl benzene

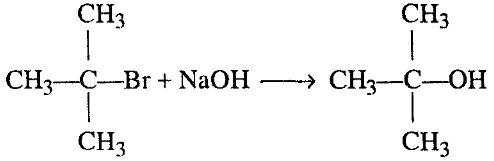


SOLUTIONS OF PROBLEMS

1. HOH is a weak nucleophile and $\overset{\ominus}{Cl}$ is not a good leaving group. So the nucleophilic substitution of ethyl chloride with water will be slow.

   $\overset{\ominus}{I}$ (from KI) is a powerful nucleophile, it displaces Cl to form $CH_3—CH_2—I$. Now I being a good leaving group, H_2O can displace it rapidly.

$$CH_3—CH_2—Cl \xrightarrow{KI} CH_3—CH_2—I \xrightarrow{HOH} CH_3—CH_2—OH$$

2. 

$$CH_3—\underset{CH_3}{\overset{CH_3}{C}}—Br + NaOH \longrightarrow CH_3—\underset{CH_3}{\overset{CH_3}{C}}—OH$$

   The above reaction follows SN1 pathway. We know that rate of an SN1 reaction increases with increasing ionising power of the solvent. Methanol has a dielectric constant of 33 and that of water is 80. Thus water is a better ionising solvent than methanol. So the rate of hydrolysis of tertiary butyl bromide increases largely when pure methanol is replaced by 50% aqueous methanol.

3. Chlorobenzene is an aromatic compound. It has delocalised *pi* electron clouds and it repels $\overset{\ominus}{OH}$. Furthermore, its Cl atom has $+R$ effect – a lone pair of electrons gets delocalised through lone pair, π conjugation. This gives the C—Cl bond a double bond character and thus the bond strength of C—Cl bond increases. This lowers the reactivity.

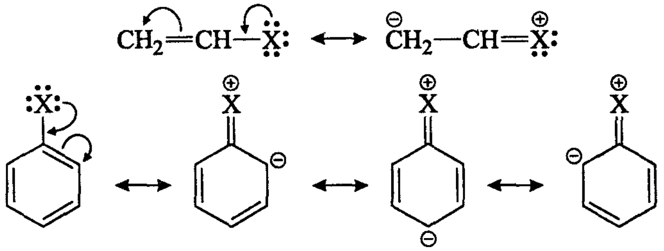
4. Organic halides give Ag*X* by SN reaction :

$$R—X + AgNO_3 \longrightarrow R—NO_3 + AgX\downarrow$$

   The above reaction is ionic reaction. Therefore, it requires the formation of halide ion from organic halides. The C—*X* bond of aryl halides as well as that of vinyl halides are very strong and hence very difficult to break heterolytically because of the following reasons :

   (i) The C—*X* bond is formed by sp^2-p overlap. This makes the bond shorter and stronger.

   (ii) The *p*-orbital electrons of the halogen atom get delocalised which gives the C—*X* bond some double bond character as shown below :



   Since halide ions do not form the said compounds, they do not precipitate silver halides.

5. Basicity is defined by the **equilibrium** constant for abstracting a proton. Thus basicity is the ability to remove $\overset{\oplus}{H}$ from an acid as represented quantitatively by the equilibrium constant. Basicity of nucleophile determines the thermodynamics of the reaction.

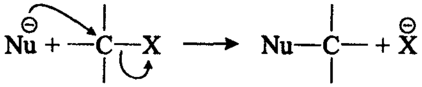
$$\overset{\bullet\bullet}{B} + H—A \overset{K\text{ equil.}}{\rightleftharpoons} B—\overset{\oplus}{H} + \overset{\ominus}{A}$$

$$K_b = \frac{[\overset{\oplus}{BH}]\,[\overset{\ominus}{A}]}{[B]\,[HA]}$$

Basicity ∝ K_b

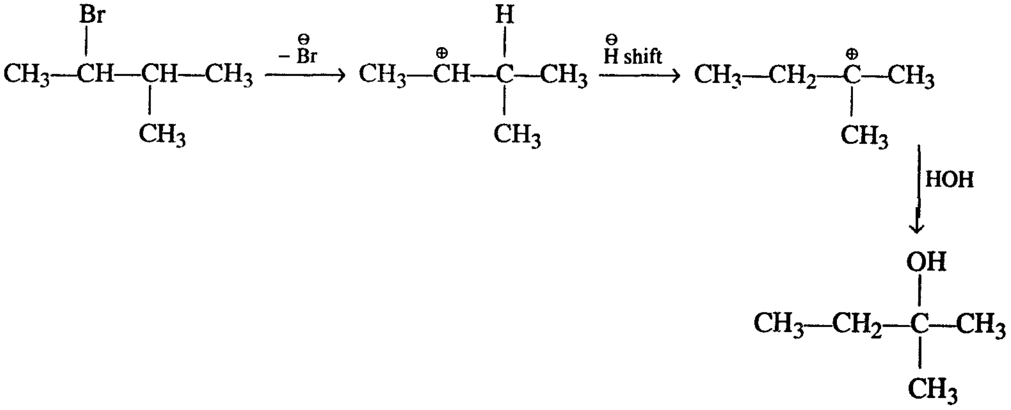
Nucleophilicity is defined by the rate of attack on an electrophilic carbon atom. Thus nucleophilicity influences the rate of the reaction as reflected by the rate constant (Kr).

In both cases the nucleophile (or base) forms a new covalent bond. If the new bond is to a proton, it has reacted as a base; if the new bond is to carbon, it has reacted as nucleophile.

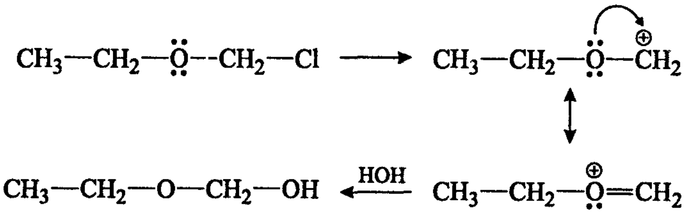


Nucleophilicity ∝ Kr

6. During an SN1 hydrolysis, ionisation produces a secondary carbocation which rearranges here by a hydride shift to more stable tertiary carbocation that reacts with HOH to form the product.

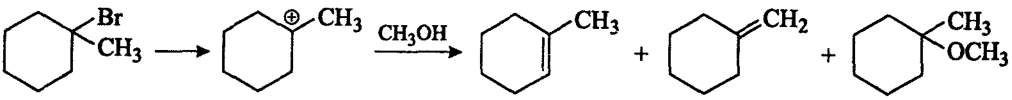


7. The rapidity of this SN1 reaction is attributed to the stability of a carbocation bonded to $-\ddot{\underset{\cdot\cdot}{O}}-$. The empty p-orbital of $\overset{\oplus}{C}$ can overlap sidewise with a filled p atomic orbital on oxygen thereby delocalising and stabilising the positive charge.



Highly stable because octet of all the atoms are complete

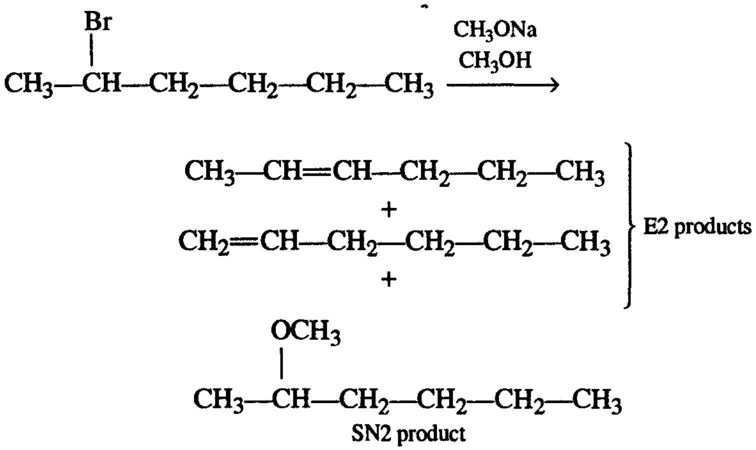
8. (a) There is no stronger base or nucleophile present, so this reaction must be first order, with an ionisation of the alkyl halide as the slow step. Deprotonation of the carbocation gives either of two elimination products, and nucleophile attack gives a substitution product.



Elimination products

Substitution product

(b) This reaction takes place with a strong base, so it is bimolecular reaction. This secondary halide can undergo both SN2 and E2 reactions. Both product will be formed with the relative proportions depending on the reaction conditions.



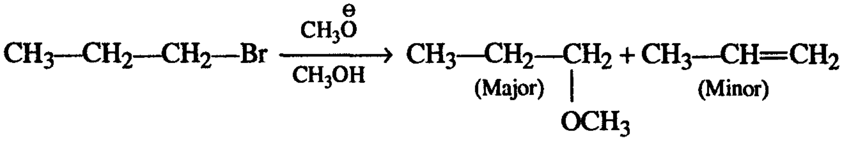
$$CH_3-\overset{\overset{Br}{|}}{C}H-CH_2-CH_2-CH_2-CH_3 \xrightarrow[CH_3OH]{CH_3ONa}$$

$$\left.\begin{array}{c} CH_3-CH=CH-CH_2-CH_2-CH_3 \\ + \\ CH_2=CH-CH_2-CH_2-CH_2-CH_3 \\ + \end{array}\right\} \text{E2 products}$$

$$CH_3-\overset{\overset{OCH_3}{|}}{C}H-CH_2-CH_2-CH_2-CH_3$$

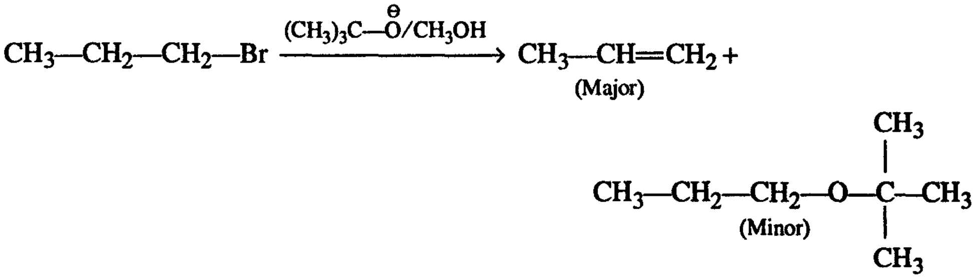
SN2 product

9. (a) The substrate is primary halide. The base/nucleophile is $CH_3\overset{\ominus}{O}$; a strong base (but not a bulky one) and a good nucleophile. Thus reaction will be SN2.



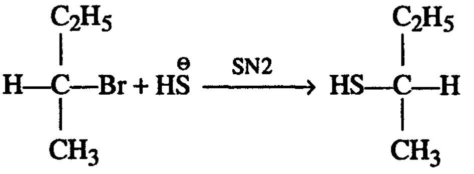
$$CH_3-CH_2-CH_2-Br \xrightarrow[CH_3OH]{CH_3\overset{\ominus}{O}} \underset{(Major)}{CH_3-CH_2-\underset{\underset{OCH_3}{|}}{CH_2}} + \underset{(Minor)}{CH_3-CH=CH_2}$$

(b) The substrate is primary halide. The base/nucleophile is a strong bulky base. Therefore, main reaction will be E2.



$$CH_3-CH_2-CH_2-Br \xrightarrow{(CH_3)_3C-\overset{\ominus}{O}/CH_3OH} \underset{(Major)}{CH_3-CH=CH_2} + \underset{(Minor)}{CH_3-CH_2-CH_2-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3}$$

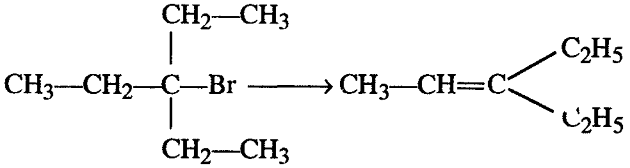
(c) The reactant is 2° alkyl halide and leaving group is attached to a stereocentre. The base/nucleophile is $H\overset{\ominus}{S}$, a strong nucleophile but a weak base. Thus reaction will be mainly SN2 causing an inversion of configuration at the stereocentre.



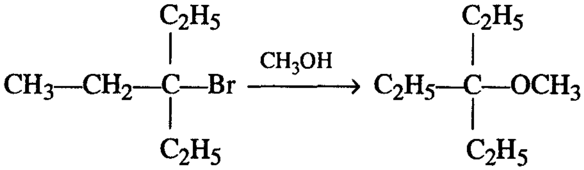
$$H-\underset{\underset{CH_3}{|}}{\overset{\overset{C_2H_5}{|}}{C}}-Br + H\overset{\ominus}{S} \xrightarrow{SN2} HS-\underset{\underset{CH_3}{|}}{\overset{\overset{C_2H_5}{|}}{C}}-H$$

Inversion of configuration

(d) The base/nucleophile is $\overset{\ominus}{O}H$, a strong base and strong nucleophile. However, the substrate is 3° halide. Therefore, the reaction will be elimination. At this higher temperature and in the presence of a strong base the reaction will not be SN1.



(e) This reaction is an example of solvolysis. The only base/nucleophile is the solvent which is a weak base. At this lower temperature the reaction will be mainly SN1.



$$CH_3-CH_2-\underset{C_2H_5}{\overset{C_2H_5}{C}}-Br \xrightarrow{CH_3OH} C_2H_5-\underset{C_2H_5}{\overset{C_2H_5}{C}}-OCH_3$$

10. Both the reactions are nucleophilic substitution reactions. Depending on the nature of alkyl group the reaction may be SN1 or SN2.

When the reagent is KCN, the nucleophile is the cyanide ion $\overset{\ominus}{C}{\equiv}\overset{\bullet\bullet}{N}$; it is an ambident nucleophile, it can attack on electrophile using its lone pair of electrons either on the carbon or on the nitrogen atom. Since carbon is stronger nucleophile (it is less electronegative than nitrogen) than the nitrogen nucleophile, the nucleophilic attack occurs mostly through the carbon atom and hence alkyl cyanide is the major product.

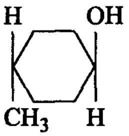
AgCN is the covalent compound, so when AgCN is the reagent, the nucleophilic attack can only occur through the nitrogen atom. Thus alkyl isocyanide is almost the sole product. Sparingly soluble AgCN gives a trace amount of cyanide ion : this in turn gives rise to trace amount of alkyl cyanide.

$$\underset{\text{Solid}}{AgCN} \qquad \underset{\text{In solution}}{AgCN} \qquad \overset{\oplus}{Ag} + \overset{\ominus}{CN}$$

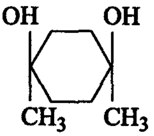
11. (a) (A); (b) (B); (c) (A); (d) (B); (e) (A); (f) (A).

12. (a) C > A > B > D (b) C > B > A > D

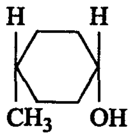
13. (i) (a)



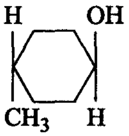
(b)



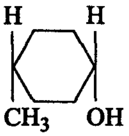
(c)



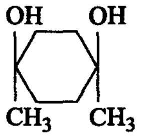
(ii) (a)



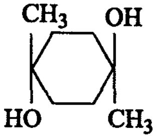
and



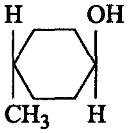
(b)



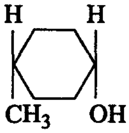
and



(c)



and



14. (a) I will be more reactive than II because steric strain in TS of I is less than the II.
    (b) IV will be more reactive than III because of the leaving power of leaving group.
    (c) VI will react more readily than the V because of the steric strain.
    (d) VII will react more readily than VIII because of the crowding around α-carbon.

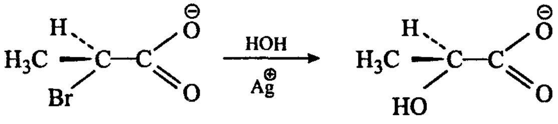
15. SN2 reaction is favoured by
    (i) Concentration of nucleophile and substrate. (ii) Stronger nucleophile.
    (a) Reaction (1) because ethoxide ion is a stronger nucleophile than ethanol.
    (b) Reaction (2) because triphenyl phosphine is a stronger nucleophile.
    (c) Reaction (2) because the concentration of nucleophile is twice than that of reaction (1).

16. Solution :
    (i) Strong base such as $R\overset{\ominus}{O}$ and higher temperature will favour elimination reaction.
    (ii) For substitution reaction, the nucleophile should be weak and neutral (say HOH or *R*OH) and the reaction should be carried out at low temperature. Under these conditions elimination is minimised.

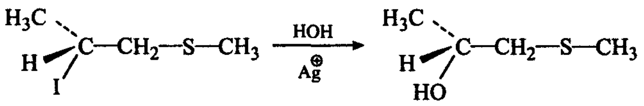
17. Although neopentyl bromine is a primary alkyl halide, the alkyl group attached to the head carbon atom is very bulky. The steric hundrance in the transition state is considerable. Therefore, the *Eac* is high and the rate is slow.

18. (a) $CH_3—Cl + CH_3\overset{\ominus}{O} \longrightarrow CH_3—O—CH_3 + \overset{\ominus}{Cl}$
    (b) $CH_3—I + \overset{\ominus}{Cl} \longrightarrow CH_3—Cl + \overset{\ominus}{I}$
    (c) $CH_3—CH_2—I + \underset{\text{(excess)}}{PH_3} \longrightarrow CH_3—CH_2—PH_2$
    (d) $CH_3—O—SO_2CH_3 + CH_3—CH_2—\overset{\ominus}{O} \longrightarrow CH_3—O—CH_2—CH_3 + CH_3—\overset{\ominus}{SO_3}$
    (e) $CH_2{=}CH—CH_2—Br + \overset{\ominus}{C}H_2—CH{=}CH \longrightarrow CH_2{=}CH—CH_2—CH_2—CH{=}CH_2$

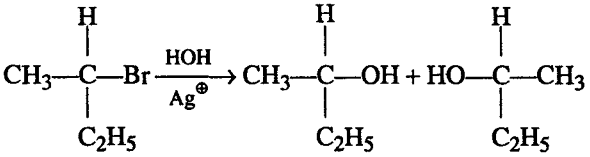
19. (a) Substrate has heteroatom on β-carbon with respect to the leaving group. Thus this reaction is an example of SN2 reaction which proceeds with neighbouring group participation. Thus there is retention of configuration.



(b) This reaction is also an example of neighbouring group participation, hence there is retention of configuration.

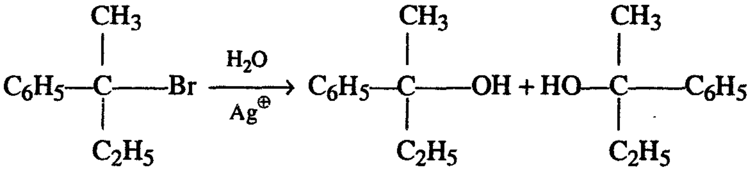


(c) SN1 reaction, hence retention as well as inversion of configuration.



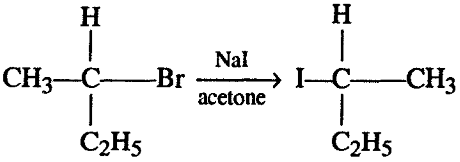
$$CH_3-\underset{C_2H_5}{\overset{H}{C}}-Br \xrightarrow[Ag^{\oplus}]{HOH} CH_3-\underset{C_2H_5}{\overset{H}{C}}-OH + HO-\underset{C_2H_5}{\overset{H}{C}}-CH_3$$

(d) SN1 reaction, hence retention as well as inversion of configuration.



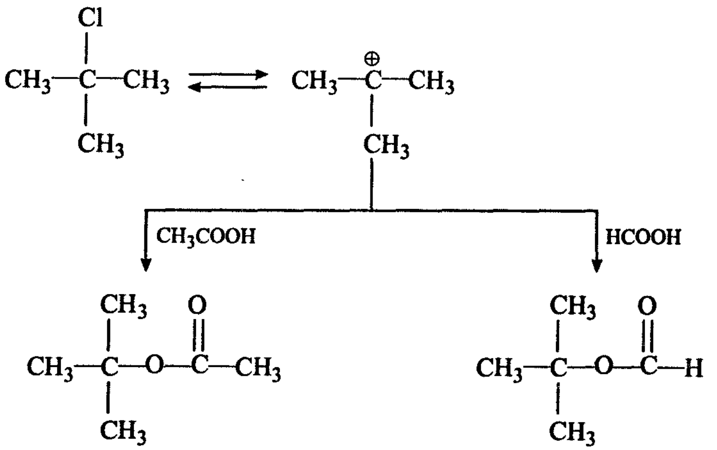
$$C_6H_5-\overset{CH_3}{\underset{C_2H_5}{C}}-Br \xrightarrow[Ag^{\oplus}]{H_2O} C_6H_5-\overset{CH_3}{\underset{C_2H_5}{C}}-OH + HO-\overset{CH_3}{\underset{C_2H_5}{C}}-C_6H_5$$

(e) Reaction is SN2, hence only inversion in configuration.



$$CH_3-\overset{H}{\underset{C_2H_5}{C}}-Br \xrightarrow[\text{acetone}]{NaI} I-\overset{H}{\underset{C_2H_5}{C}}-CH_3$$

20. (a) The SN1 solvolysis products result from attack of the respective solvent molecules on the carbocation intermediate.



Tert-butylacetate *Tert*-butylformate

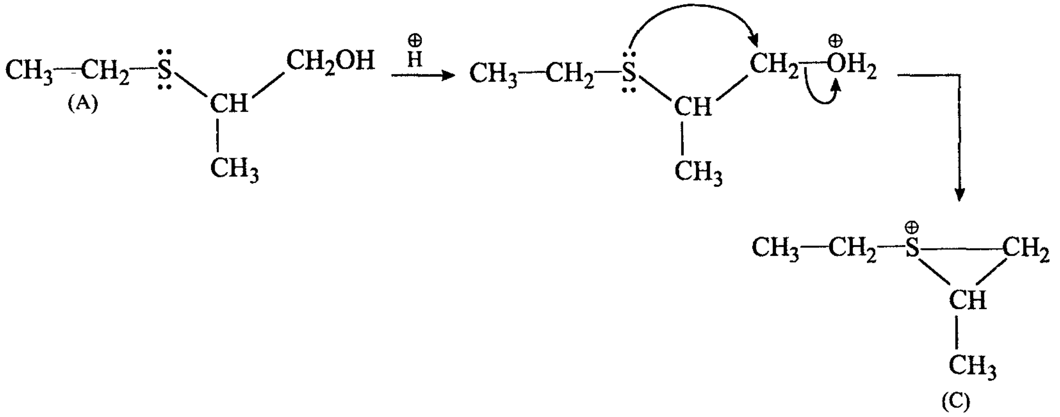
(b) The reaction is faster in formic acid, because its higher dielectric contant promotes the fomation of carbocation.

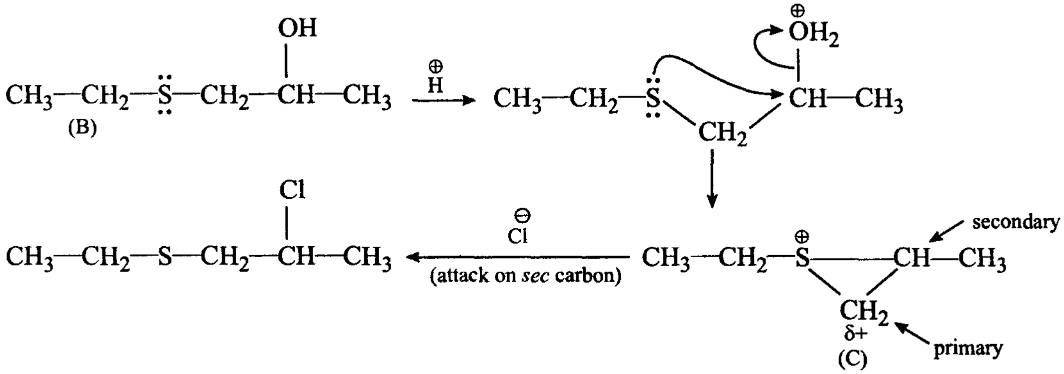
21. In this reaction iodide ion behaves as catalyst.

In methanol (polar protic solvent), the iodide ion is an excellent nucleophile and at the same time it is very good leaving group. Hence this iodide ion reacts rapidly with methyl bromide to give methyl iodide. The methyl iodide then reacts slowly with the methanol in a slow SN2 solvolysis reaction.

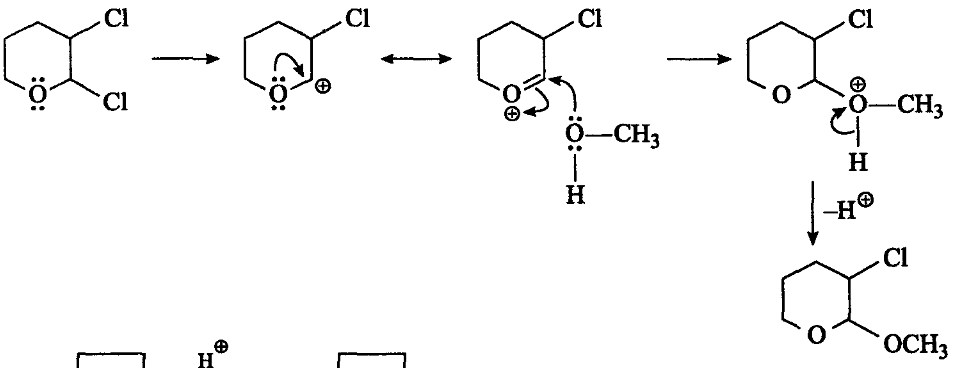
$$\overset{\ominus}{I} + CH_3-Br \xrightarrow[\text{iodide ion disappears rapidly}]{\text{faster}} CH_3-I + \overset{\ominus}{Br} \xrightarrow[CH_3OH]{\text{Slow step iodide ion reappears slowly}} CH_3-O-CH_3 + \overset{\ominus}{I}$$

22. Both of these alcohols form the same intermediate due to the neighbouring group participation by S. Due to this reason both give the same product.

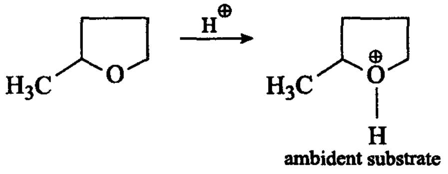




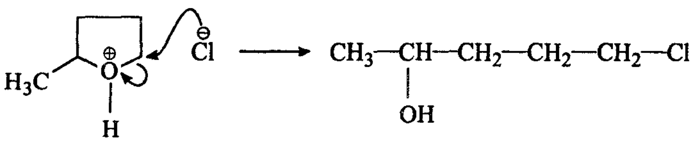
23. (a) The compound has two leaving groups-both secondary chloride. The one that leaves is next to oxygen by SN1 mechanism because halides having heteroatom at α carbon is excellent substrate for SN1 reactions.



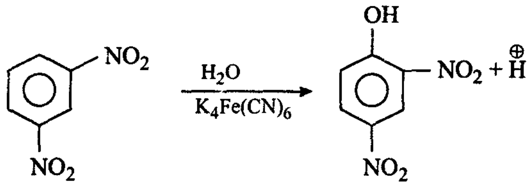
(b)



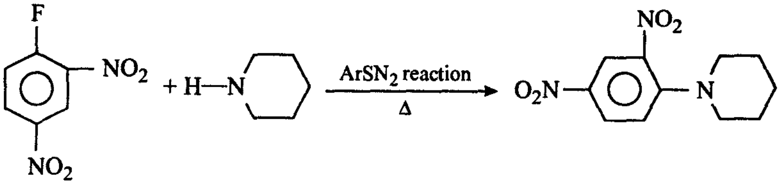
Chloride ion can attack at a primary or a secondary carbon. Since the reaction is SN2. The attack will be at primary carbon.


H₃C
H
Cl
CH₃—CH—CH₂—CH₂—CH₂—Cl
OH

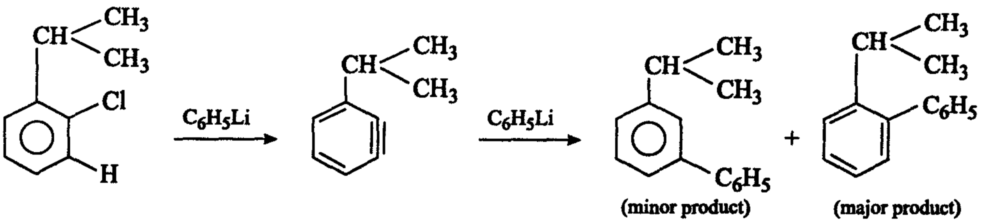
24. (a)


NO₂
NO₂
H₂O
K₄Fe(CN)₆
OH
NO₂ + H
NO₂

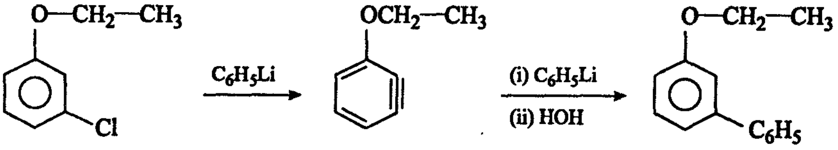
(b)


F
NO₂
NO₂
+ H—N
ArSN₂ reaction
Δ
NO₂
O₂N
N

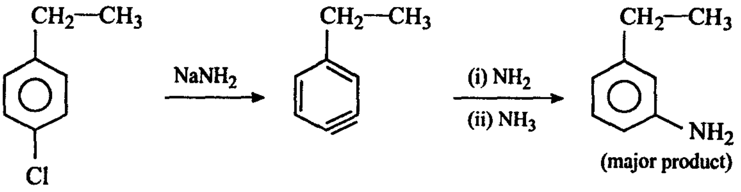
(c)


CH
CH₃
CH₃
Cl
H
C₆H₅Li
C₆H₅Li
C₆H₅
(minor product)
+
(major product)

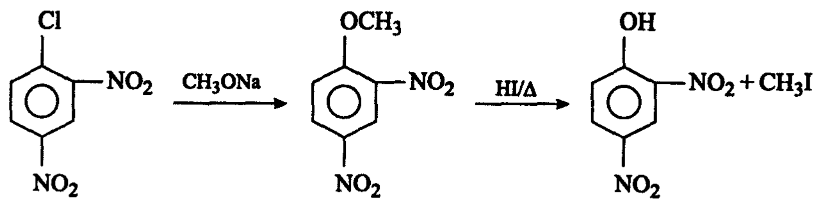
(d)


O—CH₂—CH₃
Cl
C₆H₅Li
OCH₂—CH₃
(i) C₆H₅Li
(ii) HOH
C₆H₅

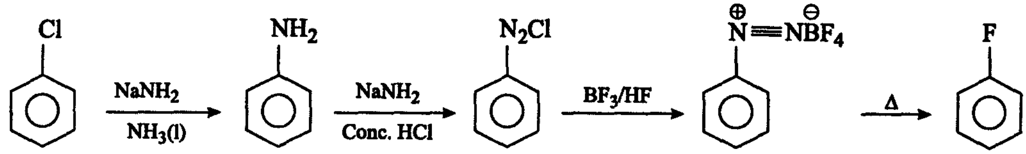
(e)


CH₂—CH₃
Cl
NaNH₂
(i) NH₂
(ii) NH₃
NH₂
(major product)

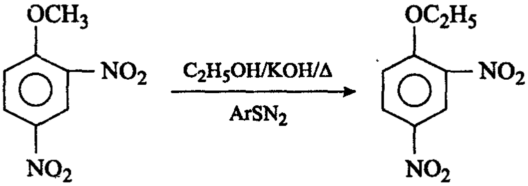
(f)


Cl
NO₂
NO₂
CH₃ONa
OCH₃
HI/Δ
OH
NO₂ + CH₃I

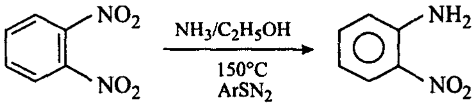
(g)


Cl
NaNH₂
NH₃(l)
NH₂
NaNH₂
Conc. HCl
N₂Cl
BF₃/HF
N≡NBF₄
Δ
F

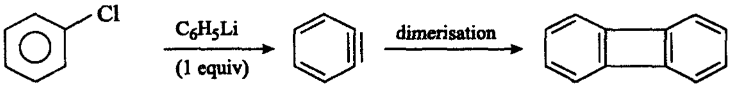
25. (a)


OCH₃
NO₂
NO₂
C₂H₅OH/KOH/Δ
ArSN₂
OC₂H₅
NO₂
NO₂

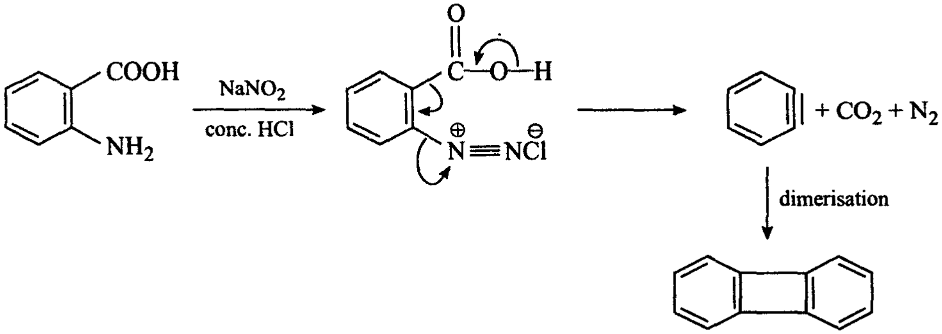
(b)


NO₂
NO₂
NH₃/C₂H₅OH
150°C
ArSN₂
NH₂
NO₂

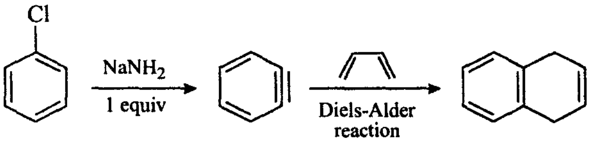
(c)


Cl
C₆H₅Li
(1 equiv)
dimerisation

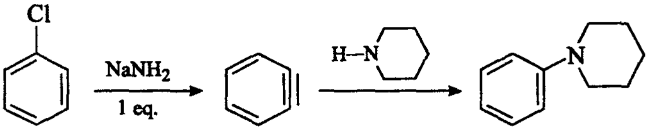
(d)


COOH
NH₂
NaNO₂
conc. HCl
O
C
O
H
N
NCl
+ CO₂ + N₂
dimerisation

(e)


Cl
NaNH₂
1 equiv
Diels-Alder
reaction

(f)


Cl
NaNH₂
1 eq.
H–N
N

INDEX

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