12 Feb 25

Ch - 9 - Hydrocarbon

Carbon and Hydrogen

Saturated
- C-C
- Alkane
- C_nH_{2n+2}
- Suffix :- ane
- Hybⁿ :- sp^3
- Shape :- tetrahedral
- ↑-S → 25%
- 109°5' or 109°28'
- C-C → 154pm

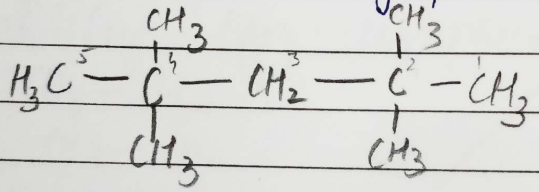
Unsaturated

Alkene
- C=C
- C_nH_{2n}
- suffix :- ene
- Hybⁿ :- sp^2
- shape : trigonal planar
- ↑-S = 33.3
- C=C :- 134pm

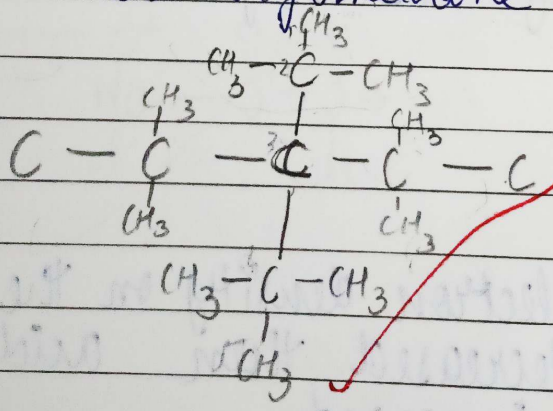
Alkyne
- C≡C
- C_nH_{2n-2}
- suffix :- yne
- sp
- linear
- 50%
- C≡C :- 122pm

Aromatic

- 2,2,4,4 - tetramethyl pentane

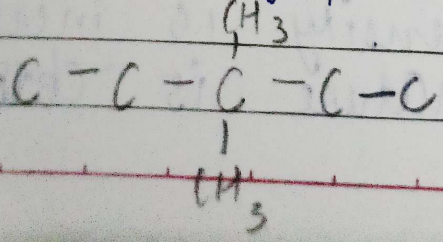


- C :- tetra - tert butyl methane

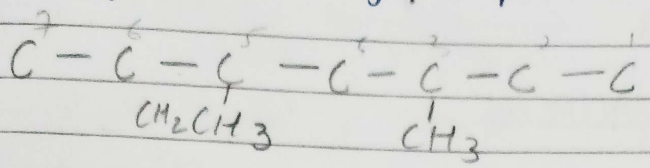


I :- 3,3 - di-tertbutyl - 2,2,4,4- tetramethyl pentane

- 3,3 - dimethyl pentane :-

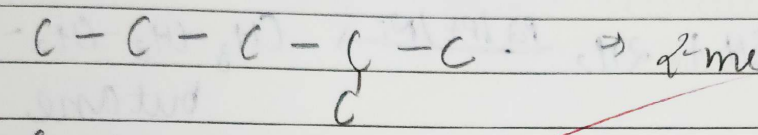


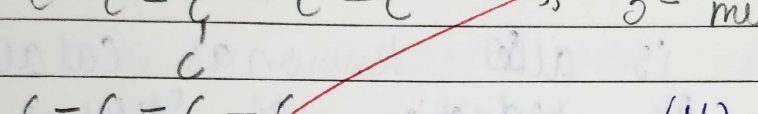
esc:- 5 - ethyl - 3 - methyl heptane

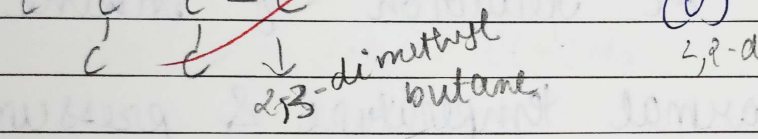


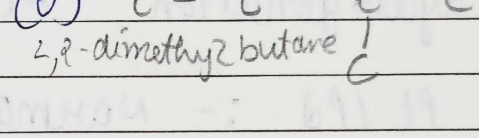
Ex 9] Isomers of Hexane :- C_6H_{14} → C_nH_{2n+2}

(i) C-C-C-C-C-C → n-hexane

(ii)  → 2-methyl pentane

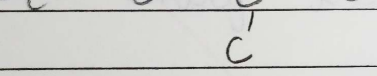
(iii)  → 3-methyl pentane

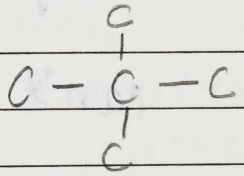
(iv)  → 2,3-dimethyl butane

(v)  → 2,2-dimethyl butane

• Isomers of pentane :- C_5H_{12}

(i) C-C-C-C-C

(ii) 

(iii) 

* Preparation of Alkane.

- From Unsaturated Hydrocarbon or Hydrogenation
- From Alkyl halide (R-X)
  - (1) Zn / dilute HCl
  - IMP (2) Wurtz Reaction
- (1) decarboxylation
  - IMP (2) Kolbe's electrolysis

CH_3CH_2Cl
I :- chloro - ethane
C :- ethyl chloride

Hydrogenation → Add H
dehydrogenation → Remove H
Hydration → Add H_2O
dehydration → Remove H_2O

① From unsaturated Hydrocarbon :-

1) Alkene (C=C)

Rx :- $CH_2=CH_2 + H_2 \xrightarrow{Pd/Pt/Ni} CH_3-CH_3$
ethene → ethane

Rx :- $CH_3-CH=CH_2 + H_2 \xrightarrow{Pd/Pt/Ni} CH_3-CH_2-CH_3$
propene → propane

Rx :- $H_3C-H_2C-C\equiv CH + 2H_2 \xrightarrow{Pd/Pt/Ni} CH_3-CH_2-CH_2-CH_3$
but-1-yne → butane

2) This method is also known as catalytic hydrogenation or reduction of Alkene.

- Pt / Pd :- Normal temperature & pressure.
  Ni :- High temperature & pressure
- Methane can't be prepared from this method.

② From Alkyl Halide (R-X) :-
R- alkyl group (long chain of C)

- $CH_3Cl + H_2 \xrightarrow[\text{dilluted HCl}]{Zn} CH_4 + HCl$
- chloro methane → methane
- $CH_3CH_2CH_2Br + H_2 \xrightarrow[\text{dilluted HCl}]{Zn} CH_3CH_2CH_3 + HBr$

- Order of Reactivity :-

$R-I > R-Br > R-Cl > R-F$
(too slow) ← (violent reaction)

Bond length ↑
Bond strength ↓

M.M. IMP

(ii) Wurtz Reaction (Naming reaction)

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

(reagent)

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

ex:- $2CH_3Cl + 2Na \xrightarrow[\text{ether}]{\text{dry}} CH_3-CH_3 + 2NaCl$

ethane

ex:- $2CH_3CH_2Cl + 2Na \xrightarrow[\text{ether}]{\text{dry}} CH_3CH_2CH_2CH_3 + 2NaCl$

Butane

→ Disadvantages :-

- We can't prepare odd no. of alkane.

ex:- $CH_3CH_2Cl + 2Na + Cl-CH_3 \xrightarrow[\text{ether}]{\text{dry}}$

$1CH_3-Cl \longrightarrow \overset{+}{C}H_3 - \overset{+}{C}H_3$

$CH_3CH_2Cl \longrightarrow CH_3CH_2CH_2CH_3$

$CH_3CH_2Cl + CH_3Cl \longrightarrow CH_3CH_2CH_3$ → mixtures of alkane

1 mol

propane

(3) Decarboxylation :- (Removal of CO_2)

$CH_3COO^-H^+ + Na^+OH^- \longrightarrow CH_3COONa + H_2O$

Acid Base

Sodium Acetate

or.

Sodium ethanoate

- $CH_3COONa^+ + Na^+OH^- \xrightarrow[\text{Soda lime}]{CaO,\ \Delta} CH_4 + Na_2CO_3$

$NaOH$ = caustic soda

CaO = quick lime

→ This method is used to decrease no. of carbon

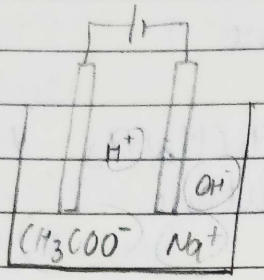
eg: 9.6)

- $CH_3CH_2CH_2COONa \xrightarrow[NaOH]{CaO} CH_3CH_2CH_3 + Na_2CO_3$ (→ Soda lime)

(ii) Kolbe's electrolysis :-

$2CH_3COO^-Na^+ + 2H_2O \xrightarrow{\text{electrolysis}} CH_3-CH_3 + 2NaOH + H_2 + 2CO_2$

(ethane gas)



* Mechanism :-

→ $2CH_3COO^-Na^+ \longrightarrow 2CH_3COO^- + Na^+$

- At anode :- Oxidation

- $2CH_3COO^- \xrightarrow{\text{loss of } e^-} 2e^- + 2\,CH_3-\overset{\overset{O}{\uparrow}}{C}-O:$

- $2CH_3-\overset{\overset{O}{\uparrow}}{C}-O: \longrightarrow 2\,CH_3 + 2\,\overset{\overset{O}{\uparrow}}{C}-O:$ (→ CO_2)

- $2CH_3 \longrightarrow CH_3 + CH_3 \longrightarrow CH_3-CH_3$ (ethane)

- At cathode :- Reduction

$2H_2O + 2e^- \longrightarrow 2H + 2OH^-$

$2H \rightarrow H_2$

* Physical properties of Alkane :-

→ C_1 to C_4 :- gases

→ C_5 to C_{17} :- liquid

→ C_{18} & above :- solid

→ Alkanes are insoluble in water.

H_2O = Universal solvent.

dissolves

⇒ polar solute + polar solvent (like dissolves like)

eg:- NaCl H_2O

- solute = less amount
- solvent = large amount

⇒ Non-polar solute dissolves Non-polar solvent

eg:- Non polar solvent :- benzene, toluene, ether, $CHCl_3$, CCl_4

⇒ They are colourless & odourless
⇒ As the no. of carbon increase, mass increase, density increase, boiling point increase
⇒ Boiling point of carbon chain.
⇒ Boiling point $\propto \frac{1}{\text{carbon chain (Branch)}}$

* Chemical reaction of Alkanes :-

1) Substitution reaction :-
- Halogenation
- Nitration
- Sulphonation

Note :- lower Alkane does not show nitration & sulphonation.

$CH_4 \xrightarrow[+X]{-H} CH_3-X$

(i) Halogenation :-
(a) At very high temp. (573K to 773K)
(b) Sunlight / Ultraviolet ray. ($h\nu$)

excess

1) $CH_4 + Cl_2 \xrightarrow[\text{homolysis}]{h\nu} CH_3-Cl + HCl$ chloromethane

Chlorination

- $CH_3-Cl + Cl_2 \xrightarrow[\text{homolysis}]{h\nu} CH_2Cl_2 + HCl$ dichloromethane
- $CH_2Cl_2 + Cl_2 \xrightarrow[\text{homolysis}]{h\nu} CHCl_3 + HCl$
  C :- chloroform.
  I :- trichloromethane.
- $CHCl_3 + Cl_2 \xrightarrow[\text{homolysis}]{h\nu} CCl_4 + HCl$
  I :- tetrachloromethane
  C :- Carbon tetrachloride
- Order of reactivity in this case for halogens is :-

1) F_2, Cl_2, Br_2, I_2.
$F_2 > Cl_2 > Br_2 > I_2$

2) Order of reactivity in terms of carbon is
$3° > 2° > 1°$

- $CH_4 + I_2 \rightleftharpoons CH_3I + HI$.
- Oxidizing agent is HIO_3 or HNO_3
  Iodic Acid

$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$

Iodinations show 2 reversible

- Halogenation :- Mechanism :- (Free Radical formation)

1) Initiation
2) Propogation
3) Termination

general :- $CH_4 + Cl_2 \rightarrow CH_3Cl +$ HCl
rxn

(1) **Initiation** :-

$Cl-Cl \xrightarrow[\text{Homolysis}]{h\nu} \dot{Cl} + \dot{Cl}$

(Free Radical Formation)

(2) **Propogation** :-

$CH_4 + \dot{Cl} \xrightarrow[\text{homolysis}]{h\nu} \dot{C}H_3 + HCl$

$\dot{C}H_3 + Cl-Cl \xrightarrow[\text{homolysis}]{h\nu} CH_3Cl + \dot{Cl}$

Step :- 2

$CH_3Cl + \dot{Cl} \xrightarrow[\text{Homolysis}]{h\nu} \dot{C}H_2Cl + HCl$

$\dot{C}H_2Cl + Cl-Cl \xrightarrow[\text{homolysis}]{h\nu} CH_2Cl_2 + \dot{Cl}$

Step :- 3

$CH_2Cl_2 + \dot{Cl} \xrightarrow[\text{homolysis}]{h\nu} \dot{C}HCl_2 + HCl$

$\dot{C}HCl_2 + Cl-Cl \xrightarrow[\text{homolysis}]{h\nu} CHCl_3 + \dot{Cl}$

Step :- 4

$CHCl_3 + \dot{Cl} \xrightarrow[\text{homolysis}]{h\nu} \dot{C}Cl_3 + HCl$

$\dot{C}Cl_3 + Cl-Cl \xrightarrow[\text{homolysis}]{h\nu} CCl_4 + \dot{Cl}$

(3) **Termination** :-

→ Side reaction : by product is formed

MCQ.

$\dot{Cl} + \dot{Cl} \longrightarrow Cl_2$

$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3-CH_3$ → ethane → by product → small amount

$\dot{C}H_3 + Cl \longrightarrow CH_3-Cl$

(2) Combustion of Alkane :-

General formula

$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O$

- $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

$\Delta_c H^\circ = -890\ KJ/mol$

- $C_4H_{10} + \frac{13}{2}O_2 \longrightarrow 4CO_2 + 5H_2O$

$\Delta_c H^\circ = -2875.84\ KJ/mol$

- High amount of heat is produced during the combustion of Alkane, so it is used as a 'Fuel'.

- **Incomplete combustion :-**

$CH_4(g) + O_2(g) \xrightarrow{\text{Incomplete combustion}} C_{(s)} + 2H_2O\ (l)$

↳ Carbon black.

- Uses of Carbon black :-
  - → Ink
  - → Printer ink
  - → Pigment
  - → filter

(3) Controlled Oxidation :-

1) $2CH_4(g) + O_2(g) \xrightarrow[523\ K,\ 100\ atm]{Cu} 2CH_3OH\ (l)$

Methanol

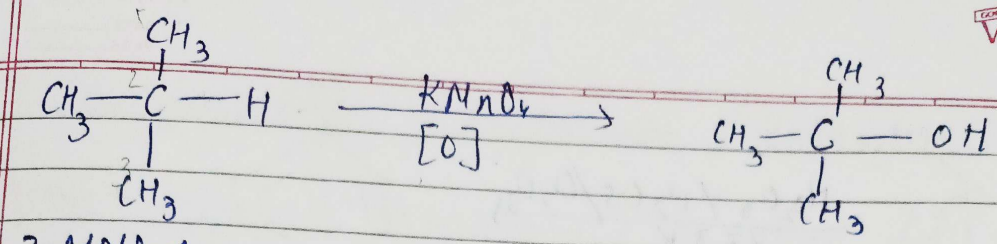
2) $CH_4 + O_2 \xrightarrow[\text{Molybdenum Oxide}]{MoO_3} HCHO + H_2O$

Methanal

3) $2CH_3-CH_3 + 3O_2 \xrightarrow[\text{Manganese acetate}]{(CH_3COO)_2Mn} 2CH_3COOH + 2H_2O$

Ethane → Acetic acid

I :- ethanoic acid

G/ 

2-Methyl propane

2-methyl propan-2-ol
(3°)

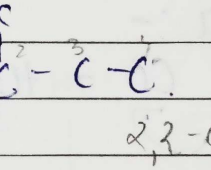
(4) Isomerisation :-

⇒ $CH_3-CH_2-CH_2-CH_2CH_2-CH_3$ (n-Hexane) $\xrightarrow[AlCl_3 \,/\, HCl]{\text{Anhydrous}}$

$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2CH_3$ + $CH_3CH_2\underset{\underset{CH_3}{|}}{CH}-CH_2CH_3$

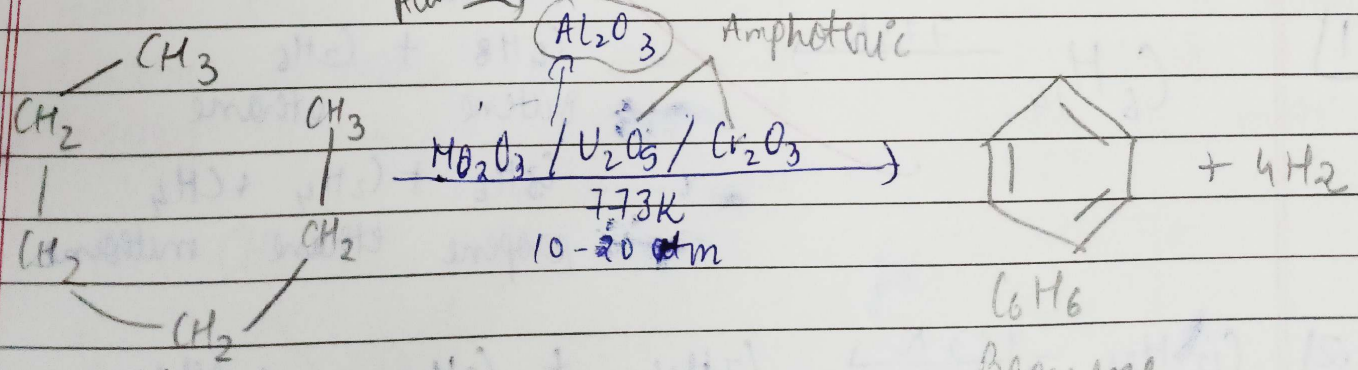
(2 methyl pentane) (3-methyl pentane)

Major Products

• $CH_3\overset{6}{C}H\overset{3}{C}H\overset{2}{C}H_3\overset{1}{C}H_3$ (2,3 dimethyl butane) +  (2,2-dimethyl butan)

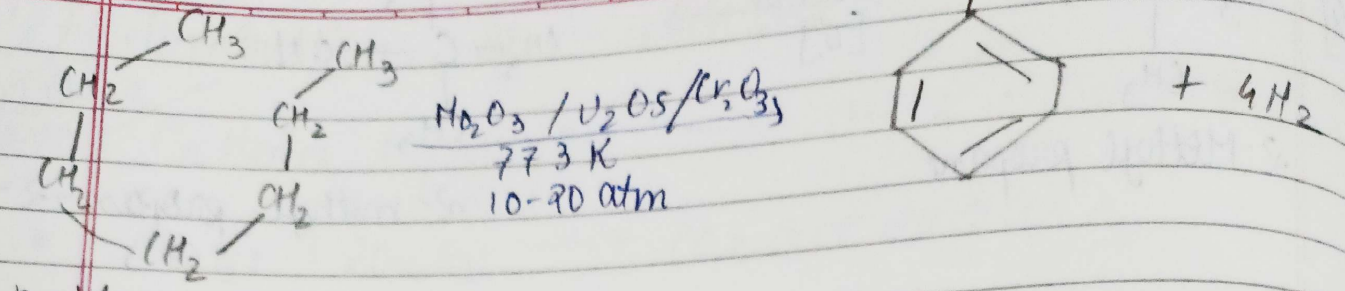
Minor Products

(5) Aromatization / Dehydrogenation / Reforming :-



n-Hexane

C6H6
Benzene



n-Heptane

(6) Reaction with steam

$CH_4(g) + H_2O(g) \xrightarrow[1273\ K]{Ni} CO + 3H_2$

carbon monoxide

↳ used in industry ← ↳ H_2 gas production

★ Nota :-

$CO + H_2$ → water gas or synthesis gas

CH_2O

(7) Pyrolysis / Cracking / Thermal Cracking

1) $C_6H_{14} \xrightarrow{773K}$

- $C_6H_{12} + H_2$ (Hexene)
- $C_4H_8 + C_2H_6$ (Butene, ethane)
- $C_3H_6 + C_2H_4 + CH_4$ (propene, ethene, methane)

2) $C_{12}H_{26} \xrightarrow[Pd/Pt/Ni]{973\ K} C_7H_{16} + C_5H_{10} +$ other product

dodecane → constituent of kerosene

Heptane, pentene

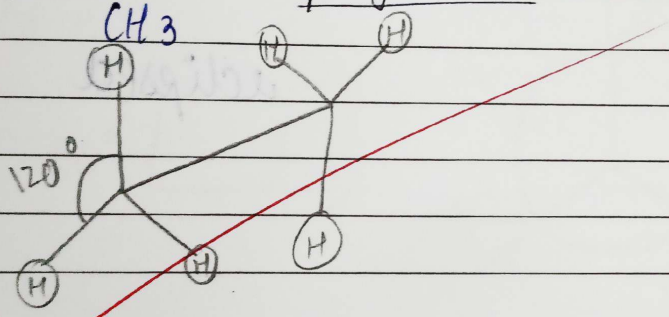
Conformation / Conformer / Rotamer :-

⇒ The different arrangement of atom in the space can be obtained by rotation of carbon-carbon single bond is called ....

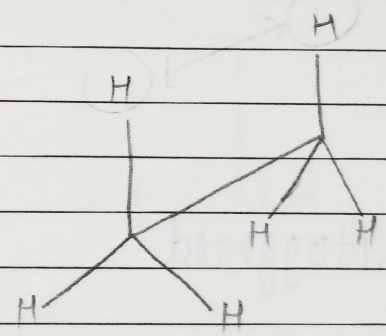
Representation

- Sawhorse projection → straight line
  - Staggered
  - eclipsed
- Newman projection → circular / circle
  - Staggered
  - eclipsed

(1) Sawhorse projection :-

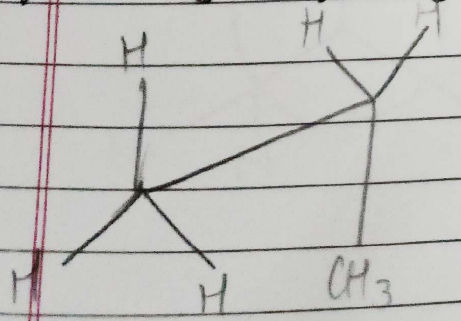


Staggered
- → more stable
- → distance is more
- → energy is less

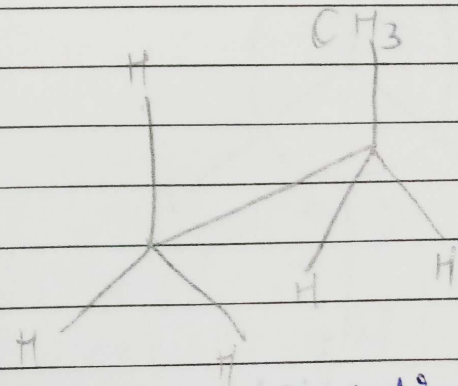


eclipsed
- → distance in minimum
- → less stable
- → energy is more

ex:- $CH_3-CH_2-CH_3$

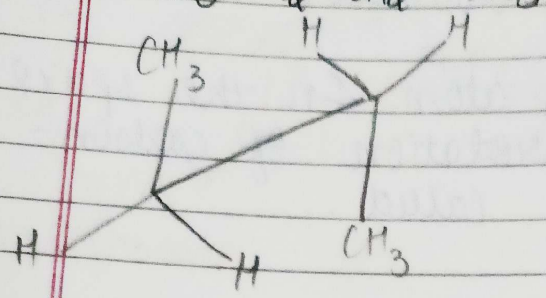


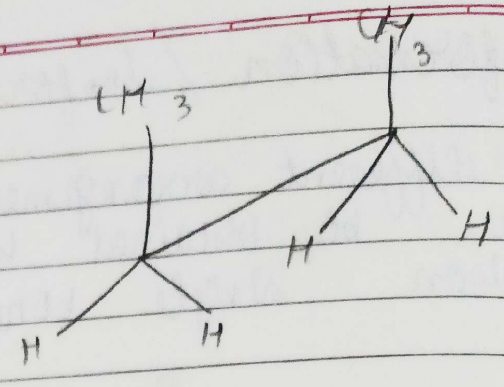
staggered



eclipsed

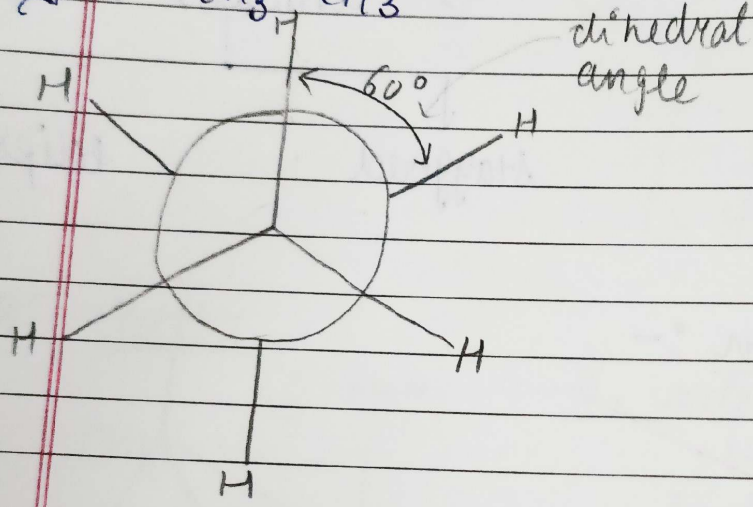
ex:- $CH_3-CH_2-CH_2-CH_3$



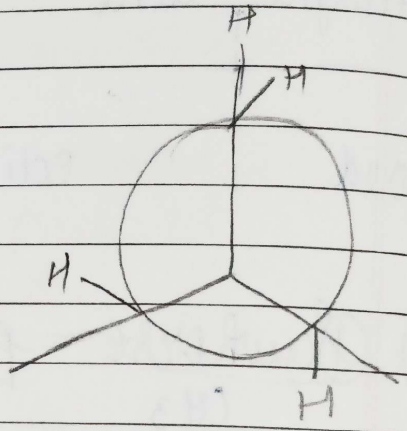


(2) Newman Projection :-

ex:- CH_3-CH_3



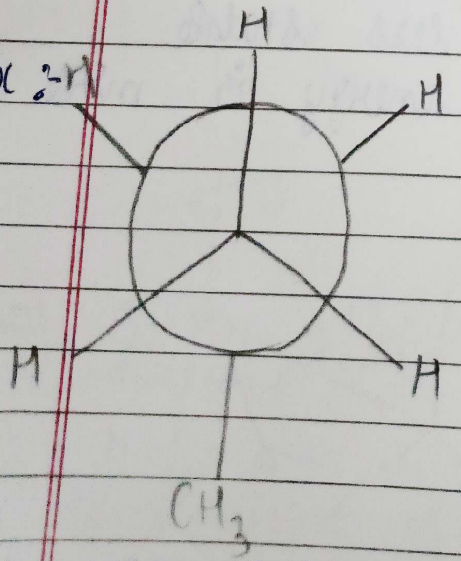
Staggered



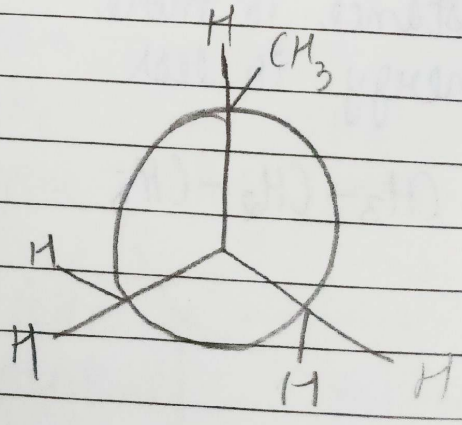
eclipsed

- Torsional strain :- Electronic repulsion b/w 2 atom is called .....

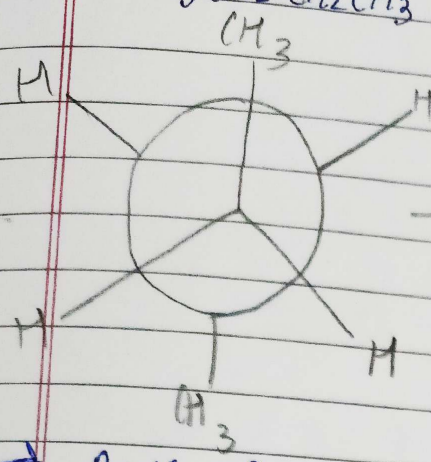
ex :-



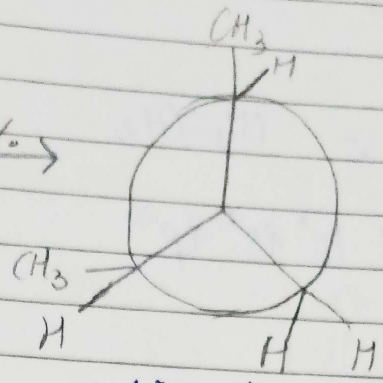
$\theta = 180°$



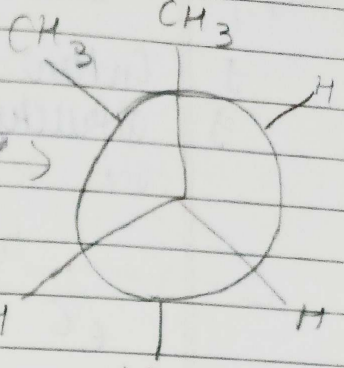
Ex:- $CH_3CH_2CH_2CH_3$



60% →



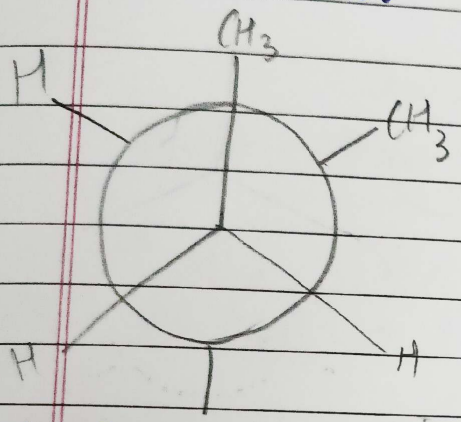
60% →



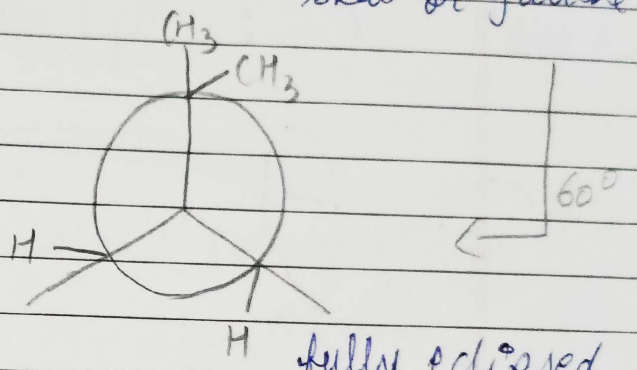
→ Anti $\theta = 180°$

eclipsed

skew or gauche

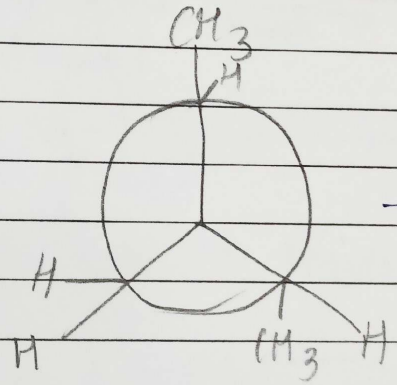


60° ←



skew

60° →



→ eclipsed

fully eclipsed
$\theta = 0°$

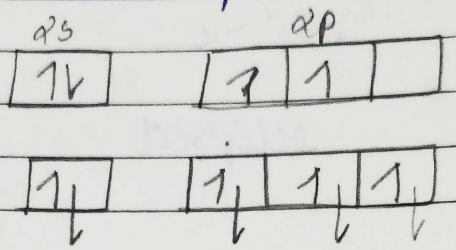
- Stability order

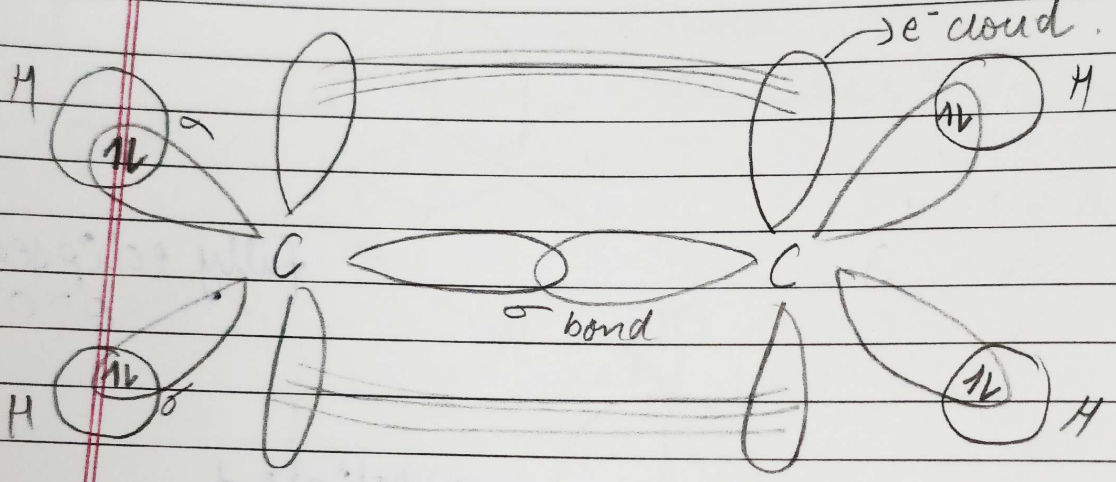
→ Anti > eclipsed > skew > fully eclipsed

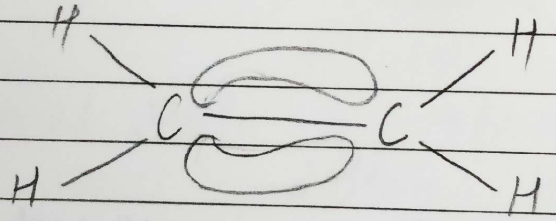
Alkene :-

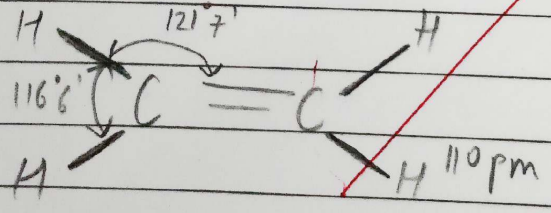
- C_nH_{2n}
- Structure :- $CH_2=CH_2$

$_6C : 1s^2 2s^2 2p^2$







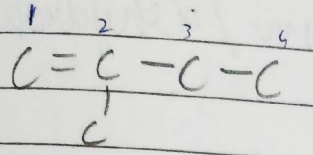


- C=C → 134 pm
- H-H → 116°6'
- C-H → 110 pm

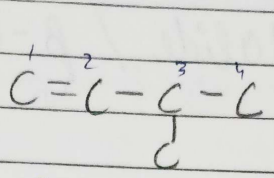
Isomers of pentene :- (C_5H_{10})

$C=C-C-C-C$ → pent-1-ene

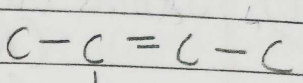
$C-C=C-C-C$ → Pent-2-ene



→ 2 methyl but-1-ene



3-methyl but-1-ene.



2-methyl but-2-ene

Preparation of Alkene :-

1) From Alkyne :-

(i) $RC\equiv CR' + H_2 \xrightarrow{Pd/C} \underset{\text{cis Alkene}}{\text{R, R', H, H}}$ (Lindlar's catalyst)

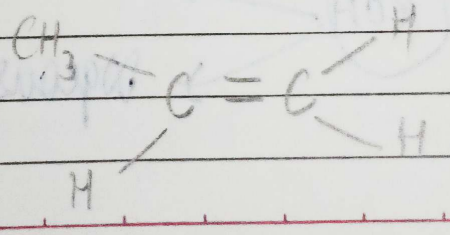
Partially reduced

Palladised Charcoal → deactivated → Sulphur → Poison or quinoline

(ii) $RC\equiv CR' + H_2 \xrightarrow[\text{liq. } NH_3]{Na} \underset{\text{trans - Alkene}}{\text{R, H, H, R'}}$

Ex:- $CH\equiv CH + H_2 \xrightarrow{Pd/C} CH_2=CH_2$

Ex:- $CH_3-C\equiv CH + H_2 \xrightarrow{Pd/C} CH_3-CH=CH_2$



dehydrohalogenation → removal of H & X.

Ex:- $CH_3-C\equiv C-CH_3 + H_2 \xrightarrow{Pd/C}$ cis-but-2-ene

(2) IMP

From Alkyl Halide / β-elimination / dehydrohalogenation

(R-X)

X = Cl, Br, I

Ex:- $CH_3CH_2Cl \xrightarrow[\Delta]{\text{Alcoholic KOH}} CH_2=CH_2 + HCl$

Chloro ethane or ethyl chloride

Ex:- $CH_3-\underset{Br}{\underset{|}{CH}}-CH_3 \xrightarrow[\Delta]{\text{Alcoholic KOH}} CH_2=CH-CH_3$ prop-1-ene

Ex:- $CH_3-CH_2-\underset{Br}{\underset{|}{CH}}-CH_3 \xrightarrow[\Delta]{\text{Alcoholic KOH}} CH_3-CH=CH-CH_3$ But-2-ene

Note:- According to Saytzeff rule in β-elimination, hydrogen is removed from the carbon where the no. of hydrogen atom is less.

Ex:- $CH_3-\underset{CH_3}{\underset{|}{C}}(CH_3)-Cl \xrightarrow[\Delta]{\text{Alcoholic KOH}} CH_3-\underset{CH_2}{\underset{||}{C}}(CH_3)$

KOH → Alc. KOH → Elimination

→ Aqueous KOH → Substitution

$-\overset{|}{C}-C$ → geminal
$\quad\;\; Cl$

(3) From Vicinal dihalide :-

↳ vic → neighbour → carbon

→ $CH_2(Cl)-CH_2(Cl)$ → Vicinal dihalide

Eg:→ $CH_2(Cl)-CH_2(Cl) + Zn \xrightarrow{\text{(dust)}} CH_2=CH_2 + ZnCl_2$

Ex:- $CH_3-CH(Br)-CH(Br)-CH_3 \xrightarrow[\text{dust}]{Zn} CH_3-CH=CH-CH_3 + ZnBr_2$
But-2-ene

Ex:- $CH_3-CH(Br)-CH(Cl)-CH_3 \longrightarrow \not\rightarrow$ (not occuring)

Ex:- $CH_3-CH(Br)-CH_2-CH_2(Br) \longrightarrow X$ (not occuring)

(4) From Alcohol by Acidic dehydration.

↓ Acid catalyst

Remove H_2O

→ Follows β- elimination

Ex:- $CH_3-\overset{\beta}{CH_2}-\overset{\alpha}{CH_2}-OH \xrightarrow[H_2SO_4]{\text{conc.}} CH_3-CH=CH_2 + H_2O$

Ex:- $CH_3-\overset{\beta_1}{CH}(OH)-\overset{\alpha}{CH_2}-\overset{\beta_2}{CH_3} \xrightarrow[H_2SO_4]{\text{Conc.}} CH_3-CH=CH-CH_3 + H_2O$

Ex:- $CH_3-\overset{\beta_1}{CH_2}-\overset{\alpha}{CH}(OH)-\overset{\beta_2}{CH_2}-CH_3 \xrightarrow[H_2SO_4]{\text{conc.}} CH_3-CH=CH-CH_3 + H_2O$

* Physical properties :-

→ C_2, C_3, C_4 → gases
C_5 to C_{18} → liquid
& above → solid

→ ethene is colourless but having faint sweet smell.
→ Other alkenes are colourless & odourless.

- Solubility :- insoluble in water
  → highly soluble in organic solvent like benzene, toluene, ether, CCl_4.
- Boiling point :- boiling point ∝ No of carbon.
- $-CH_2$ add → temperature → increases by 20 to 30 K.

* Chemical Reaction :-

(1) Addition of dihydrogen

ex. $CH_2=CH_2 + H_2 \xrightarrow{Pd/Pt/Ni} CH_3-CH_3$
ethene → ethane

ex. :- $CH_3-CH=CH_2 + H_2 \xrightarrow{Pd/Pt/Ni} CH_3-CH_2-CH_3$
→ Propane

(2) Addition of dihalogen :-

ex :- $CH_2=CH_2 + Br_2 \xrightarrow{CCl_4} CH_2(Br)-CH_2(Br)$ } Reddish orange

→ Unsaturation test

ex :- $CH_3-CH=CH_2 + Cl_2 \longrightarrow CH_3-CH(Cl)-CH_2(Cl)$
1,2-dichloro propane

- Unsaturation test :- Alkene + Br_2 + CCl_4

(3) Addition of Hydrogen halide (H-X) / electrophilic addition reaction (E^+)

→ H-I > H-Br > H-Cl

(i) For Symmetric ethene :-

ex:- $CH_2=CH_2$ + HCl ⟶ CH_3CH_2Cl
ethene

ex:- $CH_3-\overset{+}{C}H=\bar{C}H-CH_3 + H^+\bar{B}r \longrightarrow CH_3-\underset{Br}{CH}-CH_2-CH_3$

(ii) For unsymmetrical ethene :-

$CH_3-CH=CH_2 + H\bar{C}l \longrightarrow CH_3-\underset{Cl}{CH}-CH_3$

- **Markonikov's Rule** :- Negative part of halide is connected to that carbon, where no. of hydrogen is less.

$CH_3-CH=CH_2 + H^+Br^-$

↓ $CH_3-\bar{C}H-\overset{+}{C}H_2$ → $CH_3-CH_2-\overset{+}{C}H_2$ (1° less stable)

↓ $CH_3-\overset{+}{C}H-\bar{C}H_2$ → $CH_3-\overset{+}{C}H-CH_3$ (2° carbocation is more stable)

$CH_3-CH=CH_2 + HBr \longrightarrow CH_3-\underset{Br}{CH}-CH_3$ + $CH_3CH_2CH_2Br$

Major product — Minor product

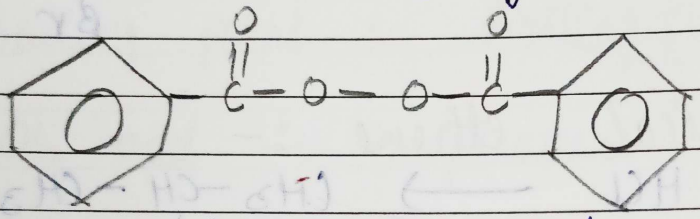
Antimarkonikov Rule / Kharash effect / Peroxide effect

- Condition :- HBr + Peroxide / HCl & HI → X
- $CH_3-CH=CH_2 + HBr \xrightarrow{\text{Peroxide}} CH_3-CH_2-CH_2-Br$
- $CH_3-CH=CH_2 + HBr \longrightarrow CH_3-\underset{Br}{CH}-CH_3$

  2- Bromo-propane

- **Mechanism** :- Follows Homolysis

H_2O_2 → Hydrogen peroxide



$[(C_6H_5CO)_2O_2]$

Benzoyl peroxide

Step 1 :- $C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \xrightarrow{\text{Homolysis}} 2C_6H_5-\overset{O}{\overset{\|}{C}}-O\cdot$

Step 2 :- $2C_6H_5-\overset{O}{\overset{\|}{C}}-O\cdot \xrightarrow{\text{Homolysis}} 2C_6H_5\cdot + 2CO_2\uparrow$

Step 3 :- $C_6H_5\cdot + H-Br \xrightarrow{\text{Homolysis}} C_6H_6 + Br\cdot$

Step 4 :- $CH_3CH=CH_2 + Br\cdot$

$CH_3-\dot{C}H-CH_2$ → $CH_3-CH-CH_2$ (Br)

1° free radical

$CH_3-\dot{C}H-CH_2$ → $CH_3-CH-CH_2Br$

2° free radical

Step 5: $CH_3-\underset{\underset{Br}{|}}{CH}-CH_2 + HBr \longrightarrow CH_3-\underset{\underset{Br}{|}}{CH}-CH_3 + Br^-$

(Minor)

$CH_3-\underset{\underset{Br}{|}}{CH}-CH_2Br + HBr \longrightarrow CH_3CH_2-CH_2Br + Br^-$

(Major)

(4) Addition of H_2SO_4 :-

Ex: $CH_2=CH_2 + H^+\ddot{O}-\underset{\underset{O}{\|}}{\overset{O}{\overset{|}{S}}}-O-H \longrightarrow CH_3CH_2-OSO_3H$

conc & cold

or

$CH_3-CH_2-HSO_4$

(Ethyl hydrogen sulphate)

Ex: $CH_3-CH=CH_2 + H-O-\underset{\underset{O}{\|}}{\overset{O}{\overset{|}{S}}}-O-H \longrightarrow CH_3-\underset{\underset{OSO_3H}{|}}{CH}-CH_3$

propyl hydrogen sulphate

(5) Addition of H_2O :-

Ex:- $CH_2=CH_2 + H_2O \xrightarrow[H_2SO_4]{\text{conc}} CH_3CH_2OH$

(H^+, OH^-; few drops)

1° Alcohol

Ex:- $CH_3-CH=CH_2 + H_2O \xrightarrow{H^+} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$

(H^+, OH^-)

2° Alcohol

Ex:- $CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 + H_2O \xrightarrow{-H^+} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3$

(H^+, OH^-)

3° Alcohol.

⑥ Oxidation :- → purple → decolourised

(i) $CH_2=CH_2 + H_2O \xrightarrow[[O]]{\text{aqueous } KMnO_4} CH_2(OH)-CH_2(OH)$

C :- ethylene glycol
I :- ethane-1,2-diol

Baeyer's reagent :- Cold aqueous $KMnO_4$ solution

$H_2O + O \longrightarrow H_2O_2$ (OH, OH)

$H-O\rightleftarrows O-H$

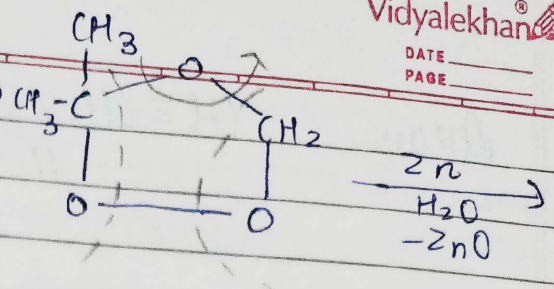
(ii) $CH_3-CH=CH_2 + H_2O \xrightarrow[[O]]{Aq.\ KMnO_4} CH_3-CH(OH)-CH_2(OH)$
prop-1-ene
propane-1,2-diol

(iii) $CH_3-CH=CH-CH_3 \xrightarrow[\text{or } H^+/KMnO_4]{\text{Acidic } KMnO_4} 2\,CH_3-C(=O)-H$
But-2-ene
ethanoic acid

(iv) $(CH_3)_2C=CH_2 \xrightarrow[[O]]{\text{Acidic } KMnO_4} CH_3-C(=O)-CH_3 + CO_2 + H_2O$
2-methyl prop-1-ene
propan-2-one

⑦ Ozonolysis :- (O_3)

(i) $CH_2=CH_2 + O_3 \longrightarrow$ ethene ozonide $\xrightarrow[H_2O]{Zn} H-C(=O)-H + H-C(=O)-H + ZnO$
Methanal

(ii) $CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 + O_3 \longrightarrow$  $\xrightarrow[H_2O]{Zn} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + HCHO$

propan-2-one Methanal

Polymerisation :-

Polymer → Monomer ⇒ Single unit.

(i) $n(CH_2=CH_2) \xrightarrow[\text{High pressure}]{\text{High temp.}} -(CH_2-CH_2-CH_2-CH_2-CH_2-)_n$

Ziegler Nata catalyst

Polymer

polythene

(ii) $n(CH_3-CH=CH_2) \xrightarrow[\text{High pressure.}]{\text{High temp.}} -(\underset{CH_3}{CH}-CH_2)_n$

propene catalyst

polypropene → milk crates

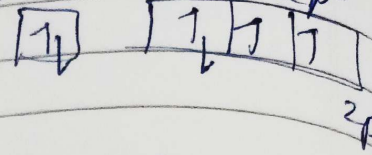
Alkynes

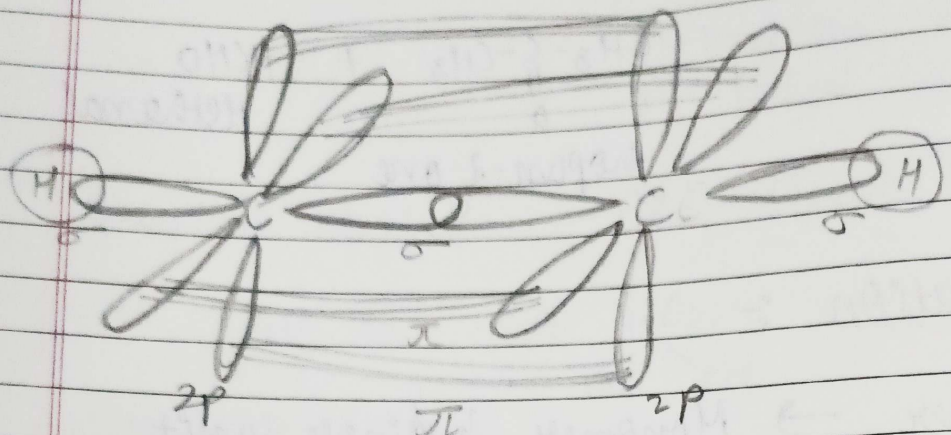
C-C

		Bond enthalpy	Bond length
→ C_nH_{2n-2}	$CH\equiv CH$	823 KJ/mol	120pm
→ sp			
→ Linear	$CH_2=CH_2$	681 KJ/mol	134pm
→ %S = 50%	CH_3-CH_3	348 KJ/mol	154pm

* Draw $CH \equiv CH$ $\quad H-C \equiv C-H$

$6C = 1s^2\ 2s^2\ 2p^2$





9.13 ex * Draw isomers of 5th member of Alkyne series
↳ Pentyne

(1) $C \equiv C-C-C-C-C$ ⇒ Hex-1-yne

(2) $C-C \equiv C-C-C-C$ ⇒ Hex-2-yne

(3) $C-C-C \equiv C-C-C$ ⇒ Hex-3-yne

(4) $C \equiv C-C-\underset{\underset{C}{|}}{C}-C$ ⇒ 4 methyl pent 1-yne

(5) $C \equiv C-\underset{\underset{C}{|}}{C}-C-C$ ⇒ 3-methyl pent-1-yne

(6) $C-C \equiv C-\underset{\underset{C}{|}}{C}-C$ ⇒ 4-methyl pent-2-yne

(7) $C \equiv C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-C$ ⇒ 3,3-dimethyl butyne

* Preparation of Alkyne :-

① From calcium carbide (CaC_2)) Industrial Method

$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$
limestone — quick lime

$CaO + 3C \longrightarrow CaC_2 + CO$
Coke — Calcium Carbide — Carbon monoxide

$CaC_2 + 2H_2O \longrightarrow CH\equiv CH + Ca(OH)_2$
$2H^+ \; 2OH^-$ — ethyne

* From Vicinal dihalide :-

Ex:- $\overset{\beta}{C}H_2Cl - \overset{\alpha}{C}H_2Cl + KOH \xrightarrow[-KCl\,-H_2O]{\text{Alcoholic}} \overset{\alpha}{C}H=\overset{\beta}{C}H_2Cl \xrightarrow[\text{sodamide}\;-NaCl\;-NH_3]{Na^+NH_2^-} CH\equiv CH$

Ex:- $CH_3 - \overset{\beta}{C}HBr - \overset{\alpha}{C}H_2Br + KOH \xrightarrow[-KBr\,-H_2O]{\text{Alcoholic}} CH_3-\overset{\alpha}{C}=\overset{\beta}{C}H_2 \xrightarrow[-NaBr\,-NH_3]{Na^+NH_2^-} CH_3-C\equiv CH$
Br Br — Br

* Physical properties :-

→ C_2, C_3, C_4 → gases
→ C_5 to C_{12} → liquid
→ C_{12} above → solid

→ All alkynes are colourless & odourless.
→ But ethyne has characteristic odour.

→ It is lighter than water.
→ It is insoluble in water.
→ It is soluble in organic solvent like benzene, ether, CCl_4
→ Boiling point

* Chemical Reaction :-

(1) Acidic Nature of Alkyne :-

(Ex) $CH \equiv \bar{C}H^+ + Na^+ \longrightarrow CH \equiv C\bar{N}a^+ + \frac{1}{2} H_2 (g)$
Acid Metal Monosodium ethynide

(Ex) $CH \equiv C\bar{N}a^+ + Na \longrightarrow Na^+C^- \equiv C\bar{N}a^+ + \frac{1}{2} H_2$
disodium ethynide.

$CH_3-C \equiv \bar{C}H^+ + N\bar{a}NH_2^- \longrightarrow CH_3-C \equiv C\bar{N}a^+ + NH_3$
propyne Base

- Order of acidic character :-

→ $CH \equiv CH > CH_3 \rightarrow C \equiv CH > CH_3-CH_2-C \equiv CH > CH_3-C \equiv C-CH_3$

→ $C \equiv C > C=C > C-C$
✓ ✗ ✗

(2) * Addition of dihydrogen / Reduction

→ $CH \equiv CH + H_2 \xrightarrow{Pd/Pt/Ni} CH_2=CH_2 + H_2 \xrightarrow{Pd/Pt/Ni} CH_3-CH_3$
ethyne ethene ethane

→ $CH_3-C \equiv CH + 2H_2 \xrightarrow{Pd/Pt/Ni} CH_3-CH_2-CH_3$

(3) Addition of dihalogen :-

ex :- $CH \equiv CH + Cl_2 \longrightarrow CH(Cl)=CH(Cl) + Cl_2 \longrightarrow CH(Cl)_2-CH(Cl)_2$

ex :- $CH_3-C \equiv CH + Br_2 \xrightarrow{CCl_4} CH_3-C(Br)=CH(Br) + Br_2 \longrightarrow CH_3-C(Br)_2-CH(Br)_2$

Note :- Unsaturation test
↳ Reddish orange → colourless.

(3) Addition of Hydrogen halide :- (H-X)

ex :- $CH \equiv CH + H^+Cl^- \longrightarrow CH_2=CH(Cl) + H^+Cl^- \longrightarrow CH_3-CH(Cl)_2$

ex :- $CH_3-C \equiv CH + H^+-Br^- \longrightarrow CH_3-C(Br)=CH_2 + H^+Br^- \longrightarrow CH_3-C(Br)_2-CH_3$

(4) Addition of H_2O :-

ex :- $HC \equiv CH + H_2O \xrightarrow[\text{or } HgSO_4,\ 333K]{H_2SO_4} CH_2=CH(OH) \xrightarrow[\text{or isomerism}]{\text{tautomerism}} CH_3-C(=O)-H$

(H^+, OH^-)

Ethanal

ex :- $CH_3-C \equiv CH + H_2O \xrightarrow[HgSO_4,\ 333K]{H_2SO_4} CH_3-C(OH)=CH_2 \xrightarrow{\text{isomerism}} CH_3-C(=O)-CH_3$

(H^+, OH^-)

propan-2-one

⑤ Polymerisation :-

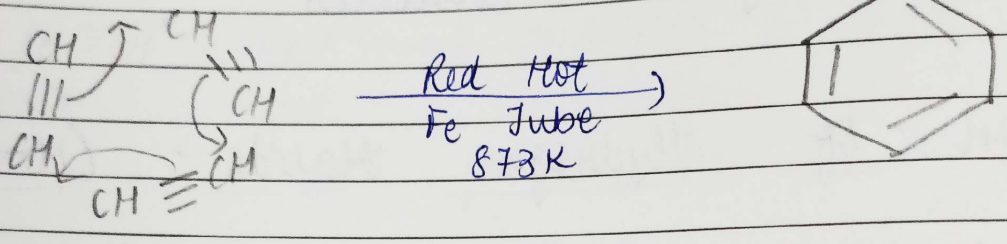
(i) Linear polymerisation :-

ex :- $n(CH \equiv CH) \xrightarrow[\text{High pressure catalyst}]{\text{High temp.}} -(CH=CH-CH=CH)_n-$

ethyne → polyethyne or polyacetylene

↳ Linear polymerisation
↳ Long chain

(ii) Cyclic polymerisation :-

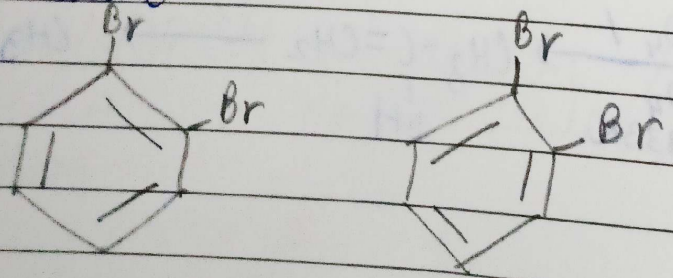
→ 

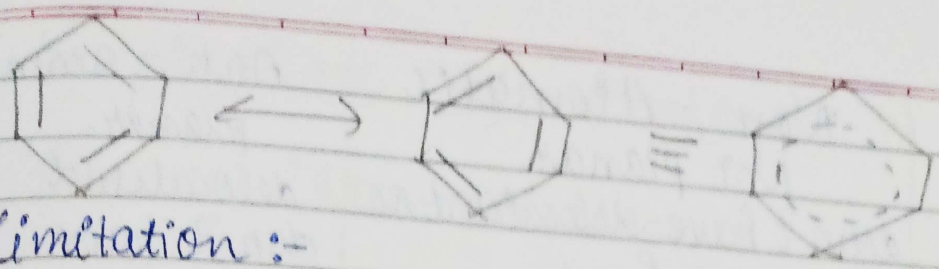
- Important Rxn :- Long chain to Cyclic chain

✳ Aromatic Hydrocarbon :- / Arenes :-
(Aroma → present smell)

- Structure Info :-
→ C_6H_6 → Benzene
→ Michael → Alkane C_nH_{2n+2}
Faraday → Alkene C_nH_{2n} → Alkyne C_nH_{2n-2}

→ Kekule

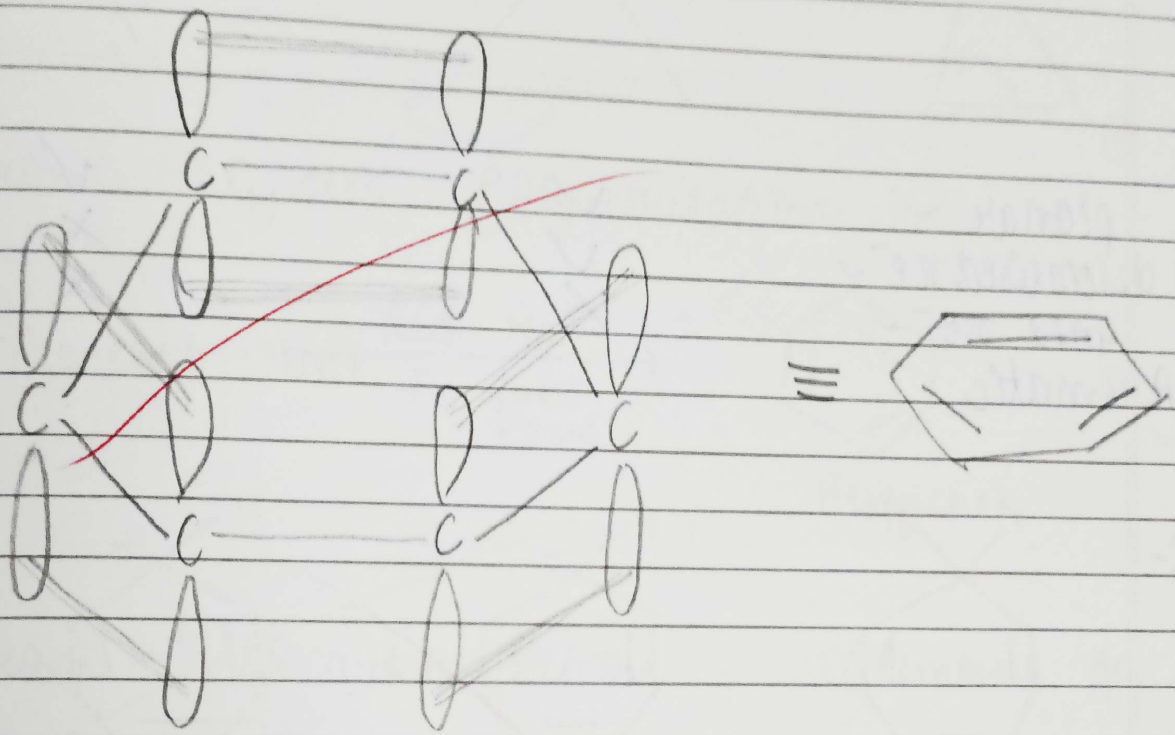




Hybrid

→ Limitation :-
→ does not explain stability.
→ Substituted benzene compound.

* Structure :-



IMP

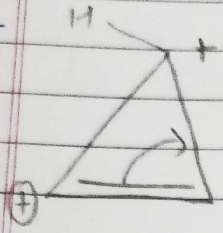
* Aromaticity of compound / Huckel Rule :-

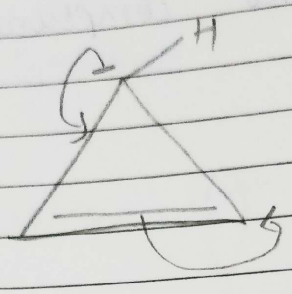
(1) Huckel Rule :-
(i) Planar / Planarity
(ii) delocalized πe^- must be present.
(iii) it must have $4n+2$ πe^- ;
$n = (0, 1, 2, 3 \ldots)$

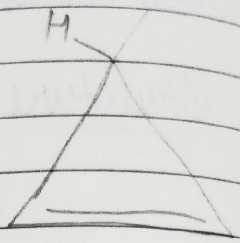
ex :- $n=0 \rightarrow 2\pi e^-$
$n=1 \rightarrow 6\pi e^-$
$n=2 \rightarrow 10\pi e^-$
$n=3 \rightarrow 14\pi e^-$

Aromatic	Non - Aromatic	Anti - aromatic
planar	Not planar	planar
delocalised πe^-	doesn't have delocalised πe^-	delocalised πe^-
$4n+2$ πe^-	does not have $4n+2$ πe^-	don't have $4n+2$ πe^-

Ex :-





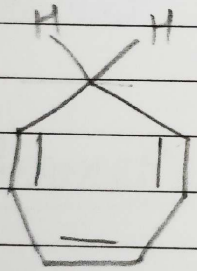


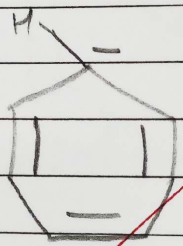
→ planar ✓ ✓ ✓
→ delocalised πe^- ✓ ✓ ✗
→ $4n+2$ πe^- ✓ ✗ ✗

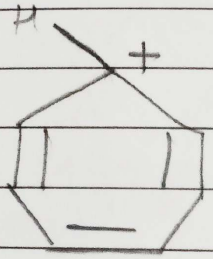
∴ → Aromatic

Anti - aromatic

Ex :-







✓ ✗ ✗

✓ ✓ ✗

✓ ✓ ✓

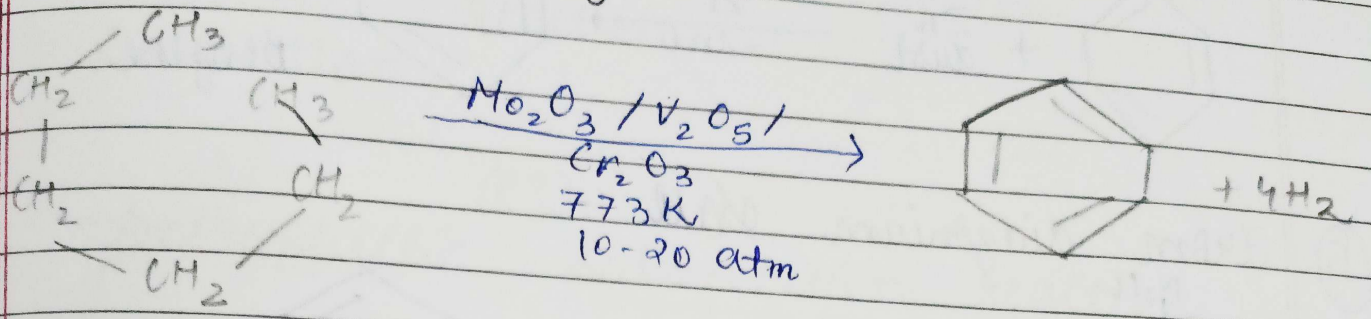
Non - aromatic

Anti - aromatic

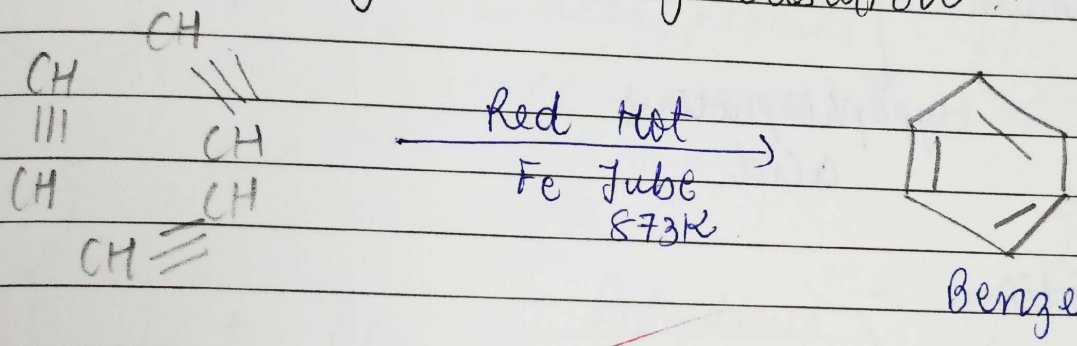
Aromatic

Preparation of Benzene :-

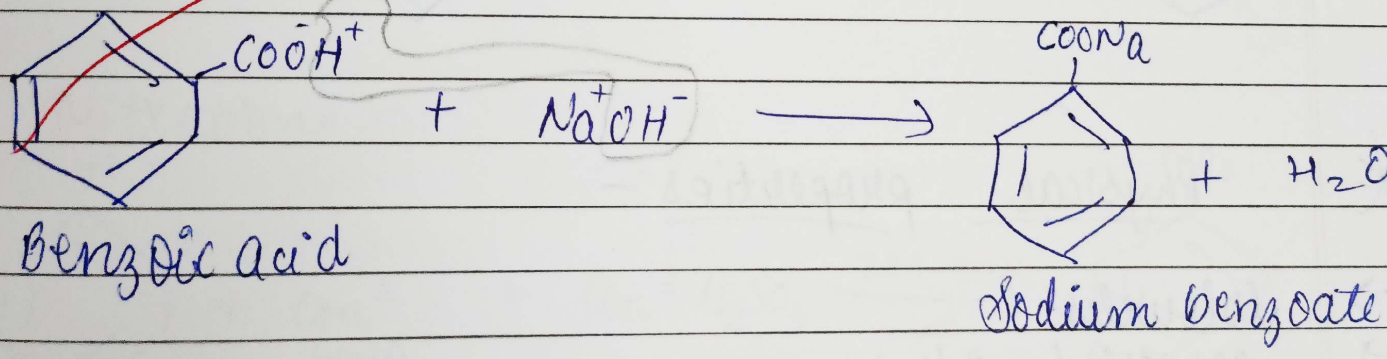
(1) From Aromatization :-

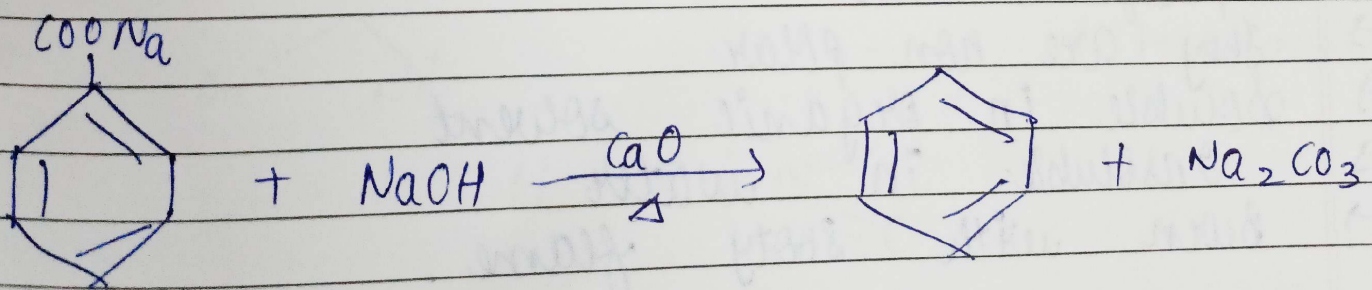


(2) From Cyclic Polymerisation :-



(3) From Decarboxylation :- (Removal of (O_2))



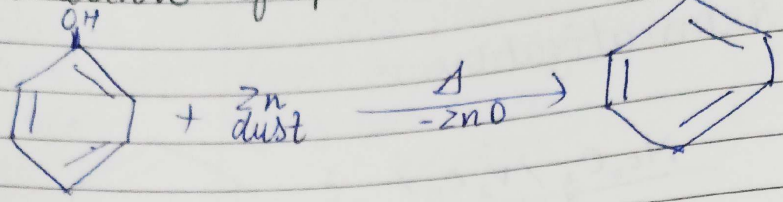


H_3PO_3 → phosphorous acid

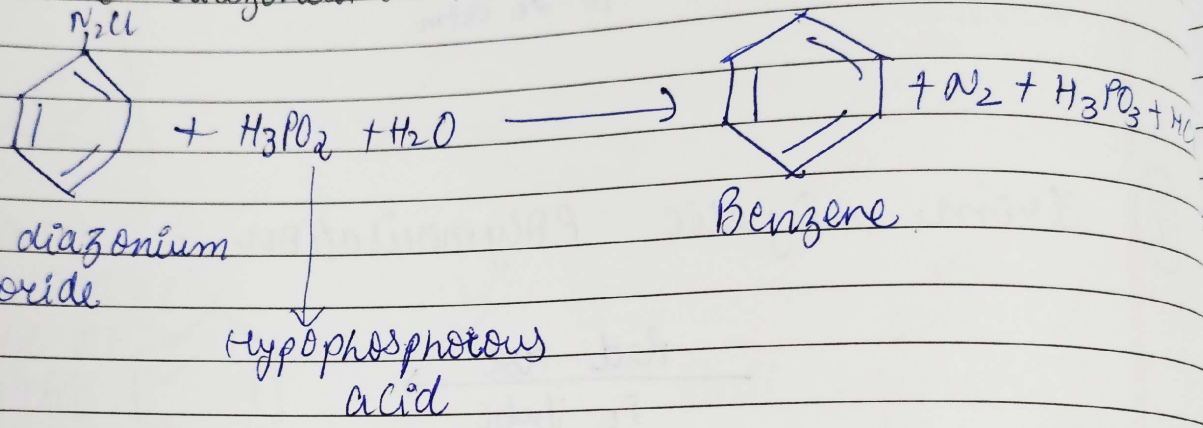
H_3PO_4 → acid

Vidyalekhan DATE PAGE

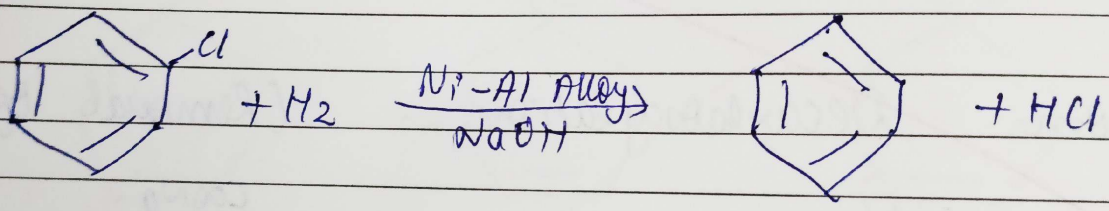
(4) Reduction of phenol :-



(5) From diazonium salt :-



(6) Reduction :-



✱ Physical properties :-

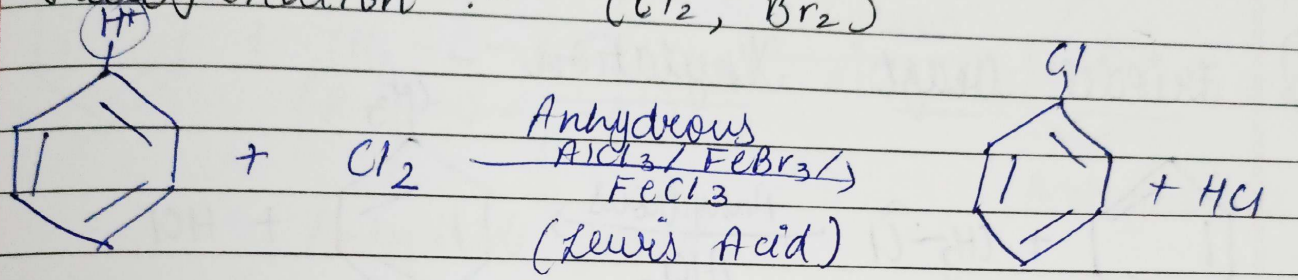
→ Colourless
→ specified odour
→ They are non-polar
→ Soluble in organic solvent
→ Insoluble in water
→ Burn with sooty flame.

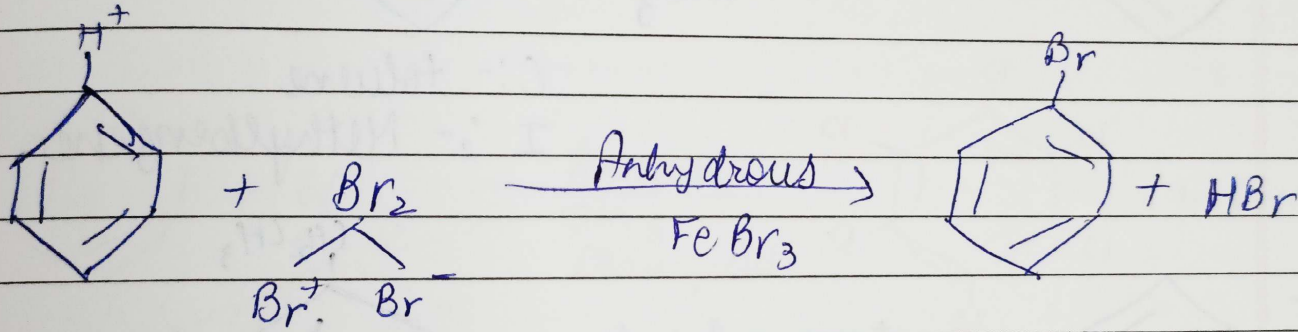
Chemical reaction :-

1. Electrophilic substitution reaction
2. Addition reaction
3. Oxidation

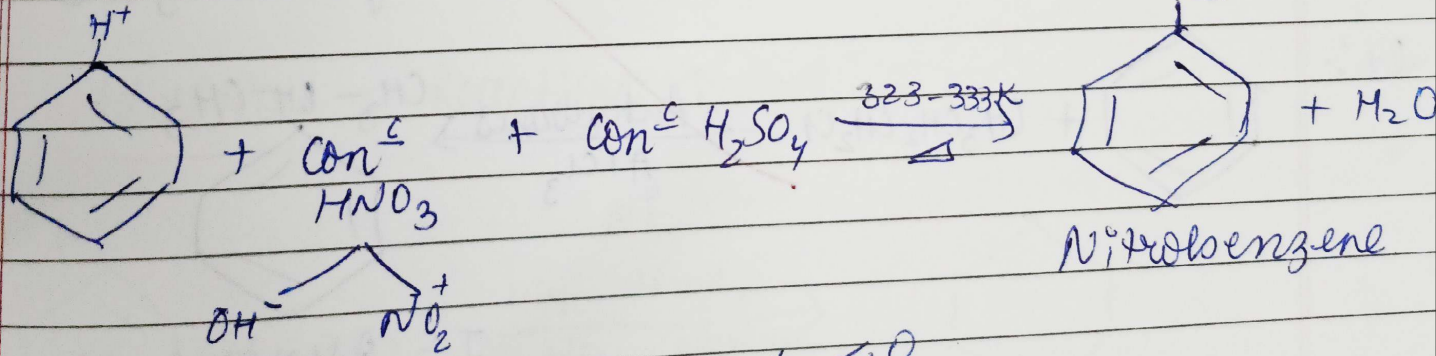
Electrophilic substitution reaction :- (E^+)

(1) Halogenation :- (Cl_2, Br_2)





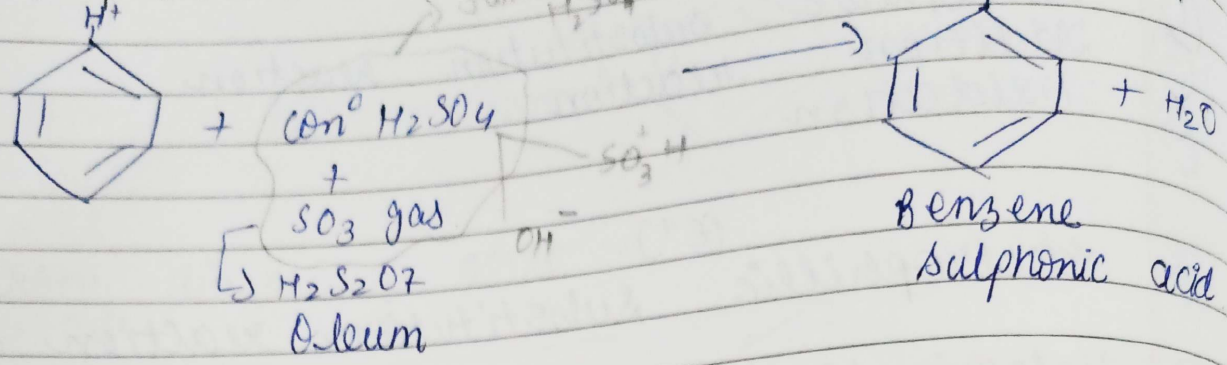
(2) Nitration :-



Nitrobenzene

$$H-\ddot{O}-\overset{+}{N}=O \leftrightarrow H-\ddot{O}-\overset{+}{N}=\ddot{O}$$

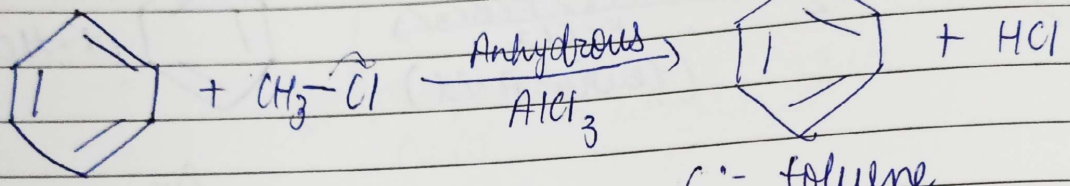
(3) Sulphonation ($-SO_3H$)



Benzene sulphonic acid

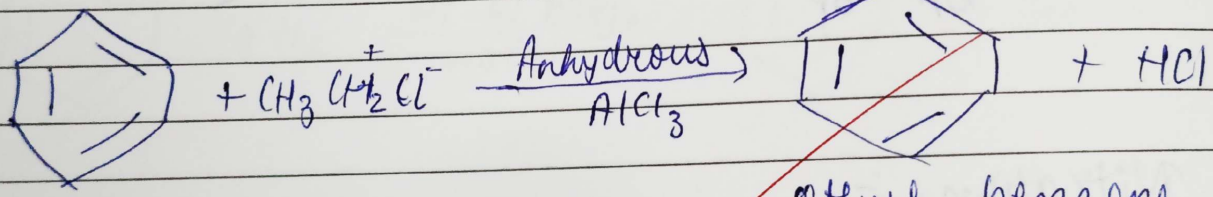
(4) Friedel Craft Alkylation :-

ex :-



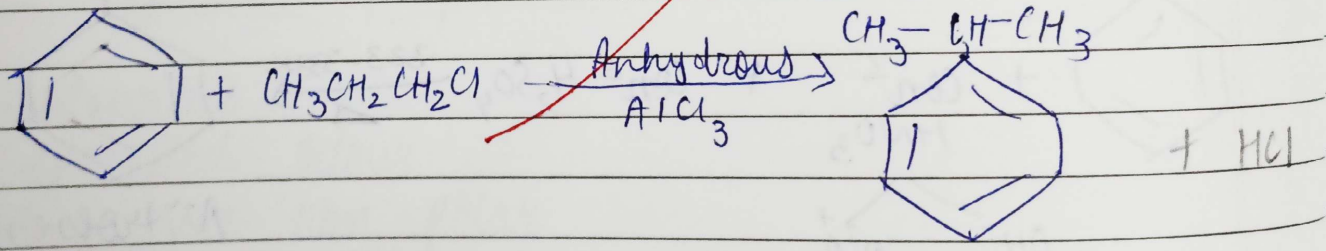
C :- toluene
I :- Methylbenzene

ex :-



ethyl benzene

ex :-



I :- Isopropyl benzene
C :- Cumene

- Hydride shifting :-

1° ← $CH_3CH_2CH_2^+ + Cl^-$
carbocation

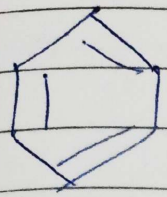
$CH_3-CH_2-CH_2^+$ → Hydride shi

$CH_3-CH^+-CH_3$
↳ 2° carbocation

(5) Friedel Craft Acylation :-

$CH_3-\overset{\overset{O}{\|}}{C}-$

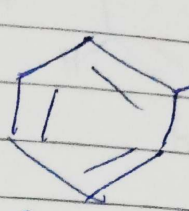
ex:-



+ $CH_3-\overset{\overset{O}{\|}}{C}-Cl$

ethanoyl chloride

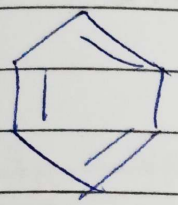
$\xrightarrow[AlCl_3]{\text{Anhydrous}}$



+ HCl

Acetophenone

ex:-



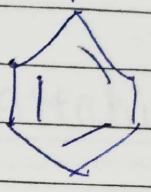
+ $CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3$

Acetic Anhydride

$(R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R')$

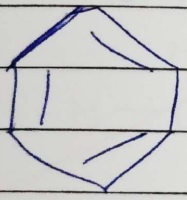
Anhydride group

$\xrightarrow[AlCl_3]{\text{Anhydrous}}$



+ CH_3COOH

Acetophenone

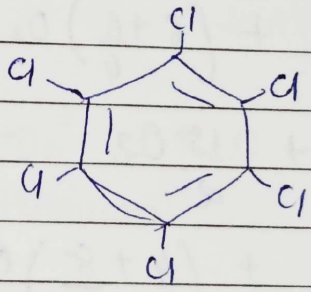


+ $6Cl_2$ (excess)

Cl^+ Cl^-

$\xrightarrow[AlCl_3]{\text{Anhydrous}}$

Dark, cold



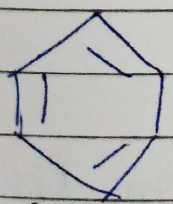
+ 6HCl

Hexachloro benzene

C_6Cl_6

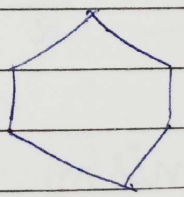
(a) Addition Reaction :-

(i)



+ $3H_2$

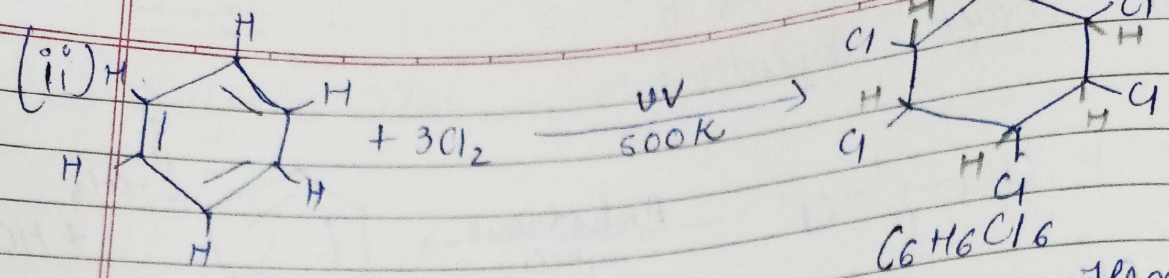
$\xrightarrow[\text{High pressure}]{Ni^\circ,\ \text{High temp.}}$



C_6H_6

cyclohexane

C_6H_{12}

(ii) 

$C_6H_6Cl_6$

Benzene Hexachloride (BHC)

or

gamma xane

(3) Oxidation :-

$$C_xH_y + \left(x + \frac{y}{4}\right) O_2 \longrightarrow xCO_2 + \frac{y}{2} H_2O$$

Isc :- $C_6H_6 + \left(6 + \frac{6}{4}\right) O_2 \longrightarrow 6CO_2 + \frac{6}{2} H_2O$

$C_6H_6 + \frac{15}{2} O_2 \longrightarrow 6CO_2 + 3H_2O$

Isl :- $C_4H_8 + \left(4 + \frac{8}{4}\right) O_2 \longrightarrow 4CO_2 + 4H_2O$

$\Rightarrow C_4H_8 + 6O_2 \longrightarrow 4CO_2 + 4H_2O$

Isc :- $C_4H_{10} + \left(4 + \frac{10}{4}\right) O_2 \longrightarrow 4CO_2 + \frac{10}{2} H_2O$

$C_4H_{10} + \frac{13}{2} O_2 \longrightarrow 4CO_2 + 5H_2O$

* Mechanism :- Electrophilic Substitution Reaction

1) generation of electrophile
2) Formation of carbocation intermediate
3) Removal of proton from carbocation intermediate.

(1) Generation of electrophile :-

(i) $Cl-Cl \xrightarrow{AlCl_3} Cl^+ + AlCl_4^-$
Chloronium ion

(ii) $CH_3-Cl \xrightarrow{AlCl_3} CH_3^+ + AlCl_4^-$
Methyl carbocation

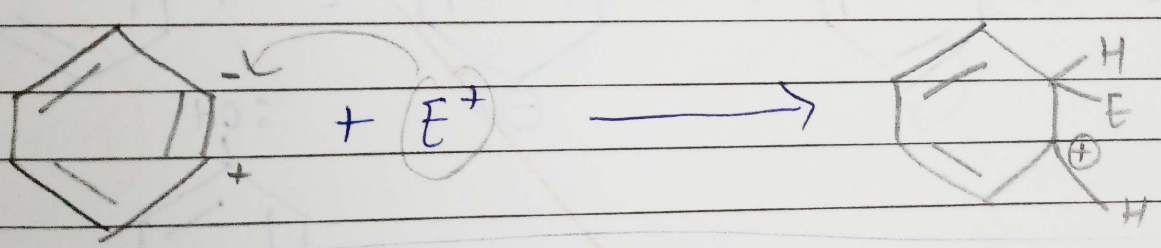
(iii) $CH_3-C(=O)-Cl \xrightarrow{AlCl_3} CH_3-C^+=O + AlCl_4^-$

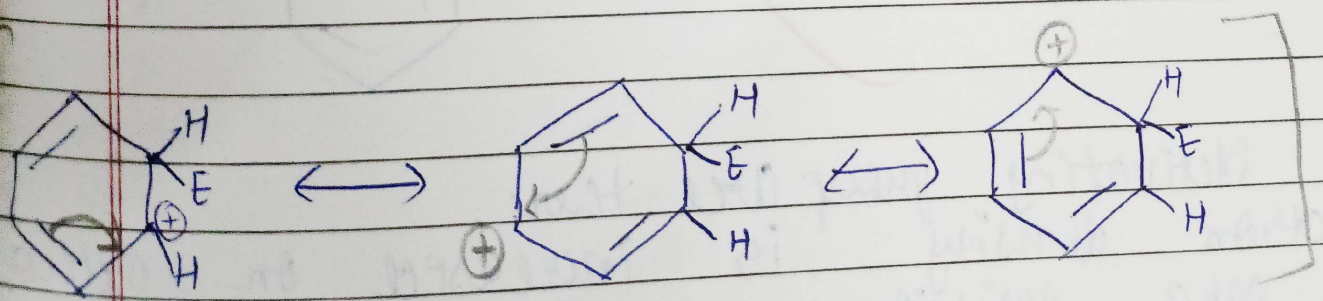
• In the case of Nitration :-

(i) $H-O-S(=O)_2-O-H + H-\ddot{O}-N(=O)=O \rightleftharpoons H-\overset{H}{\overset{|}{O}}^+-N(=O)=O + HSO_4^-$
Base

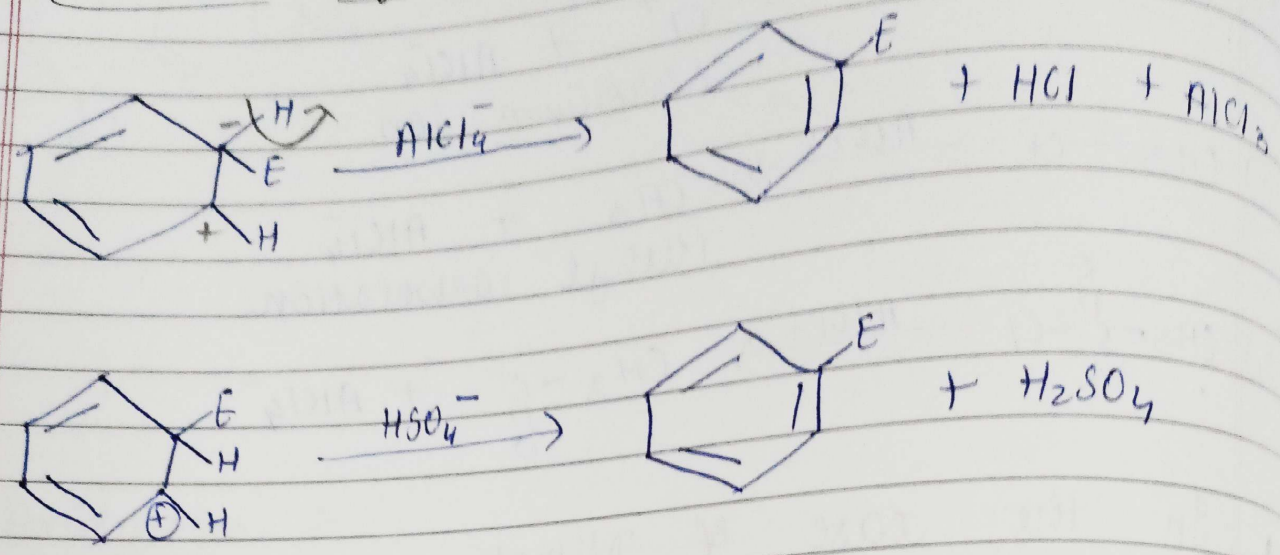
(ii) $H-\overset{H}{\overset{|}{O}}^+-N(=O)=O \rightleftharpoons NO_2^+ + H_2O$
Nitronium

(2) Formation of carbocation (Arenium ion)





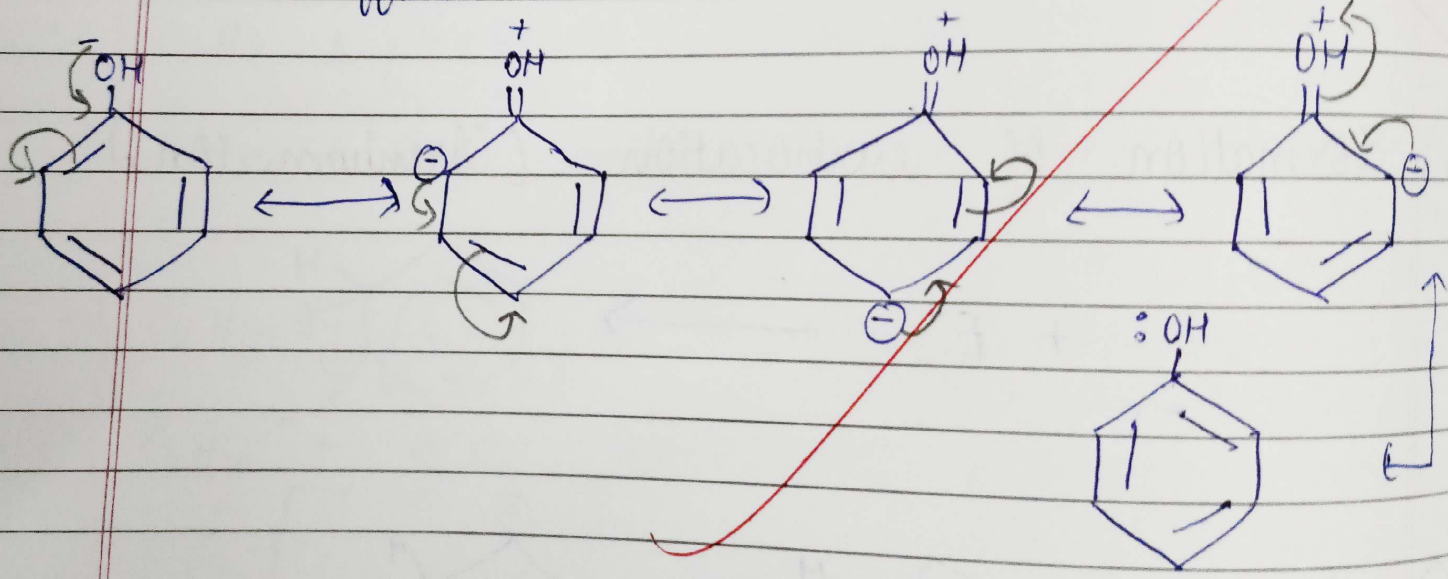
(3) Removal of proton :-



* Ortho - para directing group :-

+R - effect :- X^-, OH^-, $R-O^-$, NH_2, $R-\ddot{N}H-R$, $R-\overset{\overset{R''}{|}}{N}-R'$

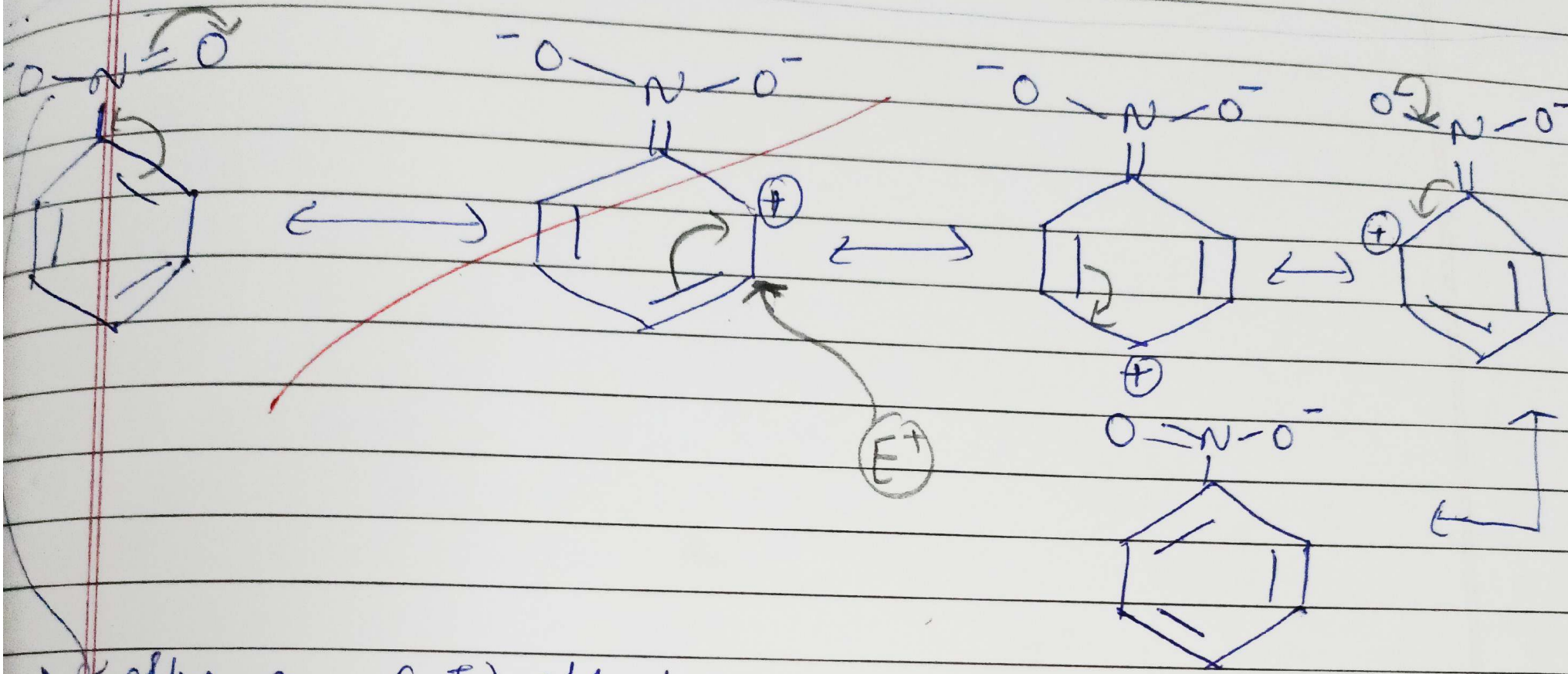
-I effect.



→ Ring Activating group are there.
→ Electron density is increased on ortho and para position.

✱ Meta Directing group :-

- -R effect :- $-NO_2$, $-CN$, $-CHO$, $-\overset{\overset{O}{\|}}{C}-$, $-COOH$



→ Strong (-I) effect.
→ Ring deactivating group
→ e^- density is increased.