Electrophile and Nucleophile.

Electrophile ⇒ Electron loving species.
have a deficiency of electrons

Electrophile may be positive and neutral species.
eg CH_2^+, CH_3^+, E^+ attack on high e^- density.

Nucleophile ⇒ nucleus loving species.
Nucleophile attack on low electron density.

Nucleophile may be negative and neutral.

⇒ All nucleophile are bases but all bases are not nucleophile.

eg ⇒ Cl^-, Br^-, I^-.

Reaction intermediates. ← Carbocation (+)
Carbonion (-)
Carbene

Carbene

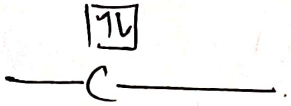
Carbon having two bond pair and 2 non-bonding electrons called Carbene.

⇒ 

 (dichlorocarbene).

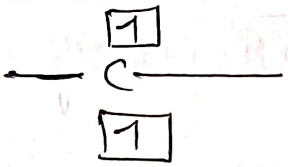
Carbene.

Singlet Carbene.



both e⁻ are in same orbital hence more Repulsion and less stability.

Triplet Carbene.



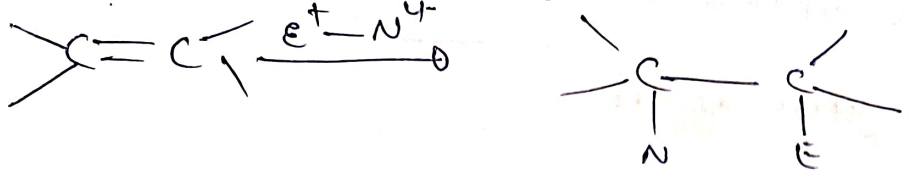
both e⁻ are in different orbital hence more less repulsion leads to more stability.

Types of Reaction.

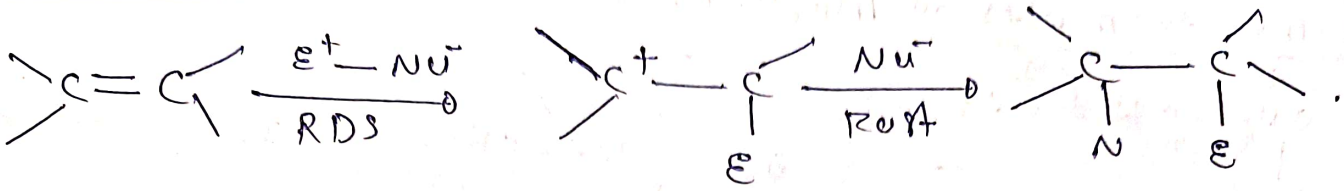
- Addition
  - Ionic addition.
    - Electrophilic Addition R
    - nucleophilic addition Reaction.
  - Free radical addition
- Substitution
  - Ionic subs.
    - ESR
    - NSR
  - Free Radical substion
- ~~Free Radical~~ Elimination.

Electrophilic Addition Reaction.

⇒ Alkene and Alkyne give EAR.



Mechanism:



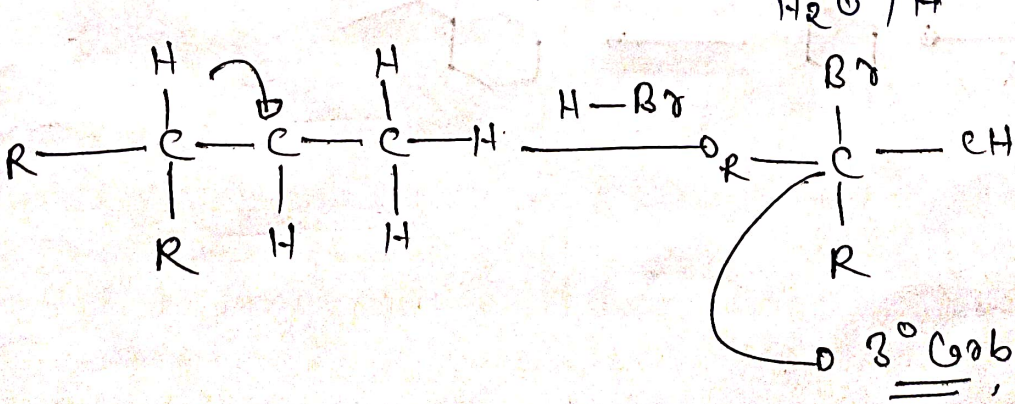
- The first step is slow step called RDS step.
- The second step is Fast step.
- The Carbocation is formed as Reaction intermediate
- order of Reaction is 2.

Application of EAR ⇒ Markovnikov Rule.

According to rule when a unsymmetric alkene is attack by unsymmetrical reagent than a negative part of reagent attached to carbon which have less hydrogen present. (i.e. attach to Carbocation).

3° > 2° > 1° ⇒ order of stability of Carbocation

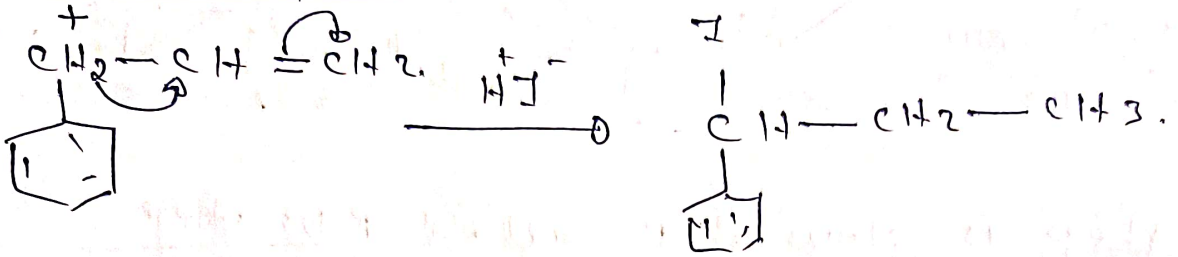
unsymmetric reagent ⇒ (H — X) (X = Cl, Br, I)



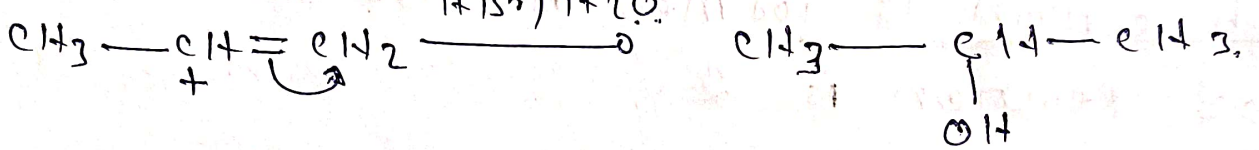
when unsymmetric reagent with H_2O_2 present then Anhmarkouniko ruled out.

and called as **Peroxide effect**.

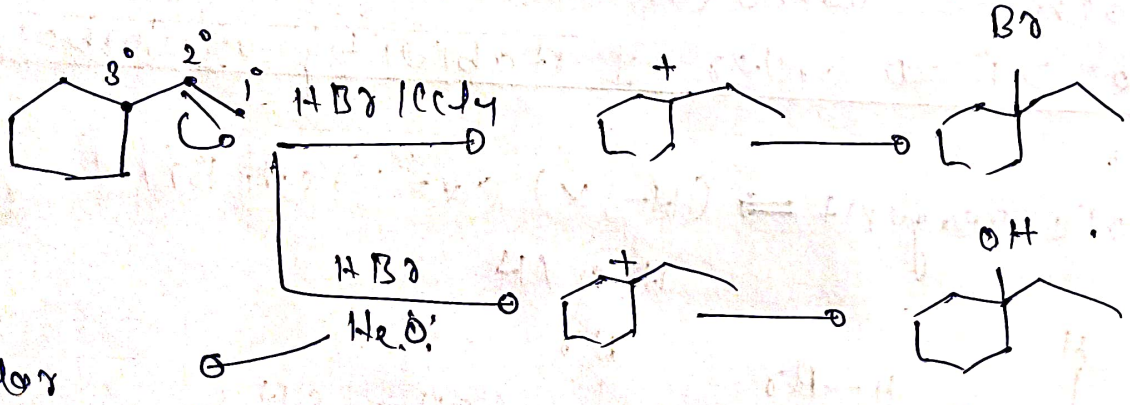
Some examples of Markouniko.



note:-



when addition of HX in alkene is take by polar protic solvent (CH_3OH, C_2H_5OH etc then solvation of (X^-) takes place that decreases the ionic mobility leads to decrease its nucleophilicity.



Polar Protic sol
Hence have
HX + PPS → OH added on Rakle Carbocation.

Note:
when cis alkene reacts with Anti-reagent form Rasmic mixture. and react with syn reagent form meso.

note:-

mesocompound. ⇒ Compound which have more than one chiral carbon but have no optical activity.

syn reagent ⇒ H_2/Ni, $KMnO_4/OH^-$

Anti reagent ⇒ X_2/CCl_4, HOX, ICl

Peroxide effect. ⇒ Application of free Radical Addition Reaction.

① Myo khorouch effect.

② Product form is Anti-Markouniko Product.

③ Here negative part of reagent attach to that carbon which have more number of ~~Carbon~~ Hydrogen.

④ H_2O_2/HX mainly present in reagent.

eg $R-CH=CH_2 \xrightarrow{HBr/R-O-O-R} R-CH_2-CH_2-Br$

(H added)

Mech.

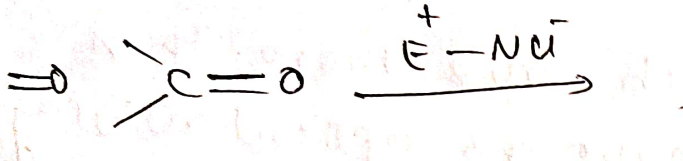
$R-O-O-R \longrightarrow 2R-O^{\cdot}$

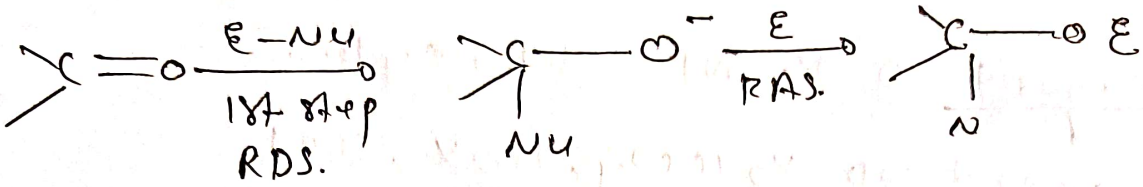
$R-O^{\cdot} + H-Br \longrightarrow R-O-H + Br^{\cdot}$

$Br^{\cdot} + R-CH=CH_2 \longrightarrow R-CH_2-CH_2-Br.$

⇒ Nucleophilic Addition Reaction (NAR).

⇒ in Aldehyde and ketone mainly.

⇒ 

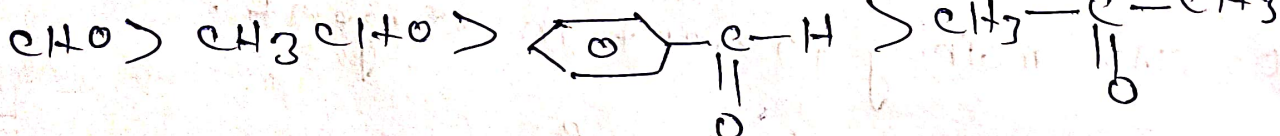
Mec:- 

(1) NAR is 2 step reaction in which 1st step is slow and second step is fast step.

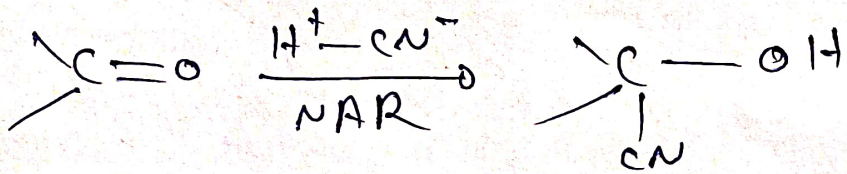
(2) order of Reaction is 2.

note:-

All Aldehyde are more reactive than ketone towards NAR.

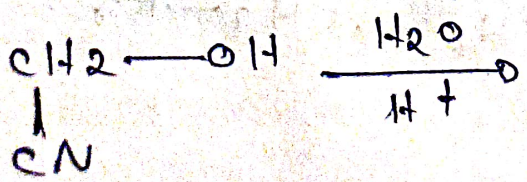


(1) Addition of HCN.



note:-

eg CN on Hydrolysis gives COOH.

⇒ 

$\Rightarrow$ $H-CH=O \xrightarrow{HCN^-} H-\underset{CN}{\underset{|}{CH}}-OH$

The addition of HCN is nucleophilic addition reaction on hydrolysing the CN it hydrolyse to COOH

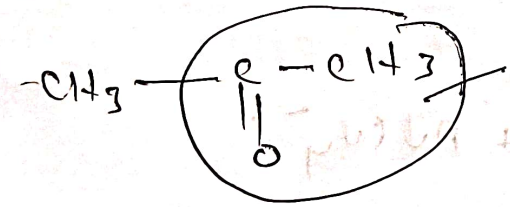
$\xrightarrow[H^+]{H_2O}$ CH_2-OH | $COOH$.

$\Rightarrow$ $CH_3-CH=O \xrightarrow[(NAR).]{HCN.} CH_3-\underset{CN.}{\underset{|}{CH}}-OH \xrightarrow[H^+]{H_2O} R-\underset{COOH}{\underset{|}{C}}-OH.$

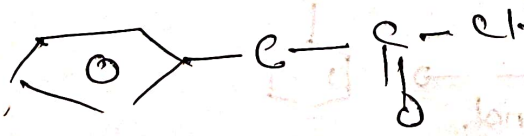
Carbonyl Test.

$\Rightarrow$ This test is only given by ~~on~~ aliphatic methyl ketone and All aldehyde.

The word aliphatic note that ketone should not with Benzene. only methyl attach to ketone.



aliphatic methyl ketone. it give Carbonyl test.



$\rightarrow$ × because Benzene present with aliphatic ketone.

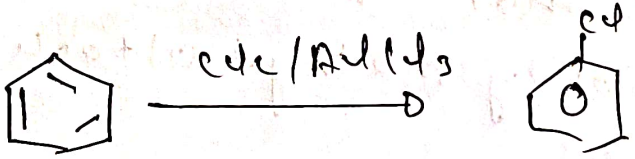
Electrophilic substitution Reaction.

G ⇒ e⁻ donating group. ⇒ ortho / para.

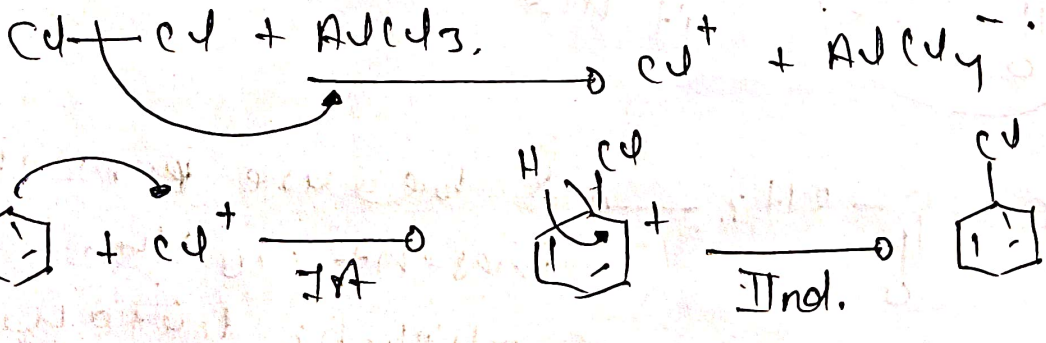
if G ⇒ e⁻ withdrawing group.
↳ meta director.

ESR
- Halogination.
- sulphonification.
- Nitration.
- Friedal craft Alkylation.
  Acylation Reaction.

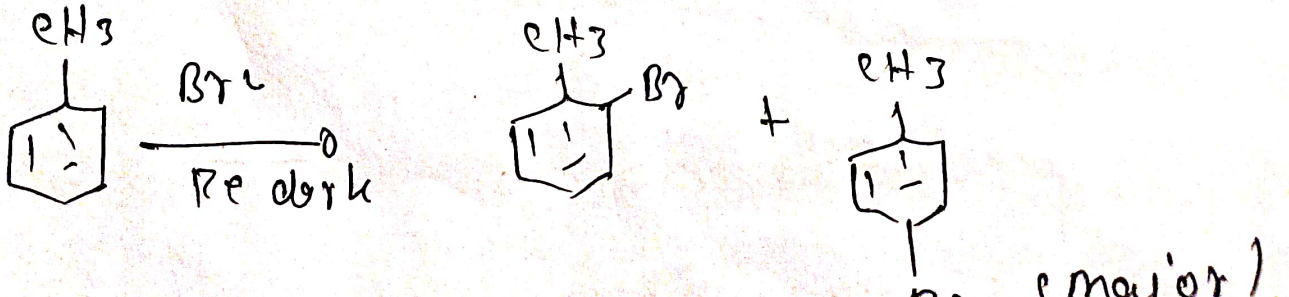
Halogination. ⇒ Addition of Halogen occur Here on Ring in presence of $CuCl_2$ / $AlCl_3$.

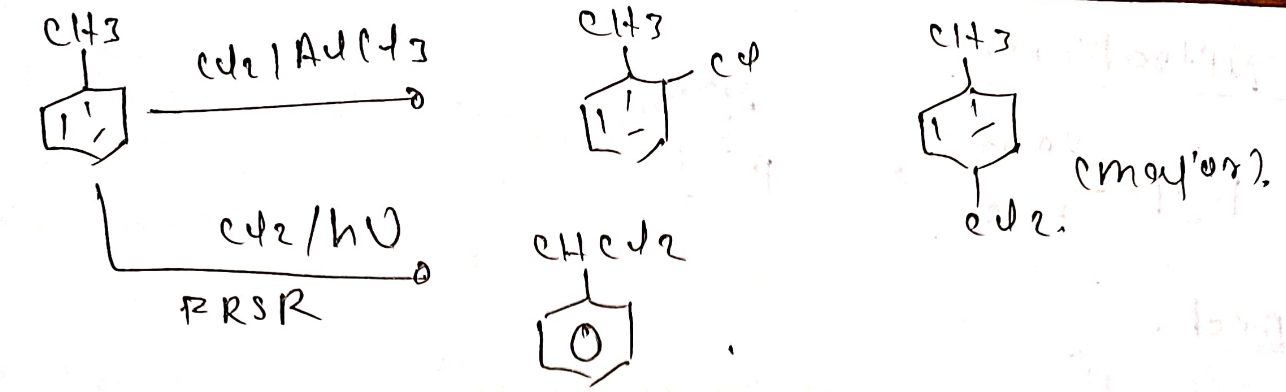


Mech:-

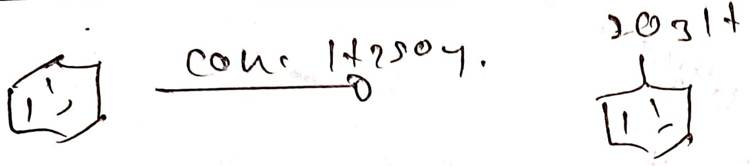


Eg.

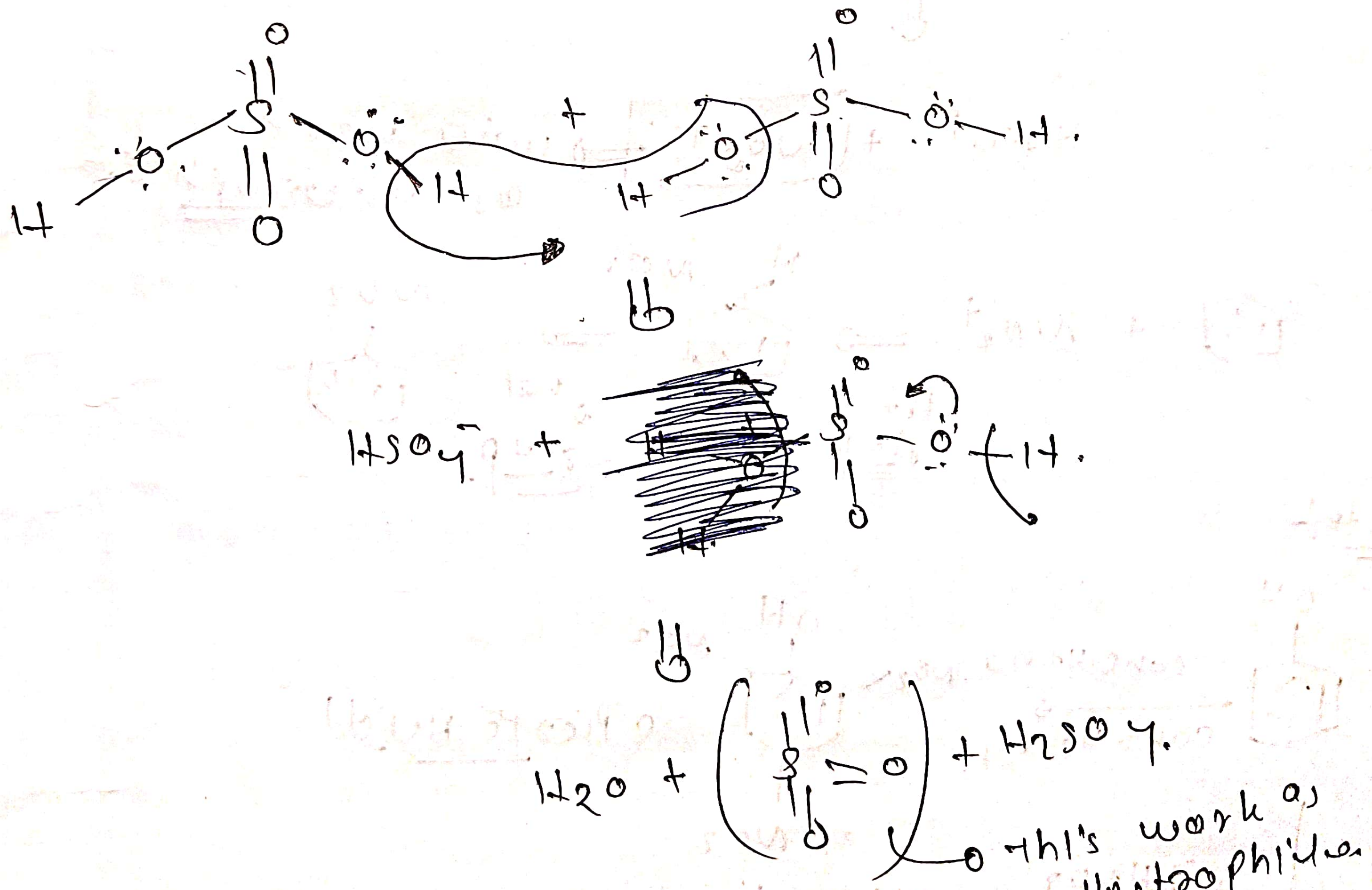


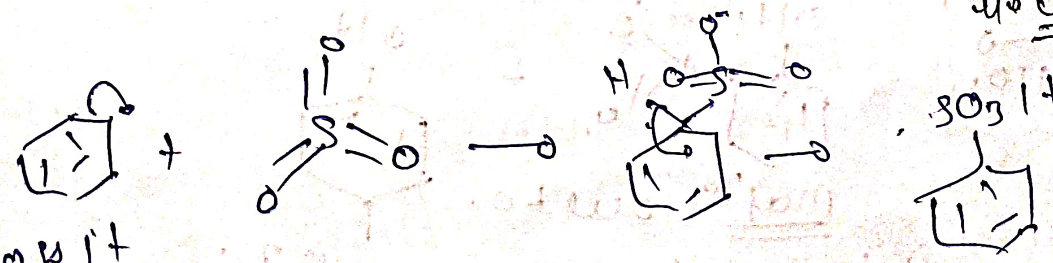


Sulphonation.



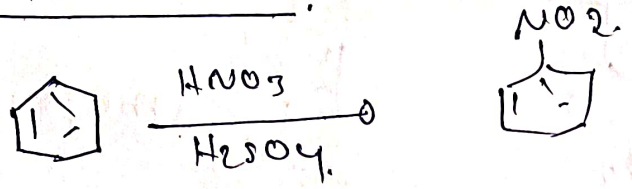
Mech.



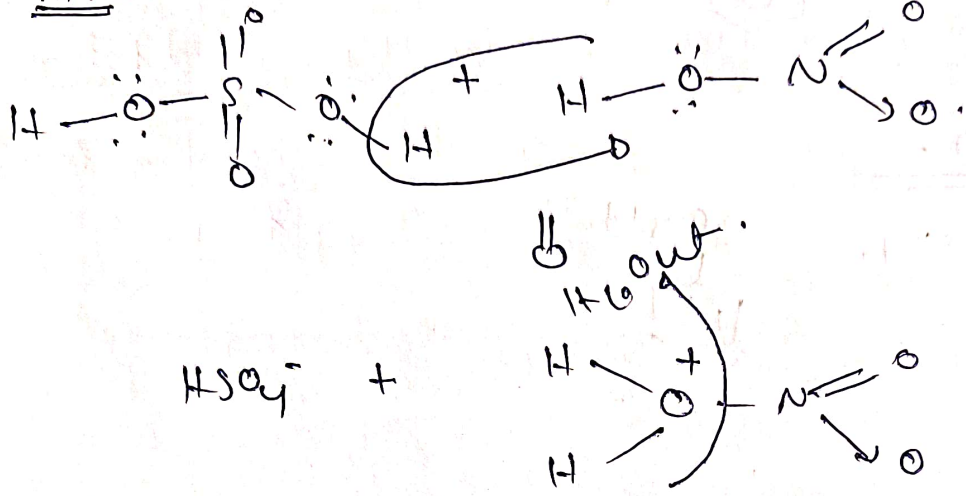


(doesn't Aromaticity)

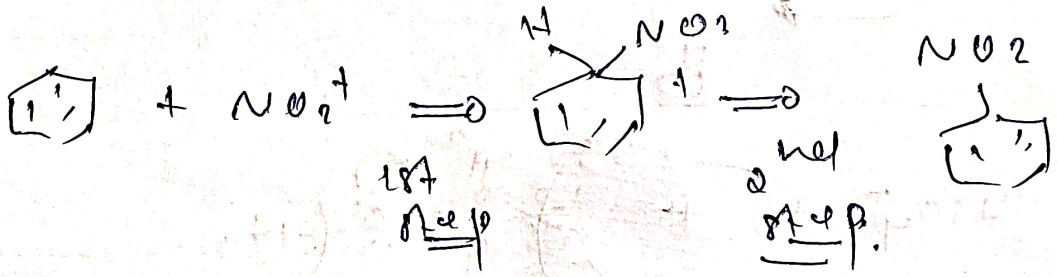
Nitration.



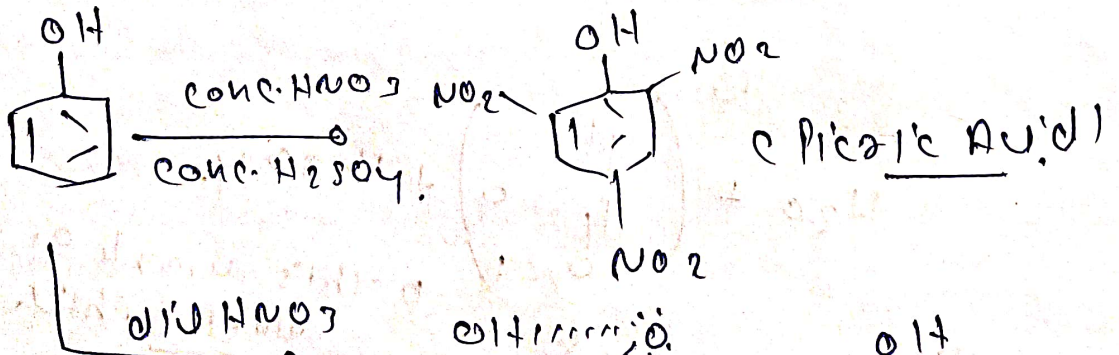
mech.



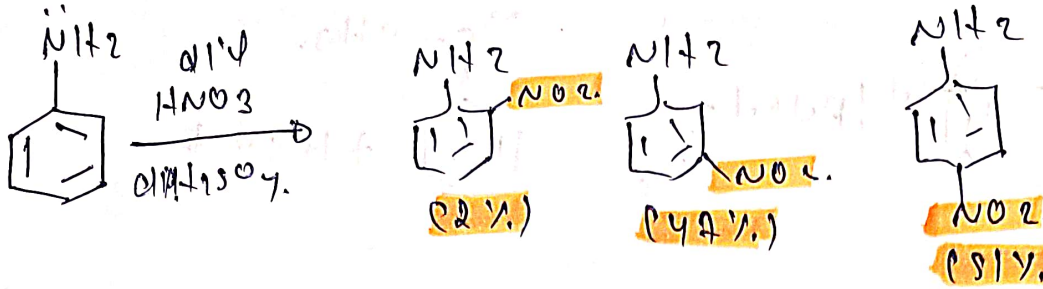
$HSO_4^+ + NO_2^+$ ⟹ will work as electrophile



note:-



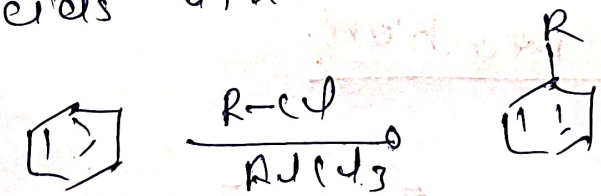
⟹ o-nitrophenol



⇒ because Here Anilinium ion form which is meta directing. so 47% NH2 form.

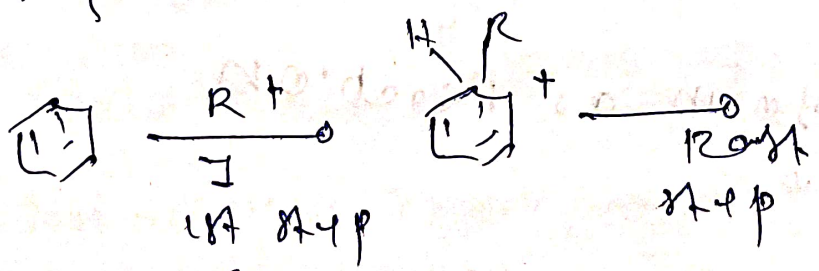
but. Para form (51%) because inductive effect do not work after 3 atom due to I-effect is distance dependence.

Friedal craft ⇒ Alkylation and Acylation takes place in presence of lewis. Acids like $AlCl_3$, $FeCl_3$.

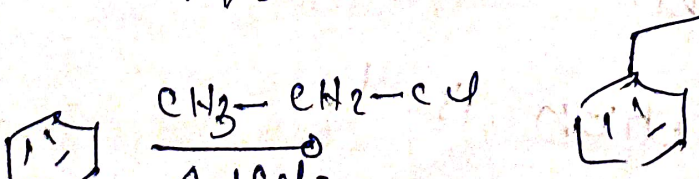


Mech:

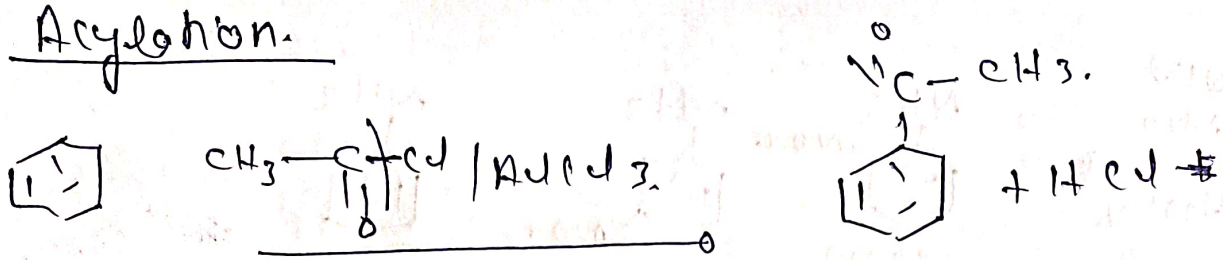
$$R\text{–}Cl + AlCl_3 \longrightarrow R^+ + AlCl_4^{\ominus}$$



Eg

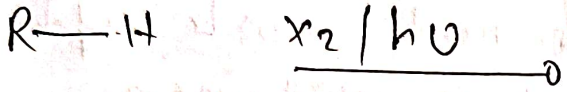


Acylation.



FREE Radical substitution Reaction. (FRSR)

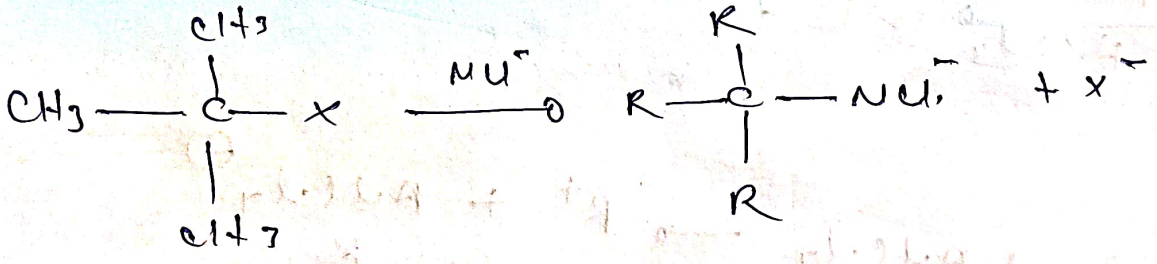
⇒ Alkanes are non-polar so they give FRSR.



mech. — initiation.
- Propagation. ⇒ (R') form.
- termination.

order ⇒ 3° > 2° > 1°.

Nucleophilic substitution Reaction.



⇒ Carbocation form as Reaction intermediate.

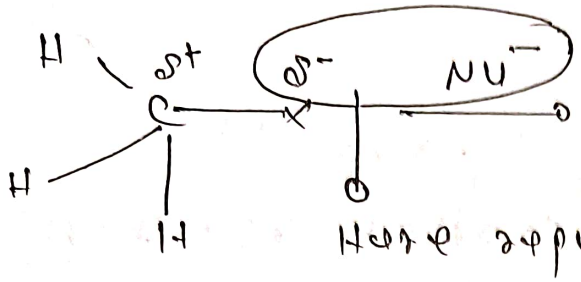
⇒ 2 step Reaction.

⇒ order of Reaction is 1.

⇒ Carbocation rearrangement takes place.

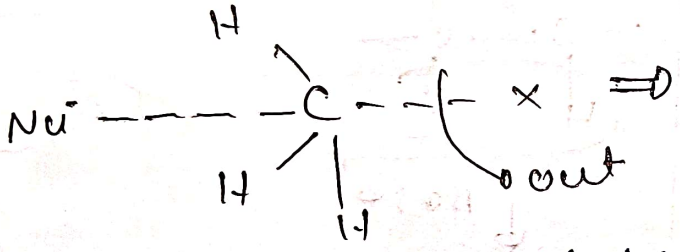
$\Rightarrow CH_3-X \xrightarrow[\text{Aceton.}]{Nu^-} Nu-CH_3.$

Here SN2 will followed.

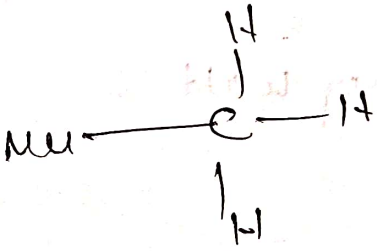


Here repulsion took place if Nu attack on carbon directly.

then. Nu^- attack on back side.



transition state).



(walden inversion).

$\Rightarrow$ SN2 is a single step reaction.

$\Rightarrow$ order of reaction is 2.

$\Rightarrow$ molecularity = 2.

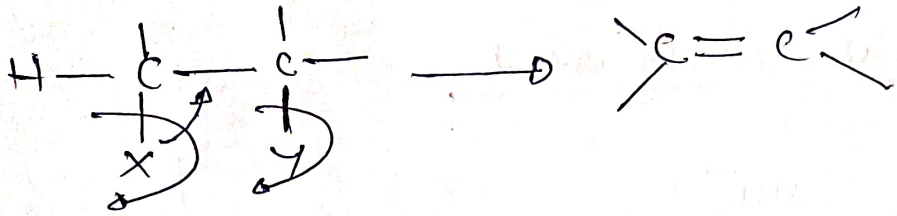
$\Rightarrow$ walden inversion occur.

$\Rightarrow$ carbocation rearrangement not occur due to formation of transition state.

$\Rightarrow$ I > Br > Cl > F.

$\Rightarrow$ 3° > 2° > 1° $\Rightarrow$ carbocation stability in SN2.

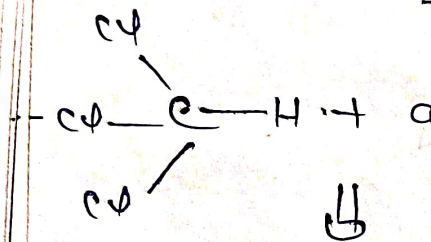
Elimination Reaction



① At least one living group is present for elimination reaction.

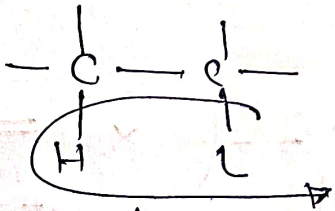
Elimination Reaction.

α elimination

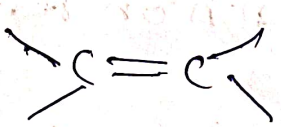


$CCl_2 + KCl + H_2O$

β- elimination.



Base.



β elimination.

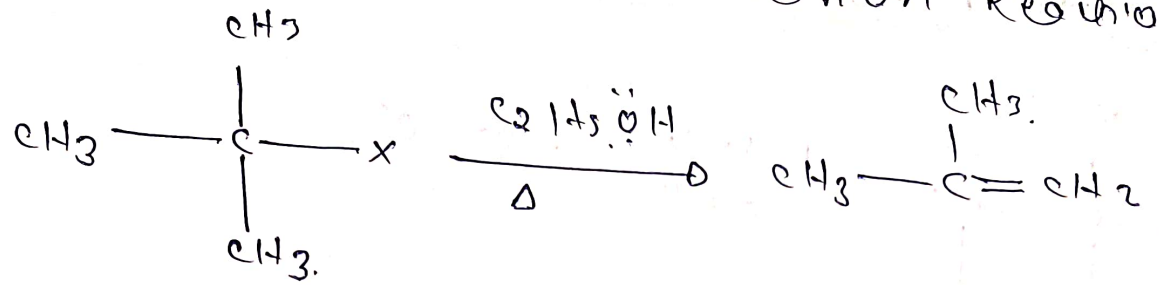
E¹ E²

note:-

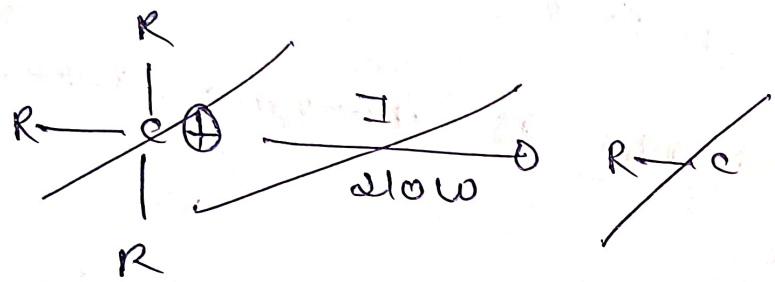
α Carbon ⇒ Carbon from which Cl is attached directly.

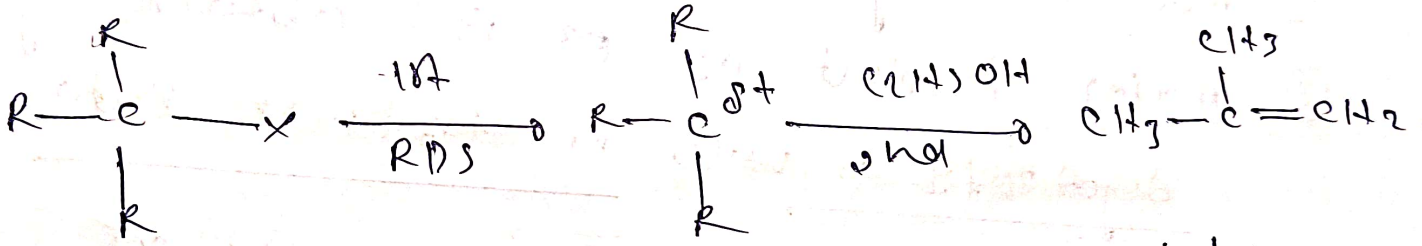
β- Halogen is not attach directly with this Carbon.

E1 ⇒ Unimolecular elimination Reaction.



Mech:-





(1) $C^{\oplus}$ formed as Reaction intermediate.

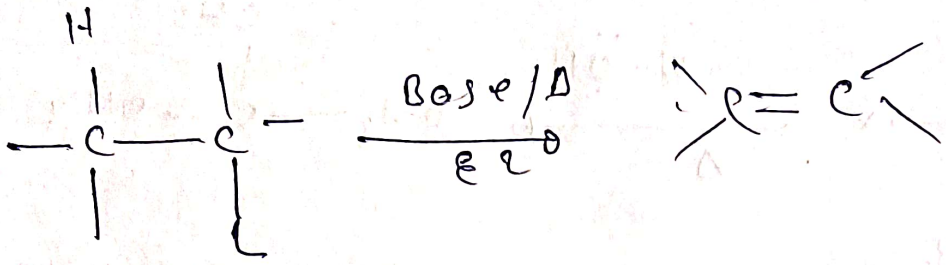
(2) E1 is 2 step reaction.

(3) $3^{\circ} > 2^{\circ} > 1^{\circ}$.

(4) major product of E1 is obtain by Saytzeff Rule.

(5) It is neither stereospecific nor stereoselective.

E2 ⇒ Bimolecular elimination R.



(1) E2 is single step reaction.

(2) order of reaction is 2.

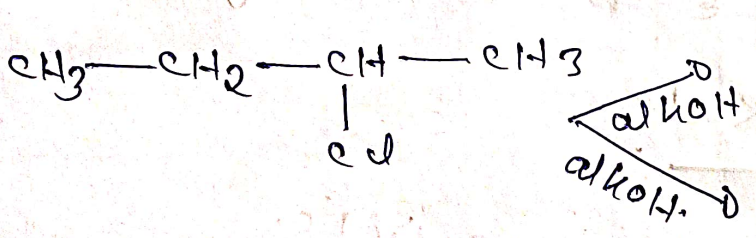
(3) no carbocation form as intermediate.

(4) molecularity = 2.

(5) major product of E2 is obtain by zaitzeff as well as Hoffman Rule.

(6) E2 is Regiospecific as well as Stereoselective Reaction.

Note :-



CH3—CH2=CH—CH3.
(more stable)
(Zaitzeff).

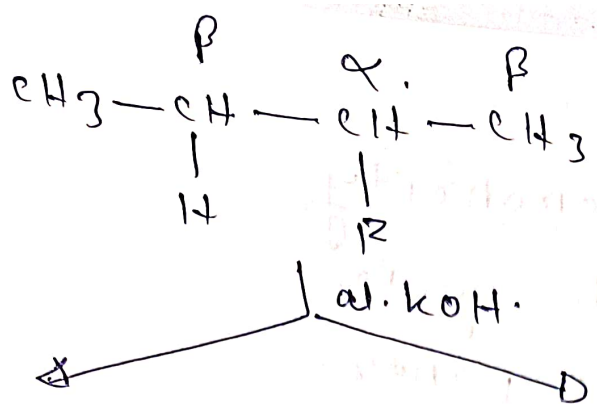
CH3—CH2—CH=CH2.

more substituted Alkene is more stable called zaitzeff Product.

less substituted alkene is Hoffman product.

note:-

#



$CH_3-CH=CH-CH_3$ — Saytzeff.

$CH_3-CH_2-CH=CH_2$ — Hoffmann.

But Here (X = F) which is weak leaving group so Hoffmann is major product and Saytzeff is minor product

---

$$R-X \xrightarrow[\text{solvent.}]{\text{alcoH}} SN1/SN2/E^1/E^2.$$

Δ

☆ $1^\circ > 2^\circ > 3^\circ \Rightarrow SN2$ and E^2.

$3^\circ > 2^\circ > 1^\circ$ (F) $\Rightarrow SN1$ and $E1$.

☆ Polar protic solvent $\Rightarrow SN1/E^1$.

Polar Aprotic solvent $\Rightarrow SN^2/E1$.

Aromaticity

Condition for Aromaticity.

① Compound must be cyclic.
② compound must be planer.
③ compound must be show Resonance.
④ $4n+2 = \pi e^-$

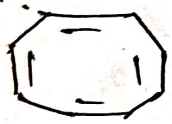
$\Rightarrow \pi = 6e^-$
$n = 6e^-$
$\Rightarrow$ Aromatic

n = 0 multiple $\Rightarrow$ Aromatic. $n = 0, 1, 2 \ldots$

note :-
$4n \neq \pi e^-$.
n = 4 multiple $\Rightarrow$ non-Aromatic
$n \neq 0$

$4n+2 = \pi e^-$s $\Rightarrow$ it's Huckles Rule

note :-



$\Rightarrow$ non-Aromatic.

Boyers strain theory

$\Rightarrow$ Also called as Ring strain theory.

$\Rightarrow$ in Boyers strain theory the difference between ideal bond angle and actual bond angle is present. in Ring.

or

Theory shows the difference between Actual bond angle and ideal bond angle.

e.g. 

Actual bond angle = 60°

ideal bond angle = 109.5°.

diff. ⇒ 49.5°.

Accounding to this theory.

⇒ maximum angle strain present in
cyclopropane > cyclobutane > cyclopentane
> cyclohexane.

⇒ maximum stability present in:-
cyclohexane > cyclopentane > cyclobutane
> cyclopropane.

note:-
Due to maximum angle strain present in cyclopropane hence it undergo addition Reaction and less stable.

Limitation of Bayers strain theory.

(1) Do not for uncorrect about longer Rings.

(2) only Applicables to small Ring.

(3) Ignores types of strain.

Isomerism → Stereoisomerism

conformers configuration

⇒ Arise due to rotation of (C–C) sigma bond

⇒ They are easily interconvertible

⇒ Can not separated easily

configurational ~~conformational~~

⇒ Arise due to ~~rotation~~ of (C=C) bond in space

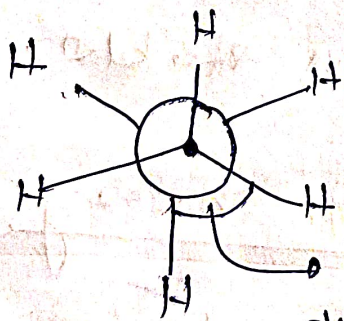
⇒ They are not easily interconvertible.

⇒ They can separated easily.

conformers isomerism.

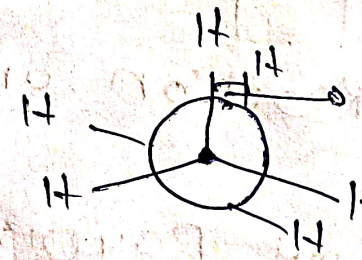
⇒ Arise due to (C–C) rotation in space.

⇒ CH_3-CH_3 (Ethane)



60° dihedral angle

⇒ Staggered form

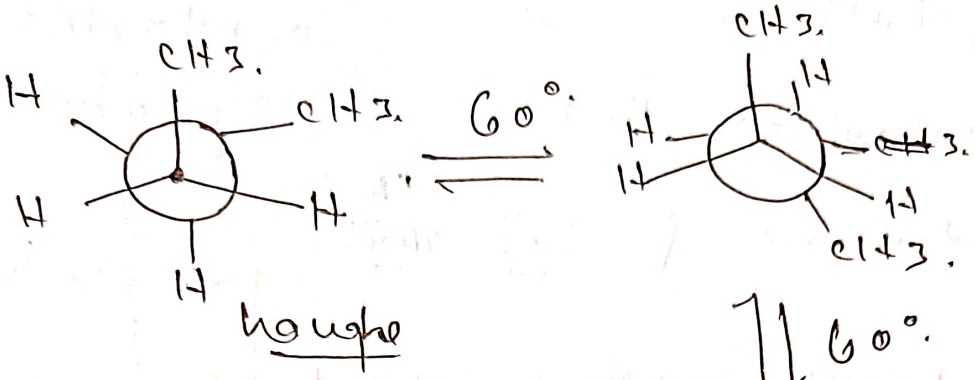


0° dihedral angle.

⇒ Eclipsed form.

⇒ conformers of Butane.

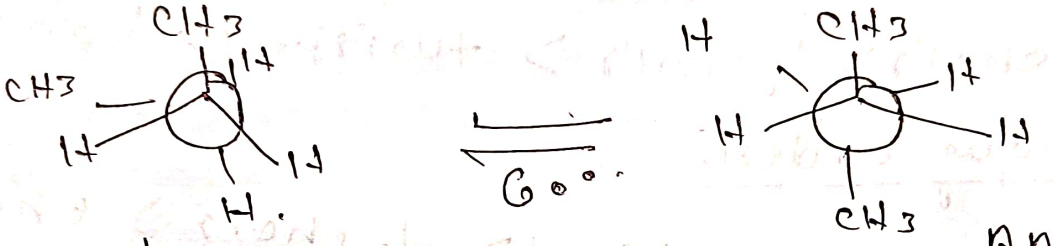
$CH_3-\overset{1}{CH_2}-\overset{2}{CH_2}-CH_3$.



Gauche

Partially eclipsed.

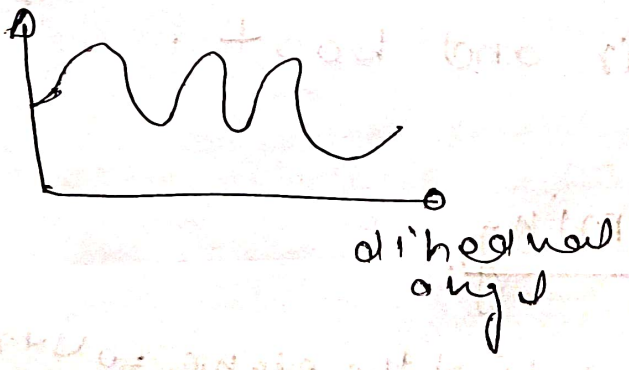
60°.



Fully eclipsed

Anti.

Stability ⇒ : Anti > Gauche > Partially eclipsed > F. eclipsed.



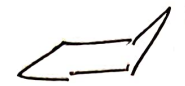
note:-

Gauche effect.

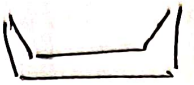
Gauche is more stable than Anti when Hydrogen bonding is present.

conformers of cyclohexane

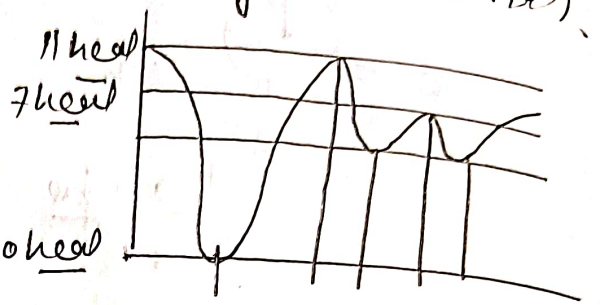
⇒ chair ⇒ 

⇒ ½ chair ⇒ 

⇒ twisted ⇒ 

⇒ Boat ⇒ 

(These are conformers of cyclohexane)



⇒ Stability order.

chair > ½ chair > twisted > boat

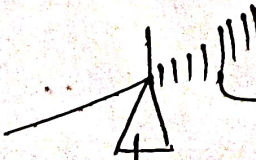
energy order.

Boat > twisted > ½ chair > chair.

note:-

The chair form are more stable then boat form because energy difference between chair and boat.

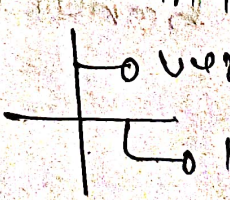
R. and S. naming



dash ⇒ behind the plane. ⇒ vertical (|)

wedge ⇒ above the plane or present in Front. and mention in Horizontal in Fisher. ⇒

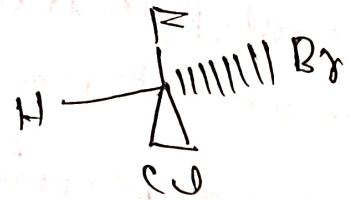
Fisher projection ⇒

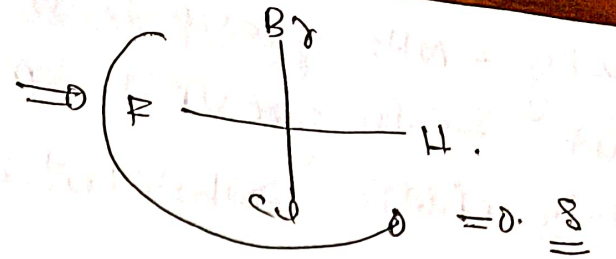


vertical

Horizontal

⇒





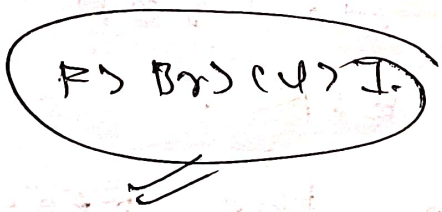
⇒ S.

R ⟶ ⟶ clockwise.

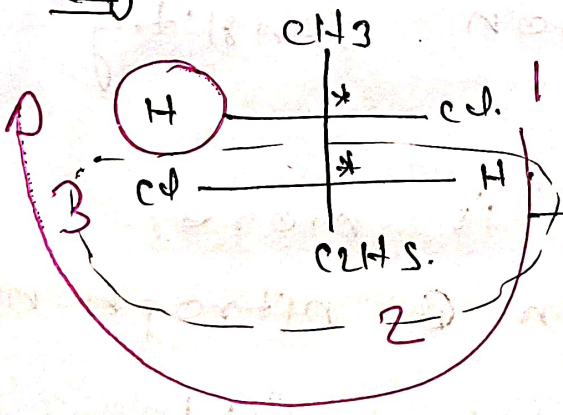
S ⟶ ⟶ Anticlockwise.

note :-

⇒ when lowest priority group like Hydrogen present on wedge (Δ) then naming should be (S) (↳) Anticlockwise.

⇒ 

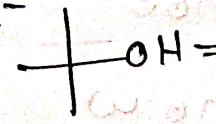
⇒

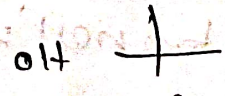


⇒ clockwise but H is on Horizontal then naming is ⇒ S.

most Prior group.

note :-





⇒ S.

⇒ Why $-NH_2$ group [illegible] but $-CHO$ group is m-directing in electrophilic substitution. explain?

⇒ Aldehyde (CHO) are meta directing in electrophilic aromatic substitution because they are electron withdrawing group.

⇒ -M (Resonance) and -I (induction) make CHO more favorable on meta position in ESR.

But $-NH_2$ is ortho and para directing because they are electron donating group in ESR.

(+M) and -I favor the Reaction and increase the electron density at a site.

⇒ Why p-nitrophenol is more soluble in water than o-nitrophenol

⇒ o nitrophenol are less soluble in water than- p nitrophenol

because → o nitrophenol show intramolecular H-bonding

→ more Neem volatile.

Mechanism of organic Reaction.

⇒ Kolbes Reaction. ⇒ Condensation. (Aldol)
⇒ Diels - Alder Reaction. ⇒ Birch reduction
⇒ Corey house synthon's. ⇒ Dickmon reaction.

Corey-House synthon's.

$$2-CH_3-X \xrightarrow{Li^\circ} 2CH_3Li$$

$$2CH_3Li \xrightarrow{Cu-X} 2CH_3-Cu-Li^\circ$$

(Gilmans Reagent).

$$2-CH_3-Cu-Li^\circ \xrightarrow{R^1-X} \cancel{2R-R} \quad R-R' + R-Cu +$$

(R-R') ⇒ unsymmetrical alkane.

Here R-X ⇒ 1° Halide

R'-X ⇒ can be 2° and 3° Halide.

Kolbes synthon's.

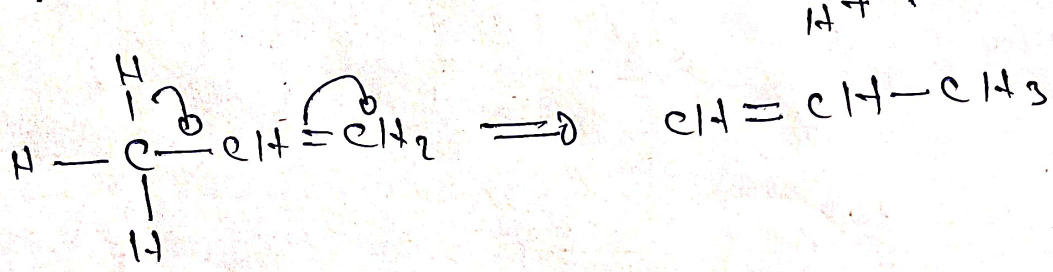
⇒ Ozonolysis of Alkene. → Topics
⇒ Hydration of alkynes.
⇒ 1 Butyne is more acidic than 1- Butyne.
⇒ Hyperconjugation.
⇒ Certain Reactions of 2023.

⇒ Hyperconjugation.

Hyperconjugation type of Delocalization of electrons.

Hyperconjugation also called as Baker Nathan effect. and also known as no bond Resonance.

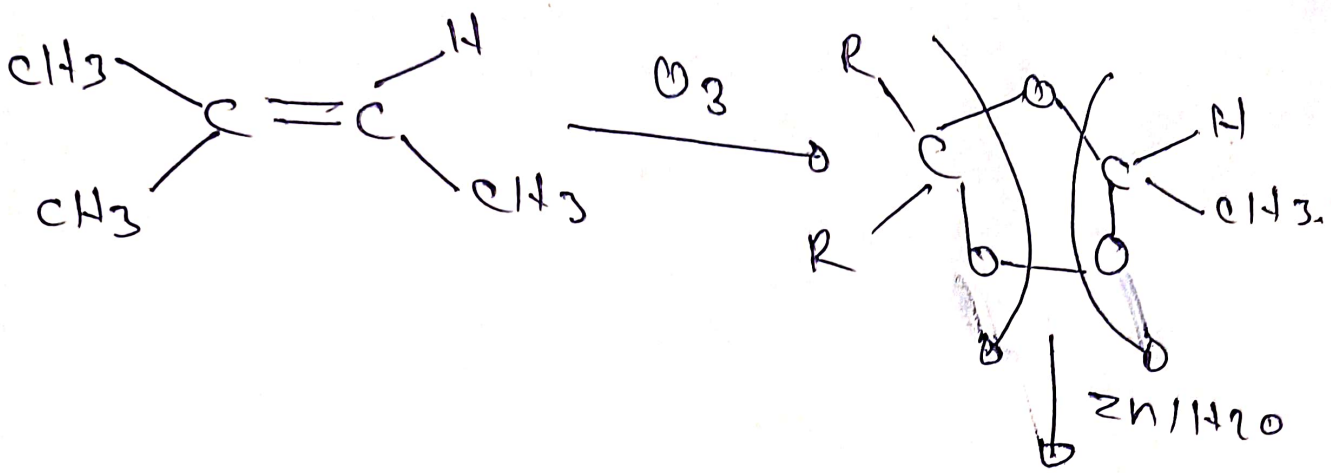
Involve delocalization of σ electrons with π- electrons of multiple bond when they are in conjugation.

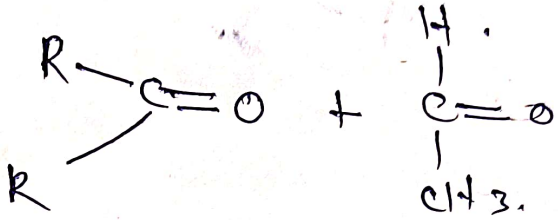


⇒ Electrophile	Nucleophile
BF_3	$\ddot{N}H_3$, $H_2\ddot{O}$
$AlCl_3$	$R-\ddot{O}H$
$FeCl_3$	F^-, Cl^-, Br^-,
$BeCl_2$	OH^-
SO_3.	CN^-.
NO_2^+	

- by means of

Ozonolysis -





Acetone (ketone).

Aldehyde.