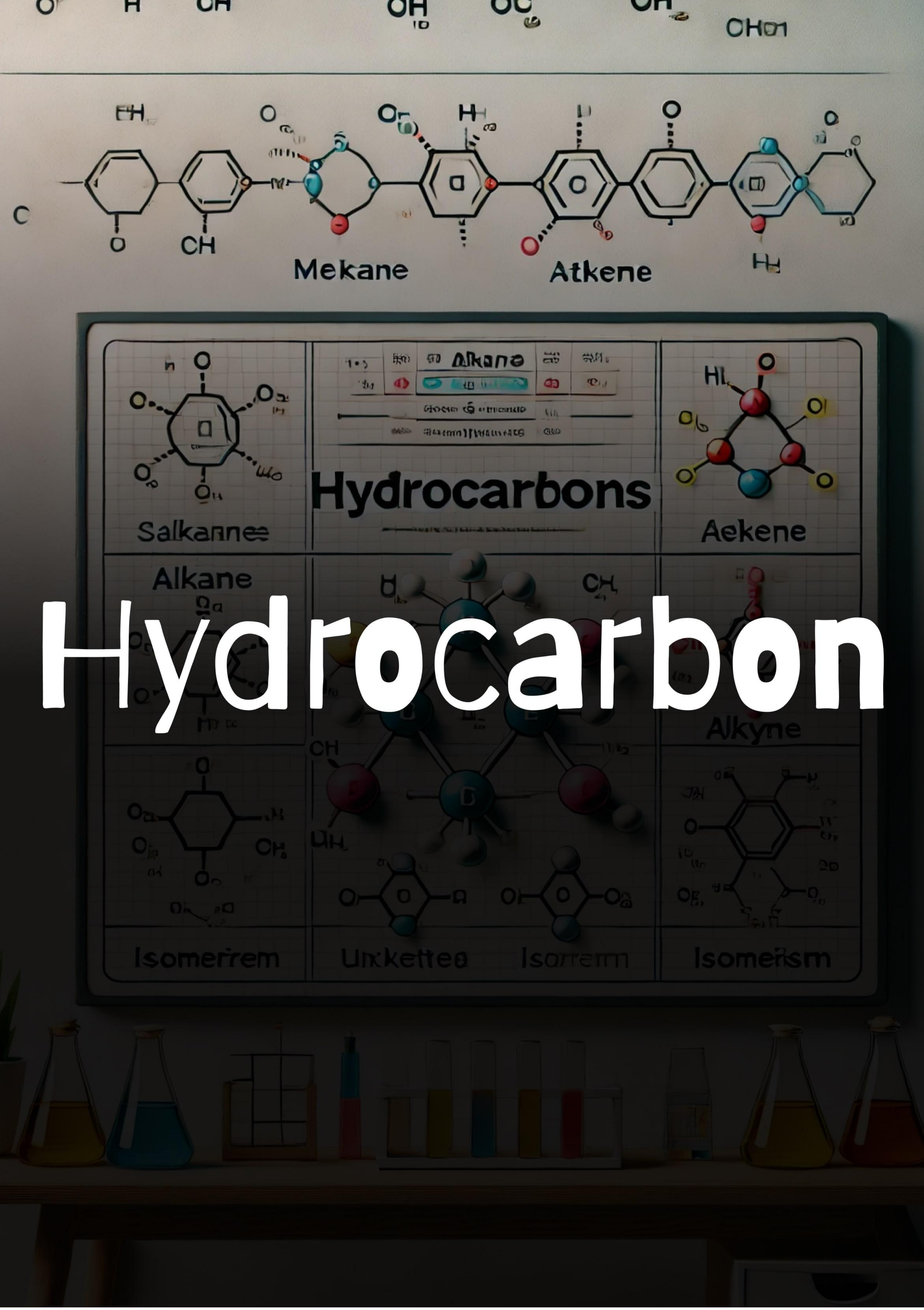


Hydrocarbon

Hydrocarbon

- Alkane

- Method of preparation:

① Grignard Reagent:

$$R-X + Mg \xrightarrow{ether} RMgX \ (G \cdot R)$$

-δ δ+

R ⟵⟵⟵ MgX → High polar bond ⟵ ⊛ Acidic — (H_2SO_4,

etc

Base Nucleophile
(Dominating nature)

⊛ —O—H
—S—H
—C≡C—H

} Active Hydrogens ↓ React with strong Base

Acidic condition + RMgX ⟶ RH + etc.

② Electrolysis method (Kolbe's electrolysis):

$$RCOOH + KOH \longrightarrow R-\overset{O}{\overset{\|}{C}}-OK$$

- Potassium salt of carboxylic acid.

- Anode:

$$R-CO-O^{\ominus} \longrightarrow R-\overset{O}{\overset{\|}{C}}-O + e^{\ominus}$$

lose of $e^{\ominus}$ oxidation

$$R-\overset{O}{\overset{\|}{C}}-O \longrightarrow R^{\cdot} + CO_2\uparrow$$

$$R^{\cdot} + R^{\cdot} \longrightarrow R-R\uparrow$$

Alkane.

- Cathode:

Reduction

$$2H^+ + 2e^{\ominus} \longrightarrow H_2\uparrow + KOH$$

Cathode ⟶ gas $H_2\uparrow$

Anode ⟶ gas ⟶ $CO_2\uparrow$ $R-R\uparrow$

$$R-\overset{O}{\overset{\|}{C}}-OK + H_2O \xrightarrow{electrolysis} R-R + CO_2 + H_2 + KOH$$

- Limitations :

① CH_4 does not form by electrolysis.

② tertiary alkane does not form gets converted to Alkene.

③ Alkane, Alkene, Alkyne → all form by kolbe's electrolysis.

④ Unsymmetrical alkanes does not form it produces mixture of products.

- Alkene :

$$\begin{matrix} CH_2COOK \\ | \\ CH_2COOK \end{matrix} \xrightarrow{electrolysis} \underbrace{\begin{matrix} CH_2 \\ || \\ CH_2 \end{matrix} + CO_2\uparrow}_{Anode.} + \underbrace{H_2 + KOH}_{cathode.}$$

- Alkyne : $C \equiv C$ —

$$\begin{matrix} CHCOOK \\ || \\ CHCOOK \end{matrix} \xrightarrow{electrolysis} \underbrace{\begin{matrix} CH \\ ||| \\ CH \end{matrix} + CO_2\uparrow}_{Aode} + \underbrace{H_2\uparrow + KOH}_{cathode.}$$

Potassium Fumarate

③ Decarboxylation of carboxylic acid salt :

$$\underset{\text{Carboxylic Acid}}{R-\overset{O}{\overset{||}{C}}-OH} \xrightarrow{NaOH} R-\overset{O}{\overset{||}{C}}-ONa$$

Sodium salt, Potassium salt } of carboxylic acid.

$$R-\overset{O}{\overset{||}{C}}-ONa + NaOH \xrightarrow{CaO} \underset{\text{Alkane}}{RH} + Na_2CO_3$$

- $\underline{NaOH + CaO}$ soda lime.

$CO_2\uparrow + NaOH$

Note : Removal of CO_2 gas in presence of soda lime.

No. of carbon decreases.

④ Wurtz Reaction.

$$R-X + 2Na + R-X \xrightarrow[\text{ether}]{\text{Dry}} R-R + 2NaX.$$

Solvent → Dry ether (No water because it react with Na)

Mech : $Na \rightarrow Na^+ + e^\ominus$

$R-X + e^\ominus \rightarrow R^\cdot + X^\ominus$

$R^\cdot + R^\cdot \longrightarrow R-R \uparrow$
Alkane

Note: CH_4 does not form by wurtz method.

$\boxed{R-I > R-Br > R-Cl > R-F}$

- Limitations.

① tertiary alkane does not form gets converted to alkene.
② Unsymmetrical alkanes does not form it produces mixture of products.
③ symmetrical forms (even no. of carbon atoms).

⑤ Corey - House method.

$$R-X + Li + CuI \longrightarrow R_2CuLi$$
Gilman's Reagent:

$$R_2CuLi + CH_3X \xrightarrow{SN_2} R-CH_3 + LiX + CuX_2$$
Alkane.

$Nu^\ominus$ Base
✓ Dominating nature.

- Physical properties of alkane:

$C_1 - C_4$ → Gas ↑
$C_5 - C_{17}$ → Liquid
$C_n > C_{17}$ → Wax solid.
↓

- Boiling ∝ M·wt (chain → ek jaisi ho}

  Boiling point ∝ $\frac{1}{Branch}$ (M·wt → constant)

- Melting point ∝ branch (M·wt → same)

  Reason → packing efficiency increases.

  Melting point :

  $C_n > C_{n+1}$ where n = even no. of carbon atom in alkane.

  $C_n > C_{n-1}$

  $C_n < C_{n+3}$

- Chemical properties :

  - Alkane is a non-polar molecule.
  - C–H has a non-polar covalent bond.

① Halogenation.

$$CH_4 + X_2 \xrightarrow{h\nu} CH_3X + CH_2X_2 + CHX_3 + CX_4$$

Mech:

$$X-X \xrightarrow{h\nu} X^{\cdot} + X^{\cdot}$$ (Initiation step) Free Radical (R)

$$CH_4 + X^{\cdot} \longrightarrow \dot{C}H_3 \times HX$$

$$CH_3^{\cdot} + X-X \longrightarrow CH_3X + X^{\cdot}$$

(Propagation step) Free Radical (L and R)

$$CH_{\dot{3}}X + X^{\cdot} \longrightarrow CH_3X_2$$

$$CH_3^{\cdot} + CH_3^{\cdot} \longrightarrow CH_3-CH_3$$

(Termination step) Free Radical (L)

- Monohalogenation :

Concept : all possible free radicals banana.

Major : Most stable free radical ke corresponding form alkyl halide

- Note : Reactivity – $F_2 > Cl_2 > Br_2 > I_2$

  $F_2 + CH_4 \longrightarrow$ carbon black + HF

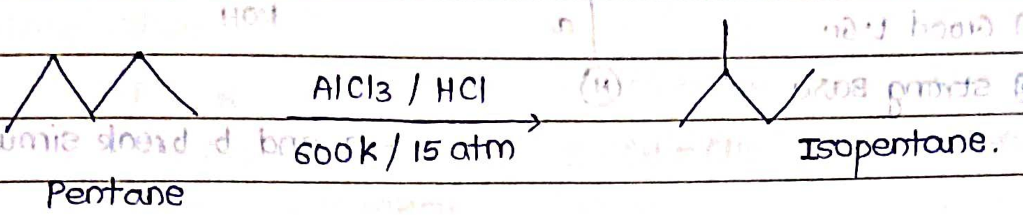
  ↓ $\Delta H = -ve$

  Release energy (Highly exothermic)

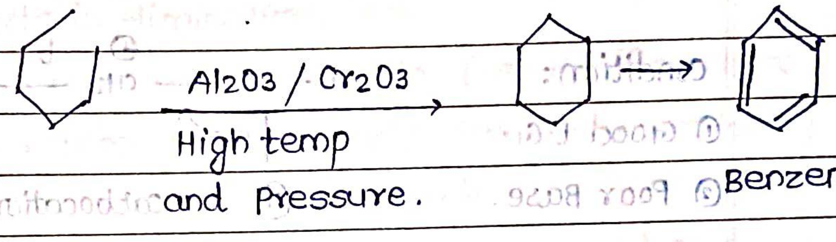
  Burn compound.

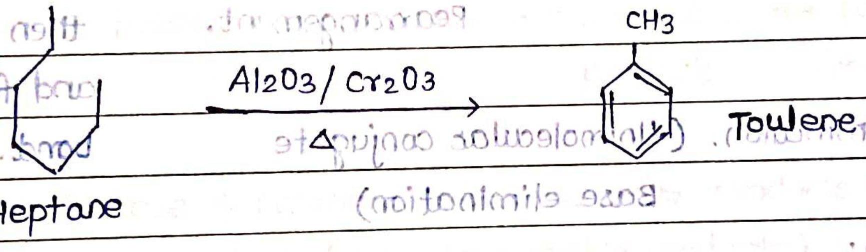
- Cl_2 is more reactive than Br_2, But Br_2 is more selective than Cl_2.

- Isomerism — Branch increase karna.



- Aromatisation :





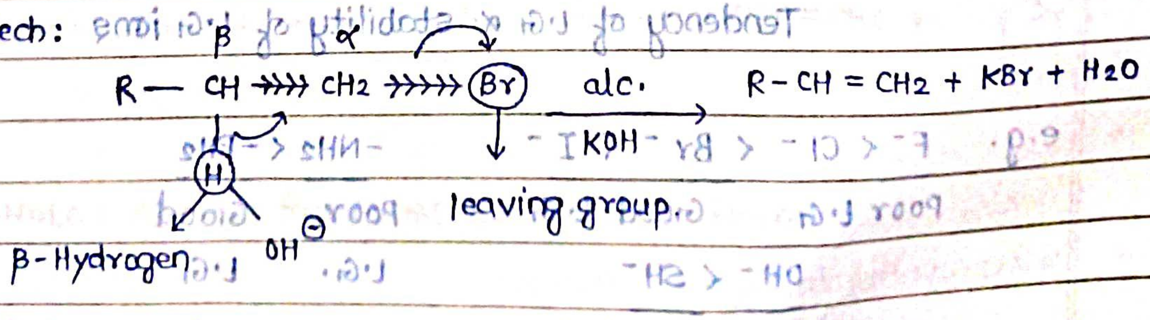
- Alkene :

- Method of preparation : elimination reaction

Removal of atoms / groups in presence of Reagent / Heat.

$R-CH_2-CH_2-OH \xrightarrow[-H_2O]{H^+} R-CH=CH_2$

Mech :

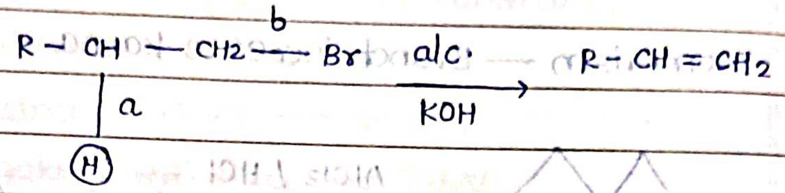


$KOH \rightarrow K^+ + OH^{\ominus}$

β-elimination.

① E_2-elimination: (Bimolecular elimination)

Condition:
① Good L.G.
② strong Base

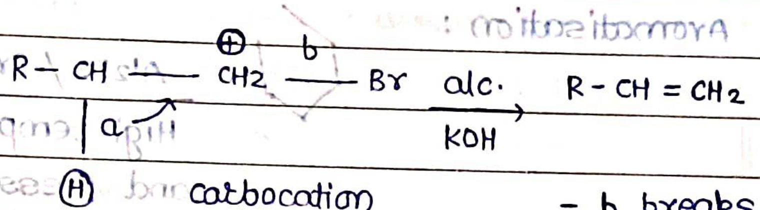


$$\underset{\underset{H}{|\,a}}{R-CH}-CH_2\overset{b}{-}Br \xrightarrow[KOH]{alc.} R-CH=CH_2$$

- a and b break simultaneously.

② E_1 – elimination (Unimolecular elimination)

Condition:
① Good L.G.
② Poor Base.



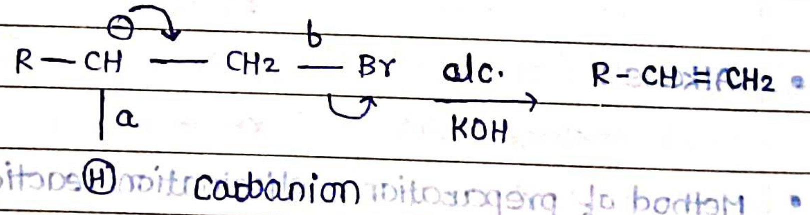
$$\underset{\underset{H}{|\,a}}{R-CH}-\overset{\oplus}{CH_2}\overset{b}{-}Br \xrightarrow[KOH]{alc.} R-CH=CH_2$$

carbocation Rearrangement.

- b breaks first then a breaks and form double bond.

③ E_1Cb – elimination. (Unimolecular conjugate Base elimination)

Condition:
① Poor L.G.
② Strong Base.



$$\underset{\underset{H}{|\,a}}{R-\overset{\ominus}{CH}}-CH_2\overset{b}{-}Br \xrightarrow[KOH]{alc.} R-CH=CH_2$$

Carbanion Character

- a breaks first and forms carbanion then b breaks.

- **Leaving Group:**

Tendency to leave group in presence of Reagent.

Tendency of L.G ∝ stability of L.G ions

e.g. $F^- < Cl^- < Br^- < I^-$
Poor L.G Good L.G

$-NH_2 < -PH_2$
Poor L.G. Good L.G.

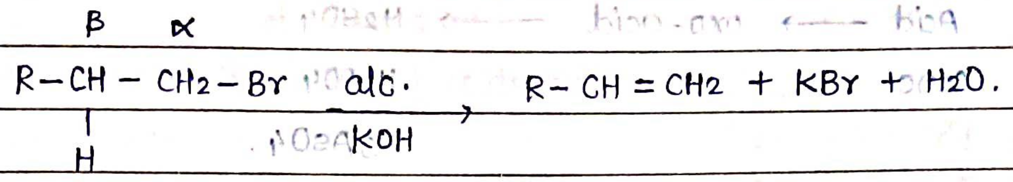
$OH^- < SH^-$
Poor L.G. Good L.G.

Note: Down the group L.G. tendency increases.

Note 2 : Neutral molecules are good L·G·

Best L·G· → N_2, H_2O.

- E_2-Elimination :



$$R-\underset{H}{\overset{\beta}{CH}}-\overset{\alpha}{CH_2}-Br \xrightarrow[KOH]{alc.} R-CH=CH_2 + KBr + H_2O.$$

① Note : Major products in elimination.

E_2 elimination → more subs. products (saytzeff products)

E_1Cb elimination → Less. subs products (Hoffman products)

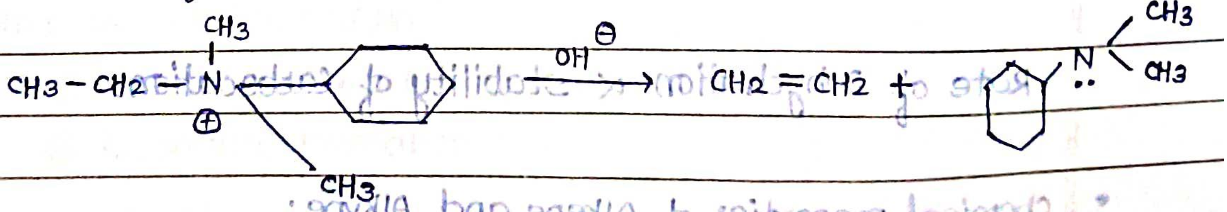
② Note : In presence of Bulky Base → less subs. products → Formed as a major products.

③ Note : In case of Resonance also less subs. products formed as a Major product (Resonance stable products).

- Stereochemistry of E_2 - Elimination :

- Anti - elimination or opposite elimination or trans elimination.
- Anti elimination + max. substituted products.

- Elimination of Ammonium salt in presence of Base :



Note : Always form less substituted alkene.

- E_1 elimination:

(a) Dehydration of alcohol in presence of oxo-acid.

Acid ⟶ oxo-acid ⟶ H_2SO_4

Conc.

H_3PO_4

H_3AsO_4.

$H_2SO_4 \rightarrow H^+ + HSO_4^-$

poor Base

- Rearrangement of carbocation takes place.

Note ⟶ (⊕) exchange hoga

-H

- phenyl

- methyl

- Ring Expansion:

Condition: Convert:

$$\text{Ring} - \overset{\oplus}{CH} -$$

3 ⟶ 4

4 ⟶ 5

5 ⟶ 6

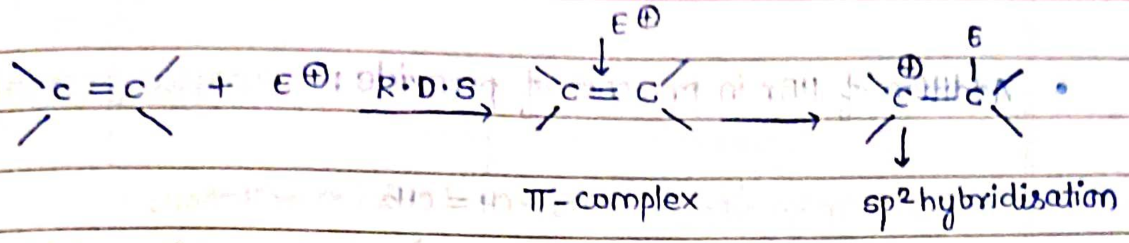
6 ⟶ ⓧ

- Note: $>C=C-OH \longrightarrow$ dehydration nahi hoga.

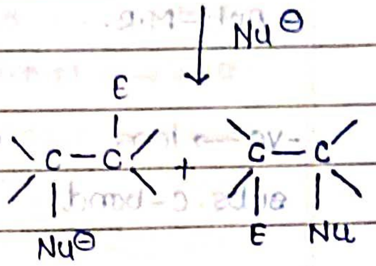
Rate of Dehydration ∝ stability of carbocation

- Chemical properties of Alkene and Alkyne:

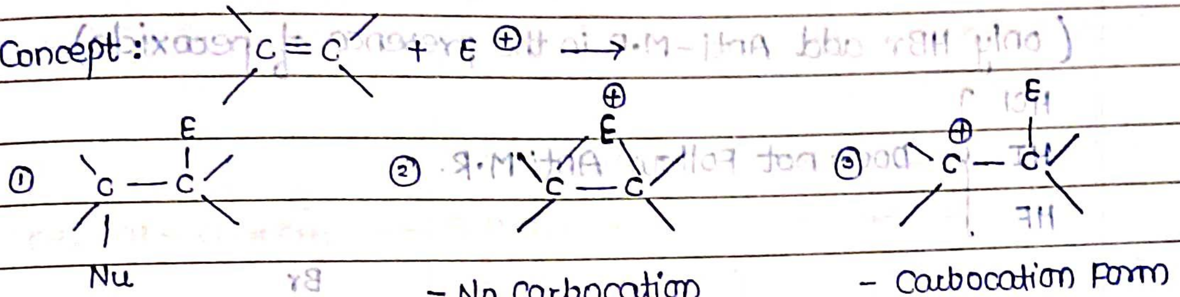
① Electrophilic Addition Reaction.



- Rate of Reaction ∝ Electron density of Alkene or stability of carbocation

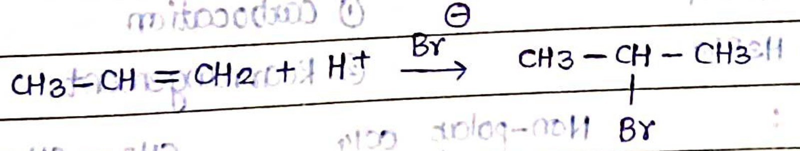


- Concept :



①	②	③
	- No Carbocation	- Carbocation Form
* alk. $KMnO_4$	- No Rearrangement	- Rearrangement.
* OsO_4	* Br_2/CCl_4	* HBr
* ozonolysis	* Br_2/H_2O	* H^+/H_2O bA
	* $Br_2/NaCl$	* HOX.
	* H·B·O	
	* OMDM	

- Addition of HBr :



$$CH_3-CH=CH_2 + H^+ \xrightarrow{Br^{\ominus}} CH_3-\underset{Br}{\underset{|}{CH}}-CH_3$$

① carbocation.
② Rearrangement.

Note : Only shifting when
① stability increases
② Resonance Formation.

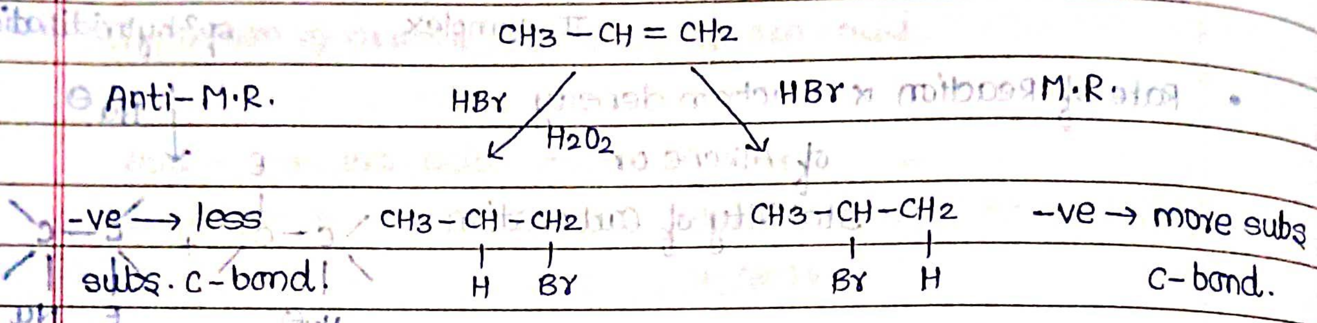
Note : Reactivity of HX :

HI > HBr > HCl > HF
↓ most acidic.

Note : Reactivity of Alkene

Reactivity ∝ stability of Carbocation

- Addition of HBr in presence of peroxide :

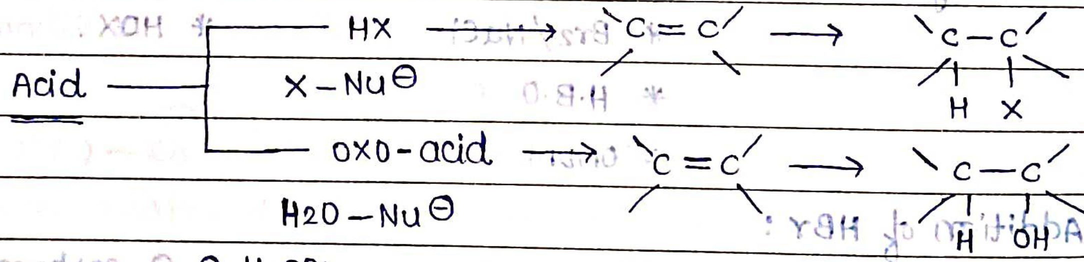


(only HBr add Anti-M.R in the presence of peroxide)

HCl
HI } Does not Follow Anti M.R.
HF

- Alkyne : $CH_3-C\equiv CH + HBr \longrightarrow CH_3-\underset{Br}{\overset{Br}{C}}-CH_3$ No Rearrangement

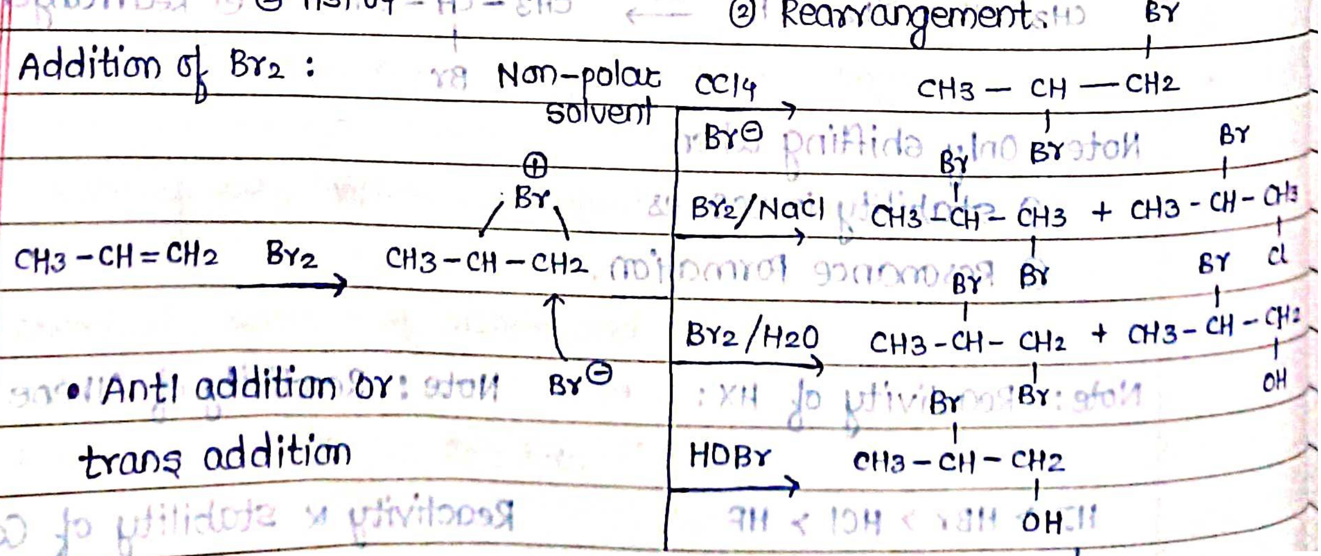
- Addition of $H_2O/H^{\oplus}$



① H_2SO_4
② H_3PO_4

① carbocation
② Rearrangement

- Addition of Br_2 :

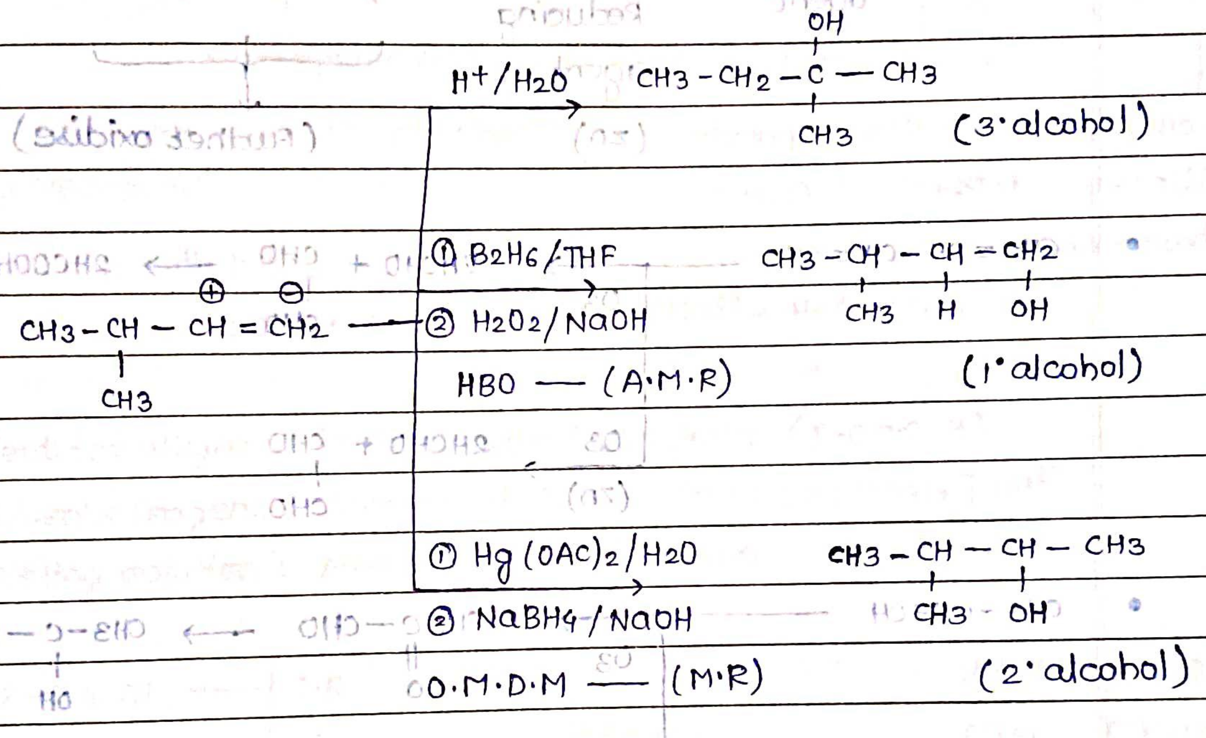


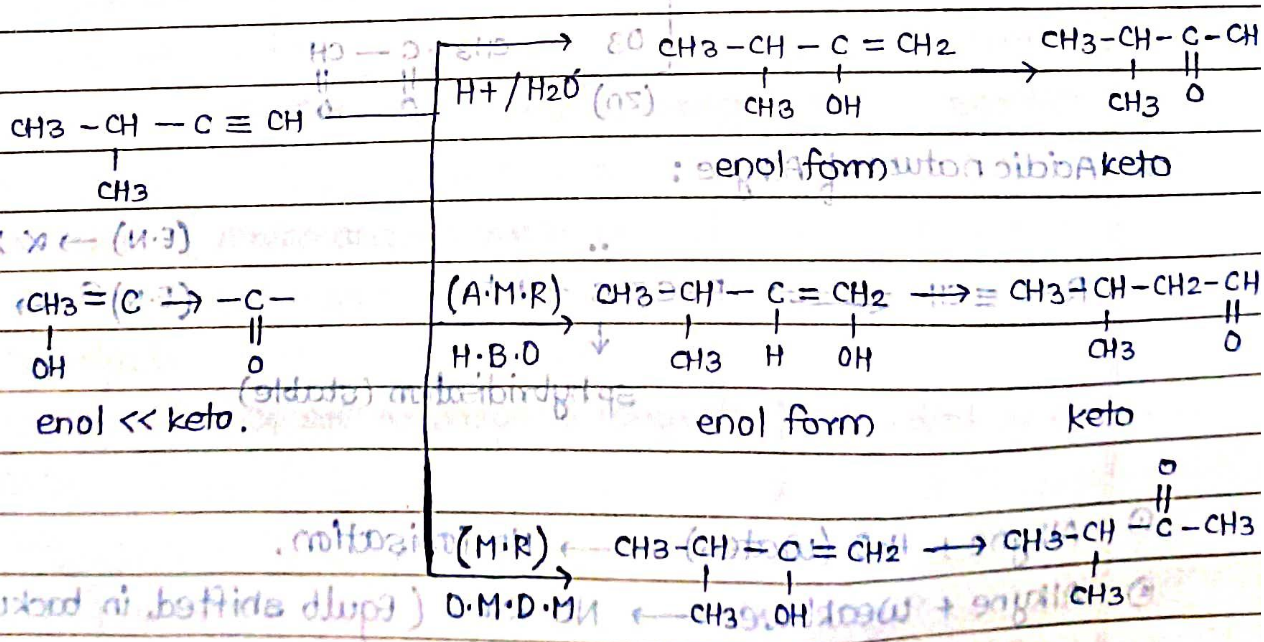
- Anti addition or:
trans addition

Page No.
Date

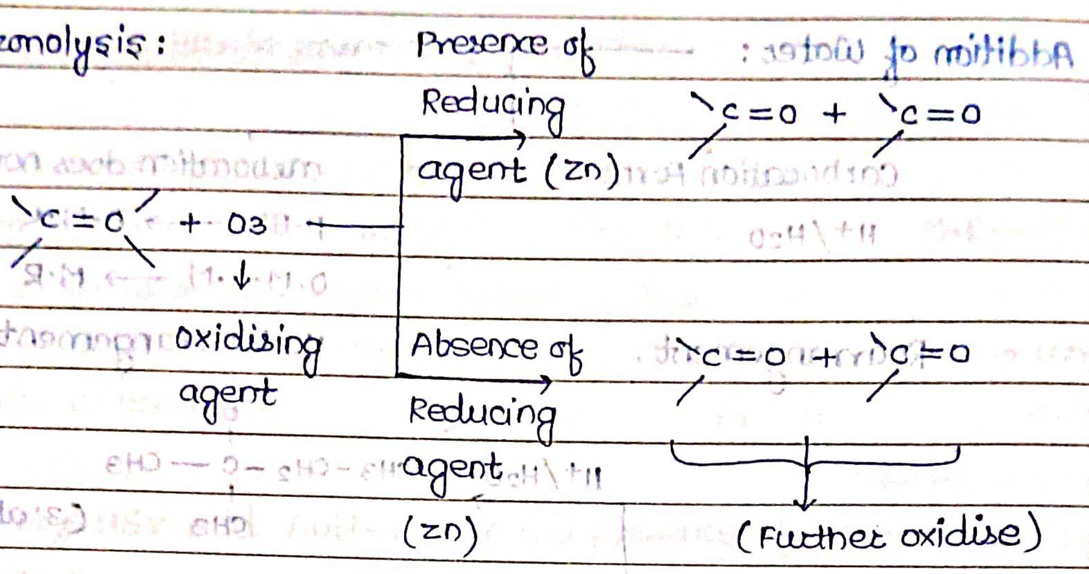
- Addition of Water :

Carbocation form	carbocation does not form
H^+/H_2O	H·BO ⟶ A·M·R
	O·M·D·M ⟶ M·R
Rearrangement.	No Rearrangement.

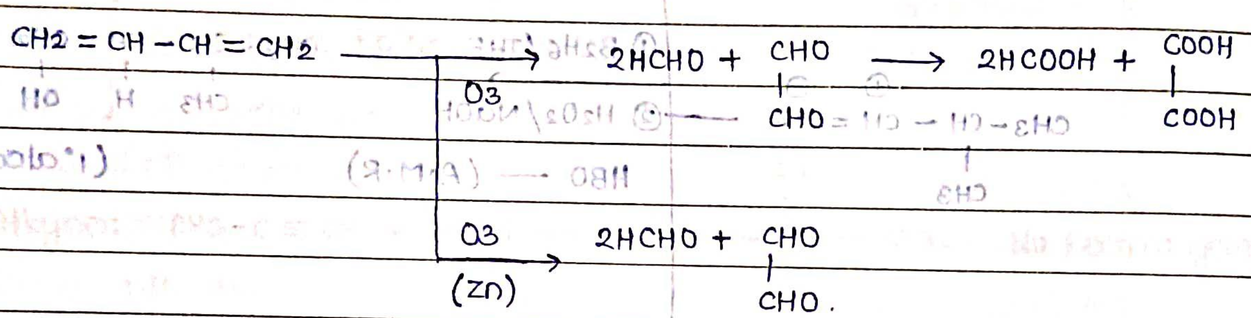
- 

- 

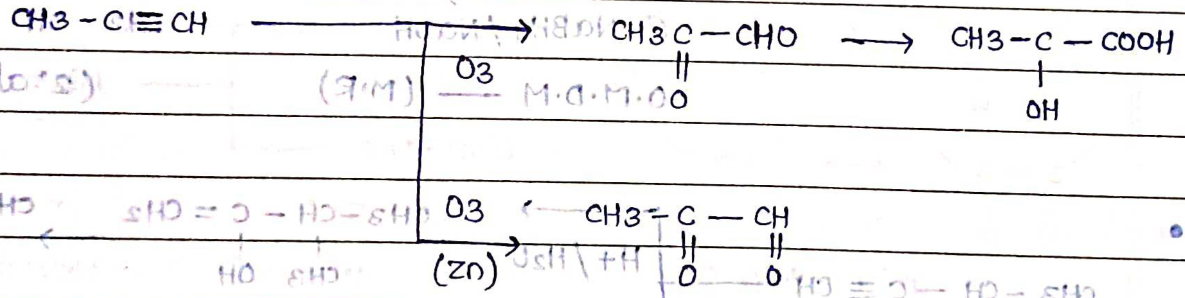
- Ozonolysis :



- $CH_2 = CH - CH = CH_2$



- $CH_3 - C \equiv CH$



- Acidic nature of Alkyne :

$$R - C \equiv CH \rightleftharpoons R - C \equiv \ddot{C} + H^+$$

sp hybridisation (stable)

$(E.N) \rightarrow \propto \%$ of s-chara

$(E.N)^{\ominus} \Longrightarrow$ stable.

① Alkyne + H_2O (water) ⟶ (No ionisation.

② Alkyne + weakbase ⟶ No Rxn. (Equlb shifted in backward direction).
NH_3, NaOH

- Note : $OR^{\ominus}$, $NH_2^{\ominus}$, $R^{\ominus}$ ⟶ strong base
  (RMgX) (RLi)

$$R-C\equiv CH + NaNH_2 \longrightarrow R-C\equiv C^{\ominus}Na^{\oplus} + NH_3$$

- Concept : $R-C\equiv C-\text{Ⓗ}$ ⟶ Very weak active Hydrogen
  ↓ Electrophilic Addition Reaction
  Very weak active Hydrogen → strong base ($>OH^{\ominus}$) | strong Metal | organo-metallic compounds.

- Reaction with Metal :

$$R-C\equiv CH + Na \longrightarrow R-C\equiv C^{\ominus}Na^{\oplus} + H_2\uparrow$$

- Test for alkyne which have active hydrogen : ($R-C\equiv C-H$)

Tollen's Reagent : Ammonical $AgNO_3$ sol^n^ or $[Ag(NH_3)_2]\,OH^{\ominus}$

Fehling solution : Ammonical $CuCl_2$ solution.

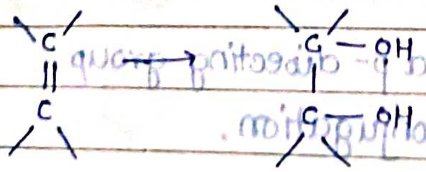
$R-C\equiv CH$ —T·R→ $\downarrow R-C\equiv C-Ag$ White ppt

$R-C\equiv CH$ —F·S→ $\downarrow R-C\equiv C-Cu$ Red or orange ppt.

Note : Alkane, Alkene, Alkyne does not show reaction with T·R and F·S

- Oxidation of Alkene and Alkyne :

① Ozonolysis
② 1% alkali $KMnO_4$ sol^n^ or Baeyer's Reagent } cis-diol
③ OsO_4 }

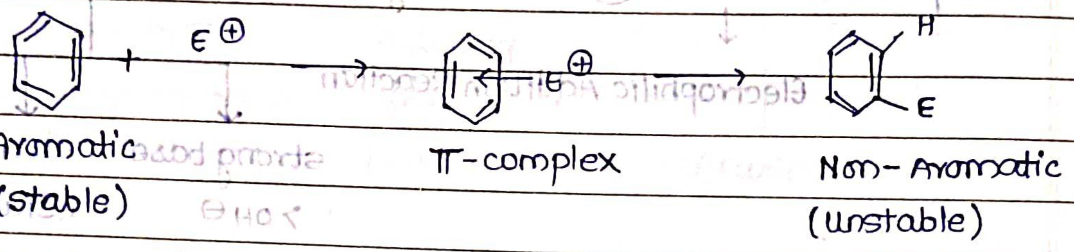


Note : only one π bond break and form cis-diol.

Page No.
Date

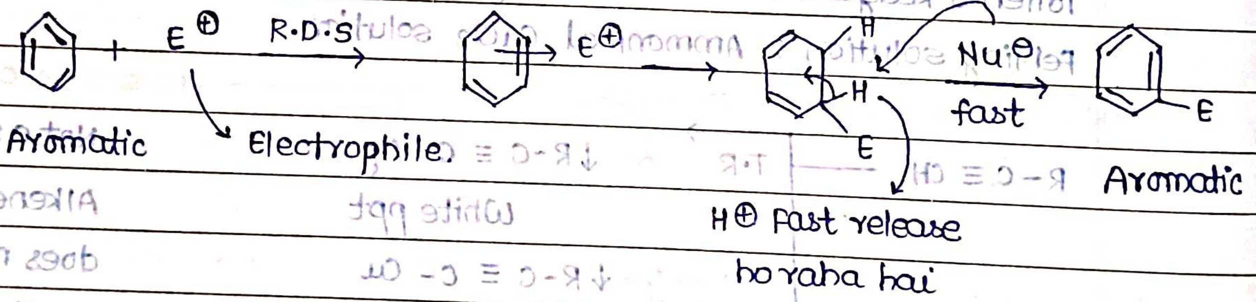
- Note — stereochemistry
  Same - same — (meso)
  Opposite — Racemic mixture.

- Electrophilic Aromatic Substitution Reaction :



Note : Aromatic compounds ⟶ $E^{\oplus}$ Addition Reaction ⟶ nahi show krte hain ?

Reason : Due to Formation of Non - Aromatic compound or due to loss of Aromaticity.



- Rate of E.A.S ∝ electron density of Benzene Ring.
  ∝ strength of Electrophile.

Electron donor group ⟶ increases Reactivity

Electron withdrawing group ⟶ decreases Reactivity.

- $-o$ or $-p$ directing group increases the electron density of benzene ring
  $-OH$, $-OR$, $-NH_2$, $-NH-R$,

- Note : ① Alkyl group also o- and p- directing group
  Reason — Due to Hyperconjugation.

 $-CH_3 > -CH_2-CH_3 > -CH(CH_3)_2$.

② X-Halogens are o- and p- directing but deactivating group.
Reason- due to high inductive effect.

③ +M effect power : $\ddot{N}H-R > -\ddot{N}H_2 > \ddot{O}H > \ddot{O}R > \ddot{O}-\overset{O}{\overset{\|}{C}}-H$

$-\ddot{N} > \ddot{O} > \ddot{C} > X$

- Note : meta- directing group decreases the electron density of the benzene ring (Deactivating group)
  Deactivating group → having multiple bond functional groups.
  $-\overset{O}{\overset{\|}{N}}\rightarrow O$, $-\overset{O}{\overset{\|}{C}}-H$, $-\overset{O}{\overset{\|}{C}}-R$, $-\overset{O}{\overset{\|}{C}}-OH$, $-\overset{O}{\overset{\|}{C}}-Cl$, $-\overset{O}{\overset{\|}{C}}-NH_2$, $-\overset{O}{\overset{\|}{C}}-OR$

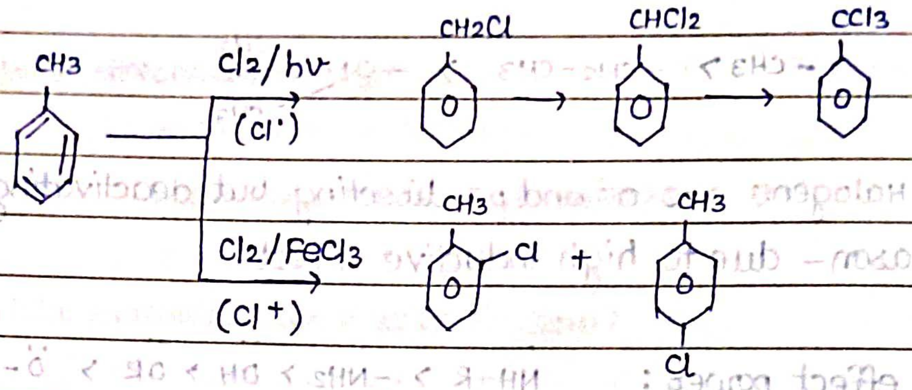
- −M power effect : $-NO_2 > -\overset{O}{\overset{\|}{C}}- > -\overset{O}{\overset{\|}{C}}-O$
  $-NO_2$, $-C\equiv N$ → strong −M effect.

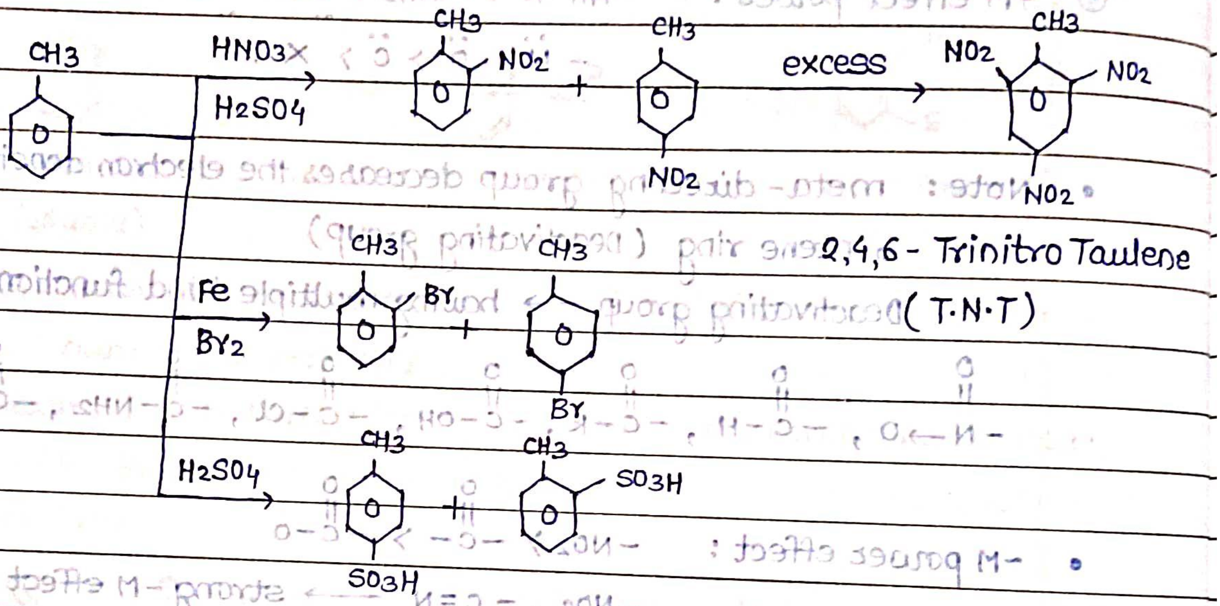
- Example of E.A.S :

	Reagent	$E^{\oplus}$
① Nitration →	conc. $HNO_3 + H_2SO_4$ →	$NO_2^{\oplus}$
② Halogenation →	Br_2/Fe or $Br/FeBr_3$ →	$Br^{\oplus}$
③ Sulphonation →	$H_2SO_4 + H_2SO_4$ →	$SO_3^{\oplus}$ ↳ Add (HSO_3) on benzene.

- Note : CH_3 → Aliphatic chain → Halogenation → $X_2/h\nu$; X_2/sunlight

 → Aromatic chain → Halogenation → $Cl^{\oplus}$ or $Br^{\oplus}$
← X_2/Metal ; $Br_2/FeBr_3$
X_2/Lewis Acid ; Br_3/Fe

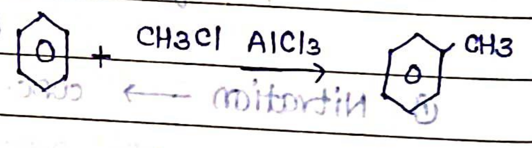


- 

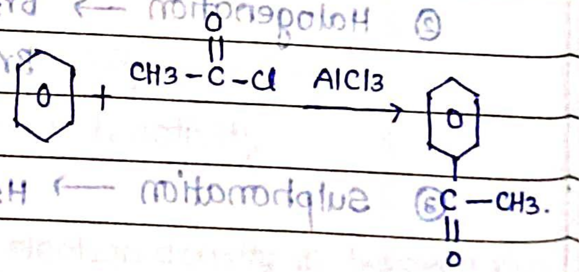
2,4,6 - Trinitro Taulene (T.N.T)

- Friedal's Craft Reaction :

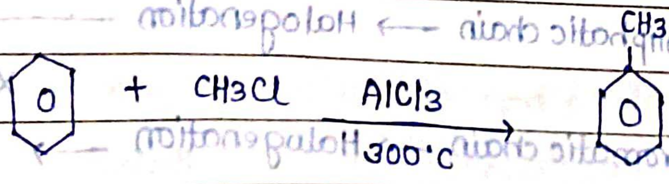
F.C.R — F.C alkylation (addition of alkyl group in Benzene Ring)



F.C. Acylation (addition of acyl $-\overset{O}{\overset{\|}{C}}-R$ group in Benzene Ring)



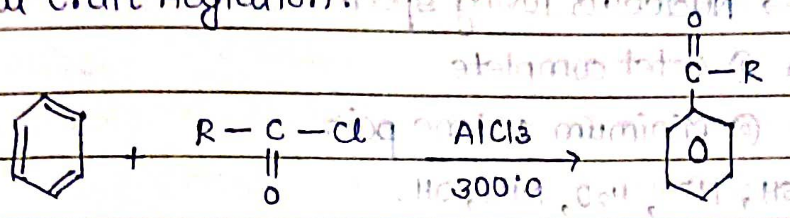
- Friedal Craft alkylation :



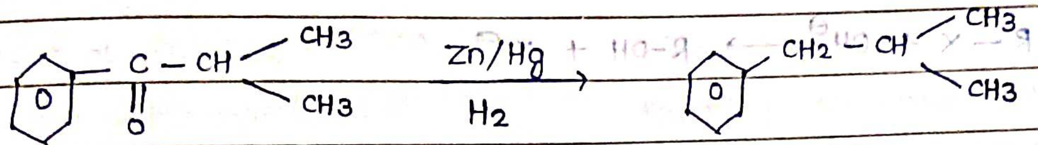
① Carbocation Formation
② Rearrangement takes place.

- Note: Alkylation does not form bulky 1° alkane (Brach 1° alkane)

- Friedal Craft Acylation:



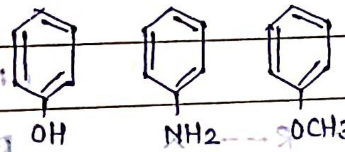
- No Rearrangement.



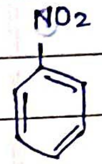
- Note:

① Primary Bulky alkane form by Acylation.

② F.C.R ⟶



⟶ No Reaction.



③ strong Deactivating group do not show Friedal crafts Reaction.