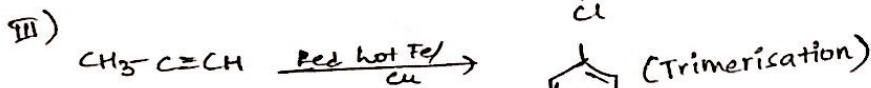
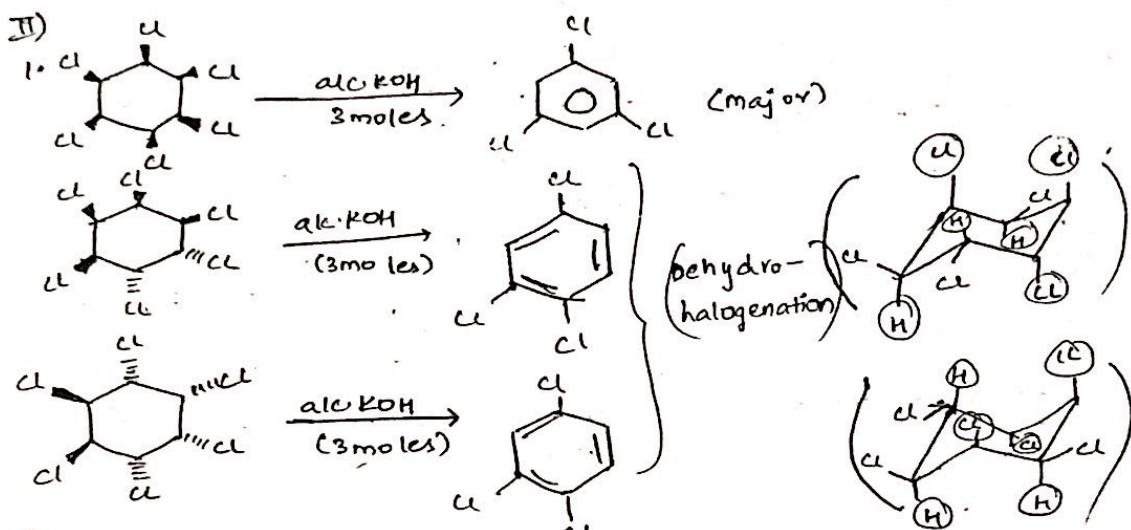
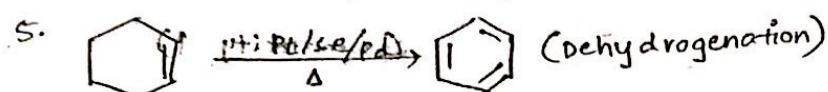
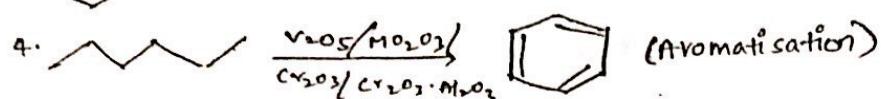
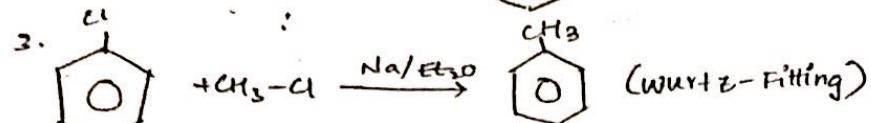
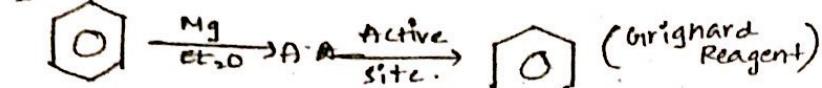
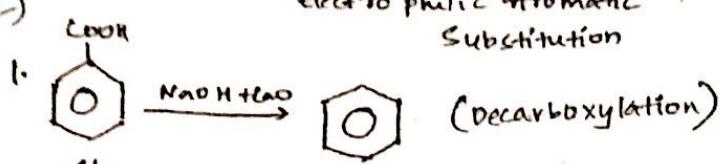


# BENZENES / EAS / Ar<sup>ES</sup>:

I) Electrophilic Aromatic Substitution

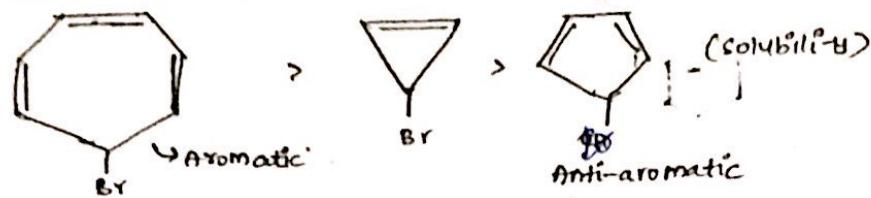


[Two hetero atoms give the preference in writing IUPAC name]

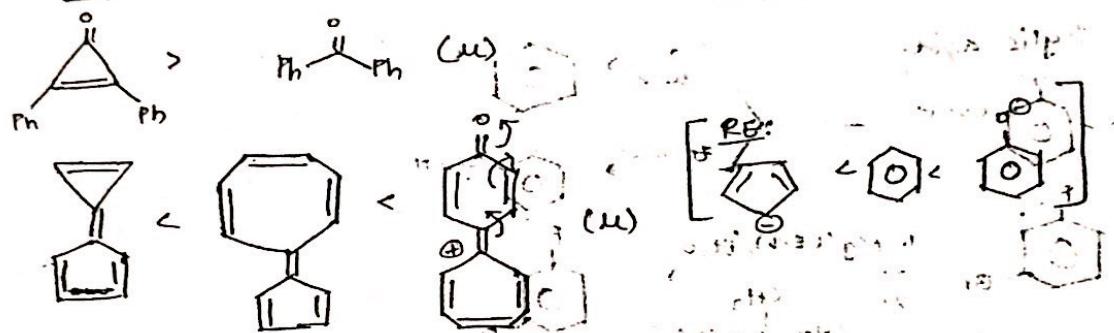
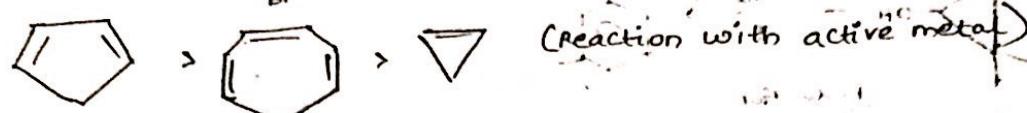
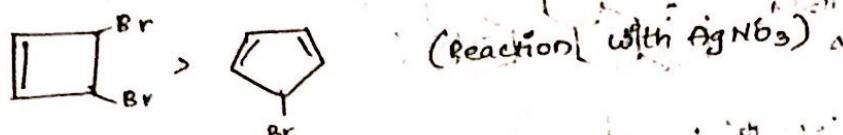
### PROPERTIES:

→ Benzene, naphthalene, anthracene etc. are insoluble.  
(Non-polar & Hydrophobic)

### ORDER OF SOLUBILITY:

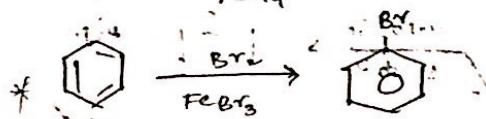
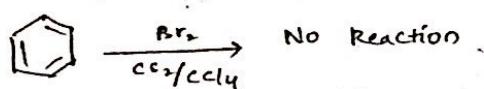
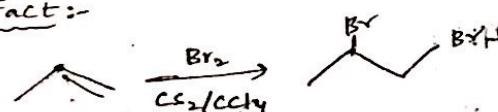


(White ionic solid)



→ Revise Resonance Energies & Stabilities.

Fact:-



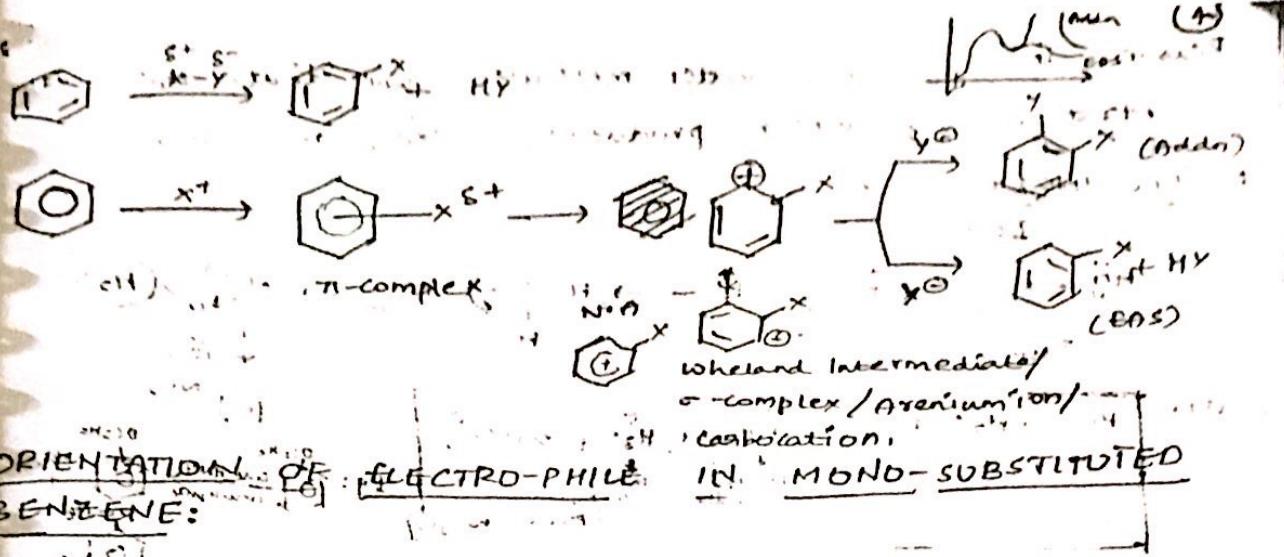
→ Electromeric effect is effectively taking place in case of  
ene > yne >  w.r.t electrophile.

→ Reagent should be slightly polar.

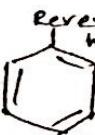
→ Most of the aromatic compounds preferably gives

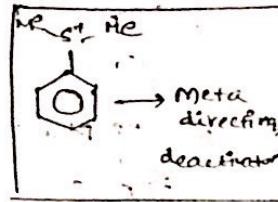
(All) substitution reactions to retain their aromaticity.

than addn reactions



### ORIENTATION OF ELECTRO-PHILE IN MONO-SUBSTITUTED BENZENE:

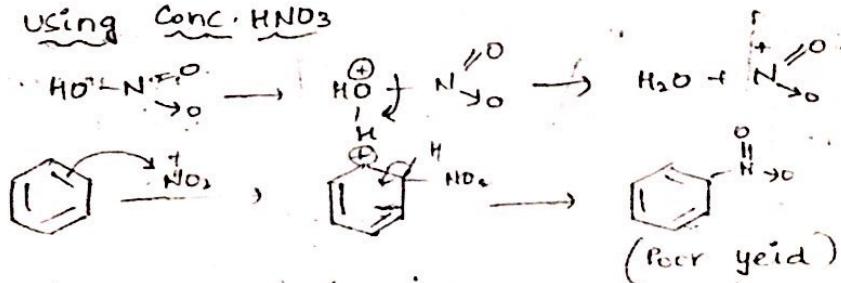
- (a)  $E^+ \rightarrow O\&P > m$   
 → Can be calculated by Arenium ion stability
- more +I      more +I      less +I
- (b)  $E^+ \rightarrow [O\&P > m]$  [Extra hyper conjugations]  
 → positive never get at ipso position.
- (c)  $E^+ \rightarrow [m > O\&P]$  [if + at ipso cause +ve, +ve repulsions]
- (d)  $+M \rightarrow -O^-, -CH=CH-COOH, -O-CH_3, -NH_2, -X, -CH=CH, -PA$  [O&P > m]
- (e)  $-M \rightarrow [-CHO]$   $M > O\&P$   
 -NO<sub>2</sub>, -CENR, -COOR, -COR, -OH, -SO<sub>3</sub>H
- (f)   $E^+ \rightarrow M > O\&P$

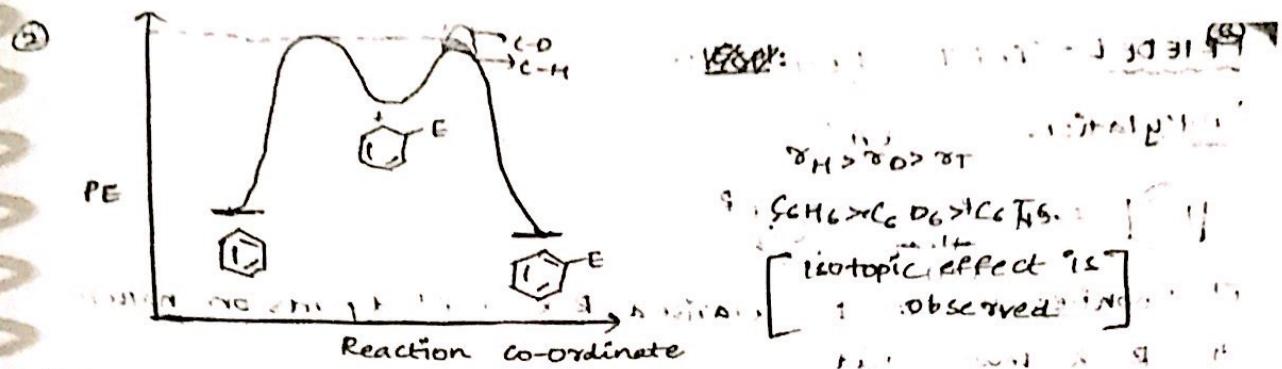


Eg:

### NITRATION:

#### 1) Using Conc. $HNO_3$





→ For Benzene, in both the cases, 1<sup>st</sup> step is slow step (PES)

→ Sulphonation, Iodination, follows graph ② and all others follows graph ①. [Nitration, chlorination etc.]

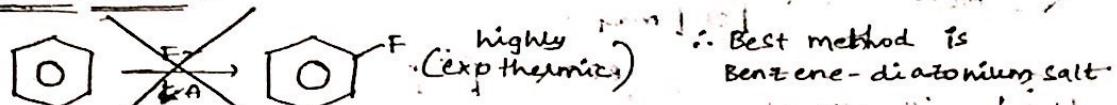
→ Reason: i) steric

(graph-2) ii) Less Bond strength

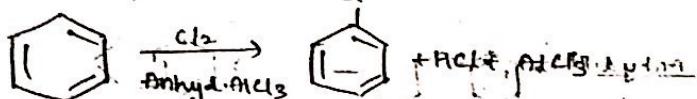
∴ It is unstable, get ready to loss of Electrophile / C-H bond.

### 3) HALOGENATION:-

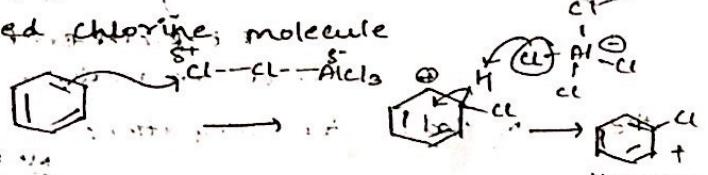
#### a) Fluorination:-



#### b) Chlorination:



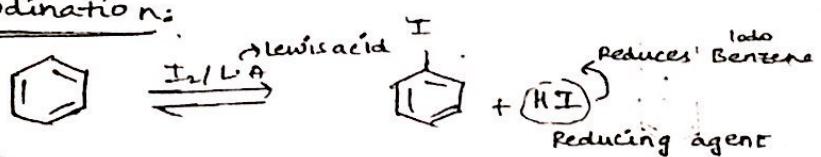
→ Electrophile is polarised chlorine molecule



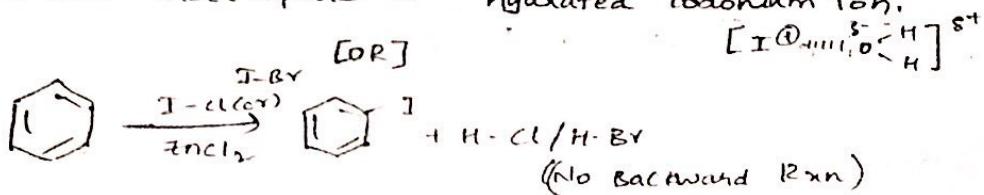
#### c) Bromination:



#### d) Iodination:



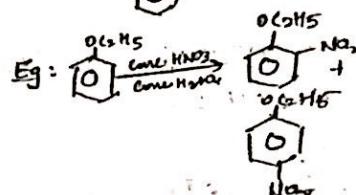
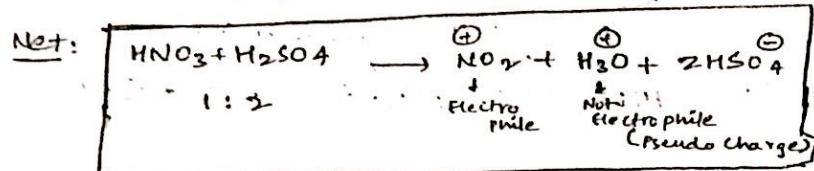
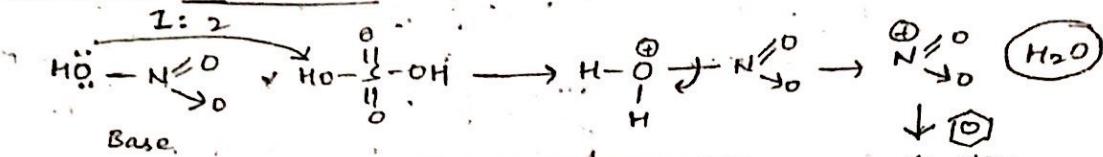
→ To get the better yield of Iodo-benzene, carry the reaction either in presence of ( $\text{HNO}_3/\text{HIO}_3/\text{HgO}/\text{Base}$ ), then the observed electrophile is hydrated Iodonium ion.



(5)

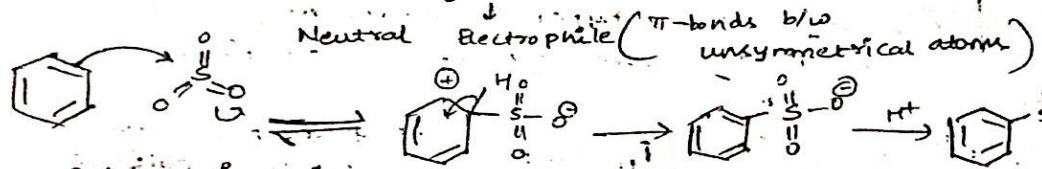
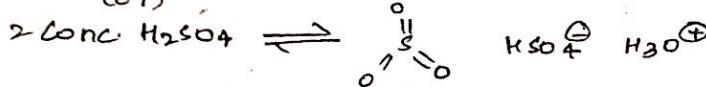
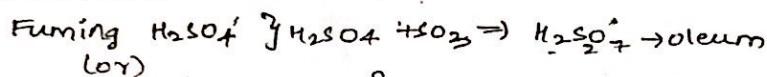
Reason: The generated water molecules will dilute the acid concentrations by which products of  $\text{NO}_2$  decreases

b) Conc.  $\text{HNO}_3 + \text{Conc. H}_2\text{SO}_4$ :



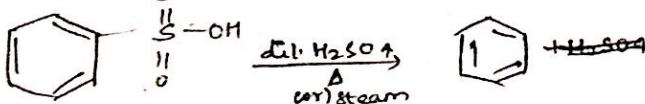
c)  $\text{CH}_3\text{COO}^{\ominus}$   $\text{NO}_2^{\oplus}$  } other reagents  
 $\text{BF}_4^{\ominus}$   $\text{NO}_2^{\oplus}$  } used as Nitrating  
 Solid  $\text{N}_2\text{O}_5$  agent

2) SULPHONATION:-

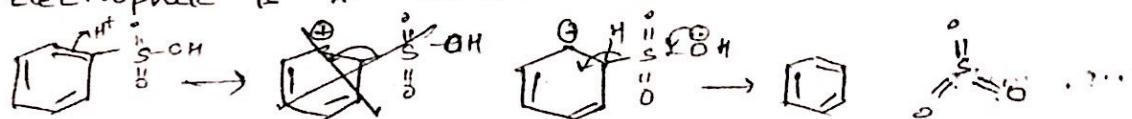


- At high temperature, desulphonation favours (40°C) (100°C)
- At low temperature, sulphonation favours (40°C) (40°C)
- Under Conc.  $\text{H}_2\text{SO}_4$ , sulphonation favours whereas in dil.  $\text{H}_2\text{SO}_4$ , desulphonation favours.

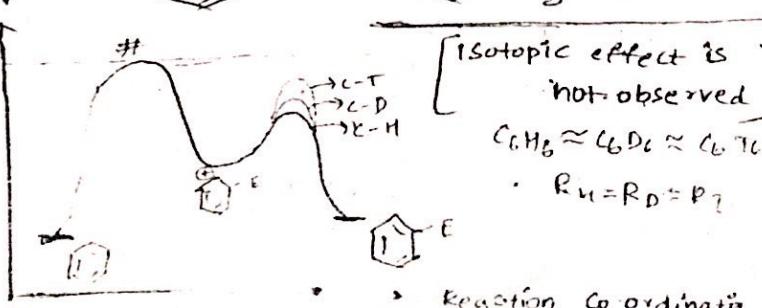
Mechanism for desulphonation =



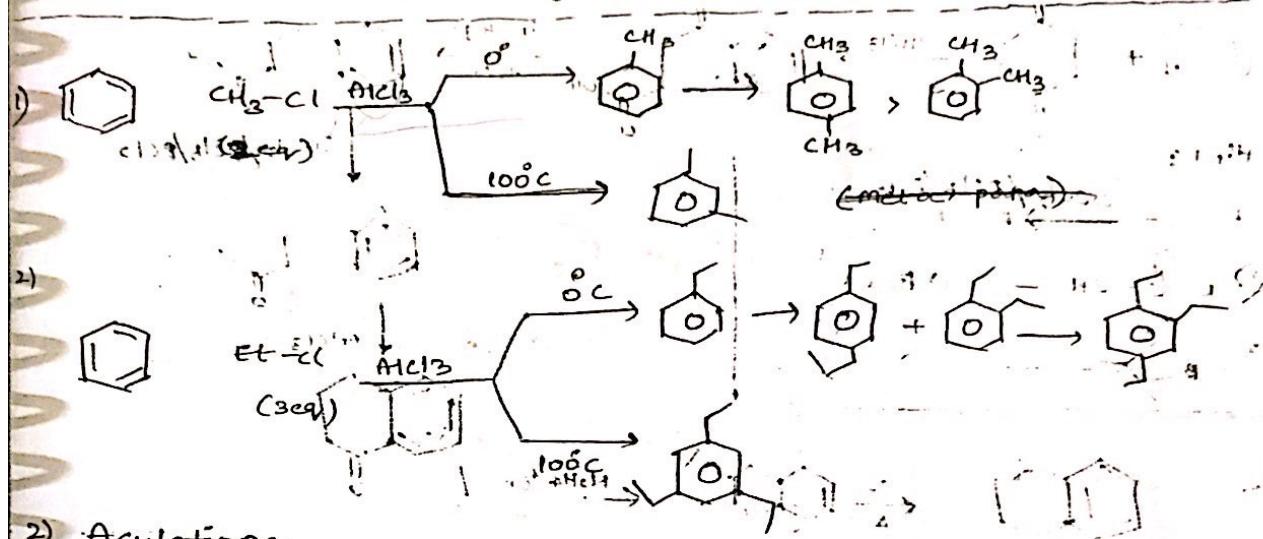
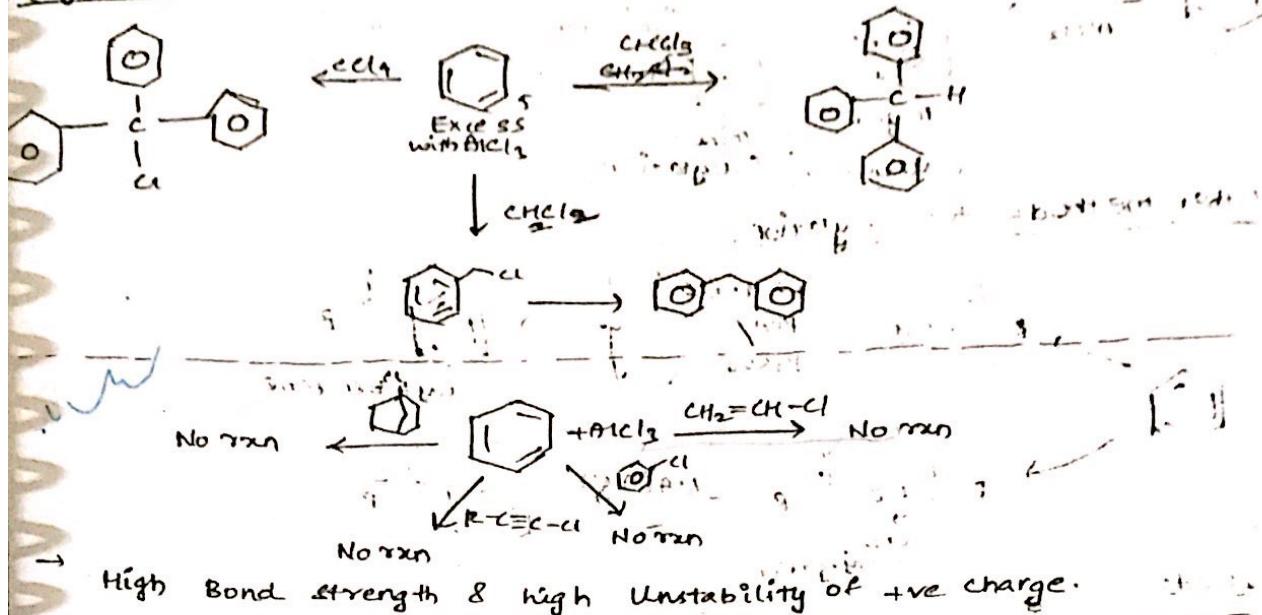
→ Electrophile is  $\text{H}^+$  attacks at ipso position



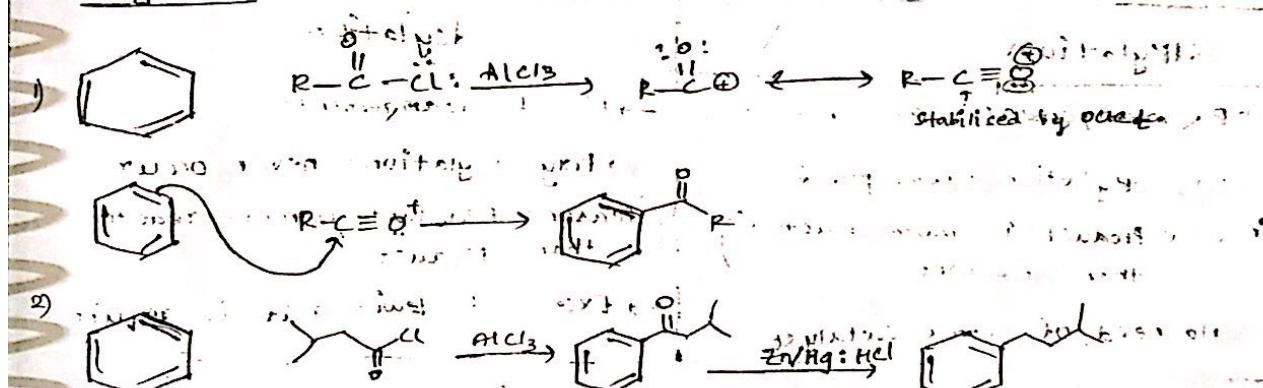
KINETIC DATA:



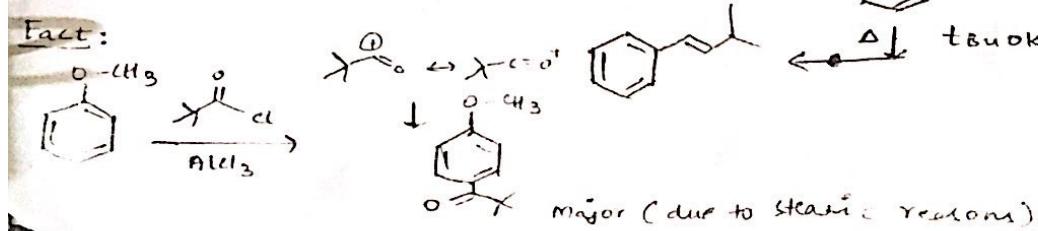
## Nucleophilic aromatic substitution



## Acylation:-



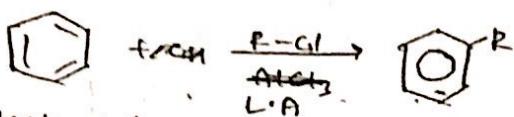
→ Rearrangements never takes place



## FRIEDEL-CRAFTS REACTION:-

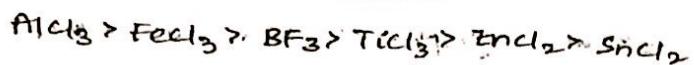
(7)

### 1) Alkylation: (EAS)

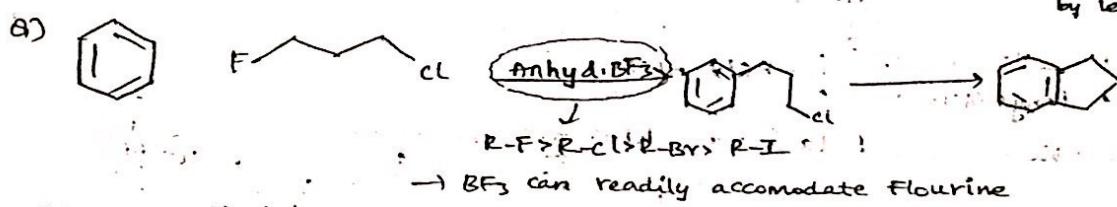
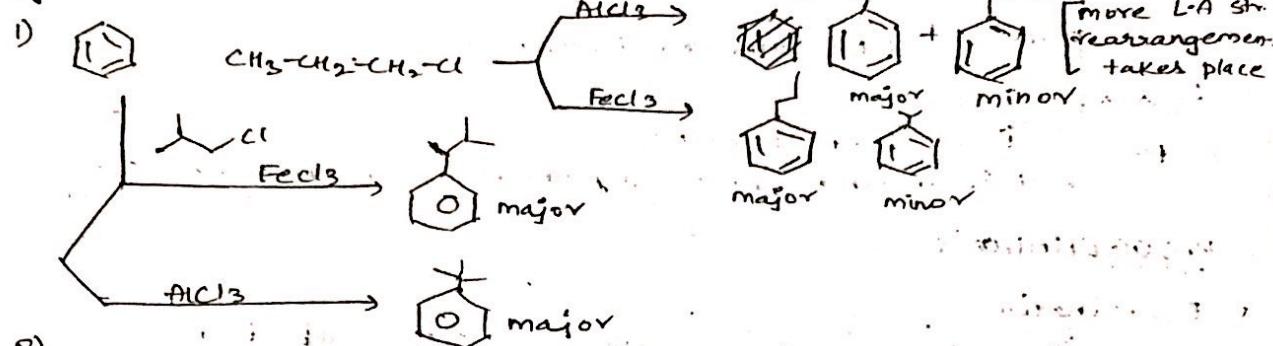


Electrophile: It can be polarised,  $\text{R-X} \leftrightarrow \text{R}^+$  depends on nature of the R & Lewis acid.

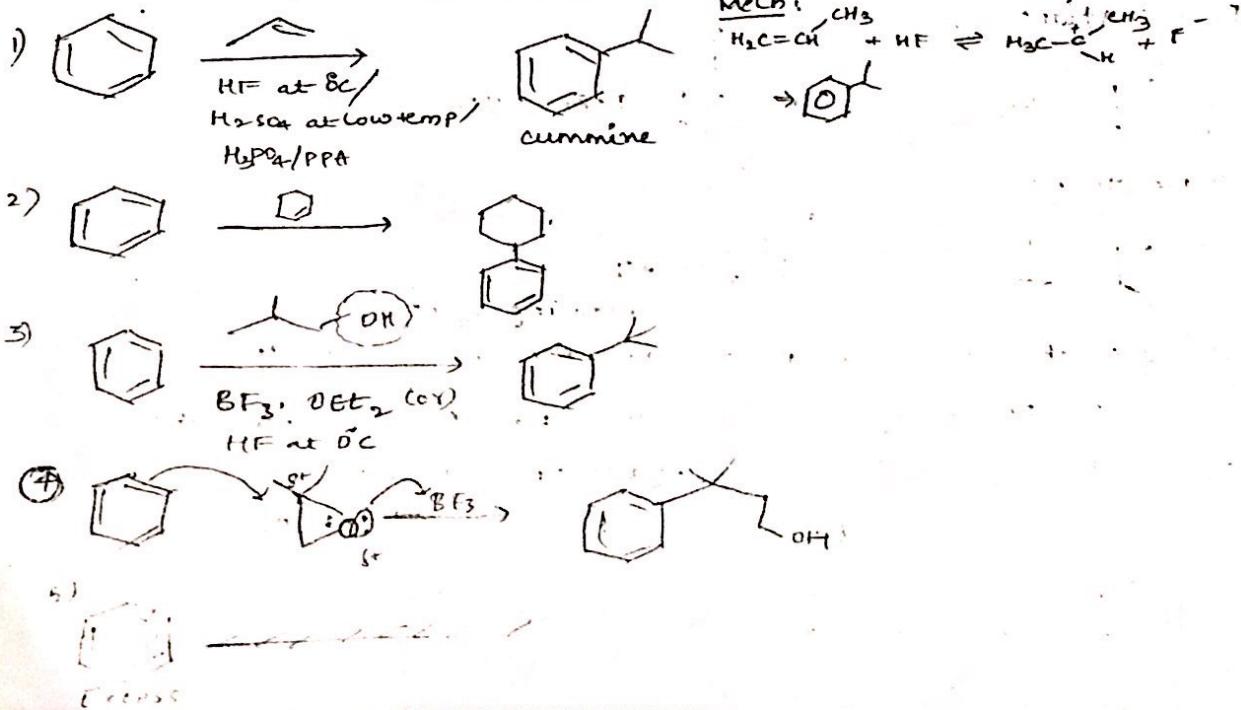
### Strength of Lewis acids:-



Eg:-



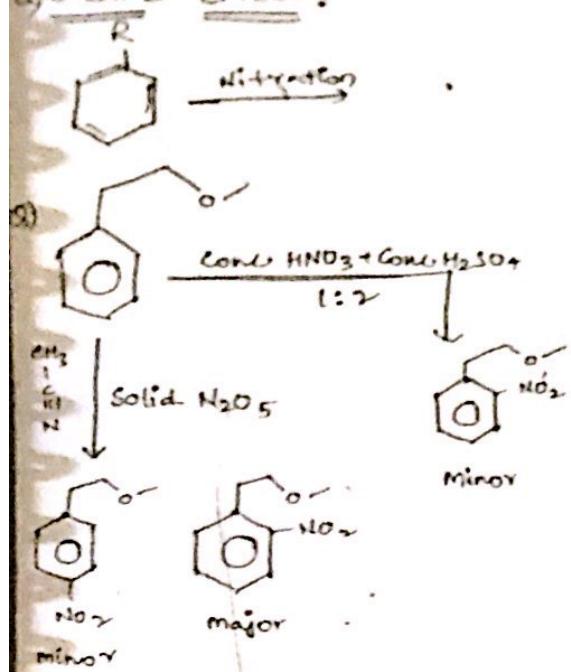
### Other methods for alkylation:-



## of ORTHO vs PARA:

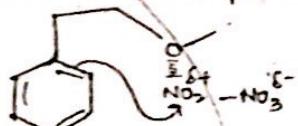
depends on following factors:

### a) Steric effect:

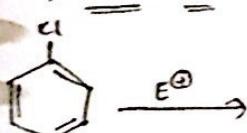


R	O	P	M
-CH <sub>3</sub>	56	37	51
-C <sub>2</sub> H <sub>5</sub>	45	49	6
-iso prop	30	62	8
-tbut	16	73	11

Reason:- Reaction proceeds through 6<sup>th</sup>



### b) SIZE OF THE ELECTROPHILE:-

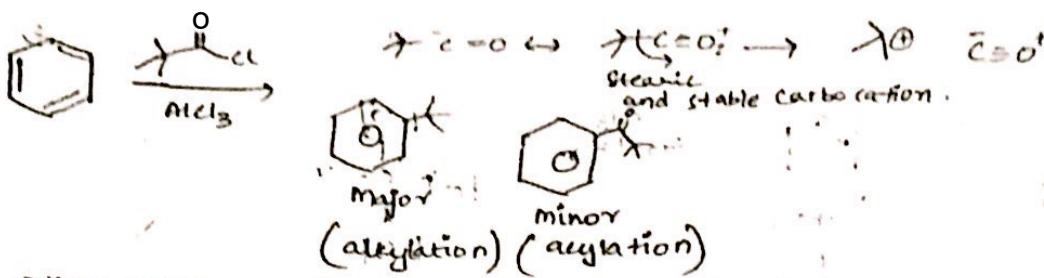


E <sup>+</sup>	O	P
chlorination	39	55
Nitration	30	69
Bromination	11	87
Sulphonation	1	99

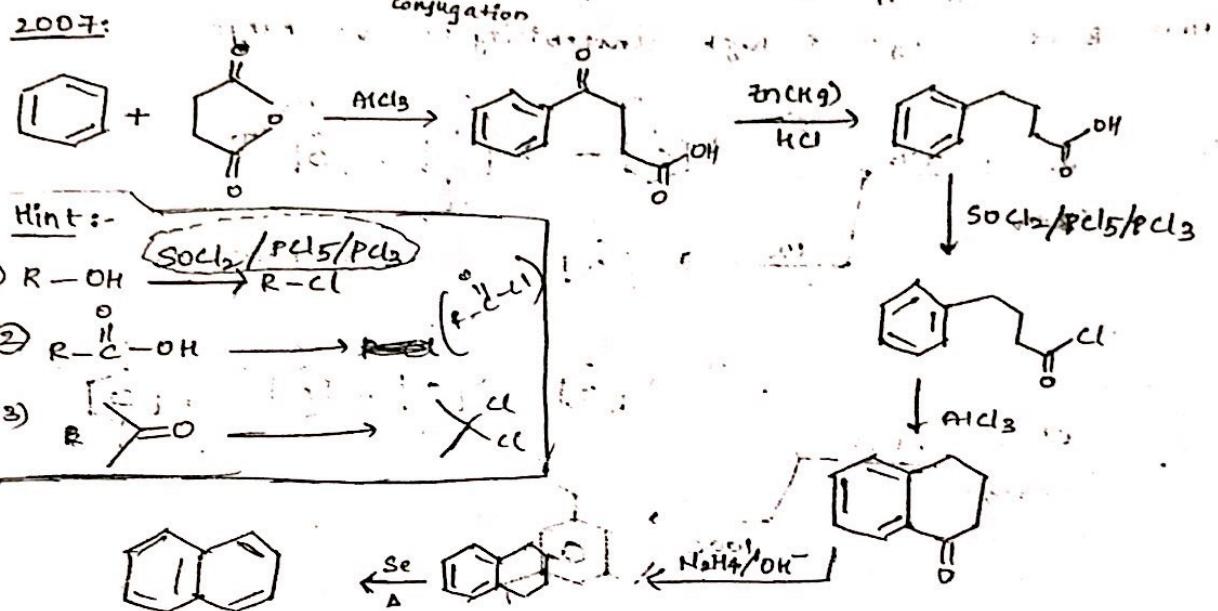
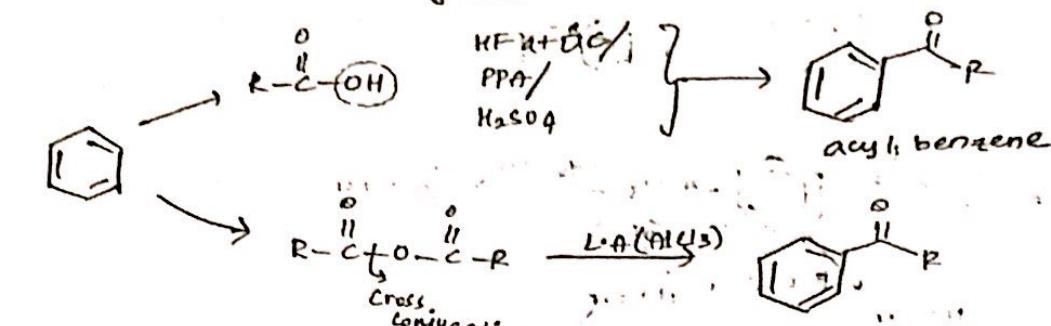
### c) Electronegativity:-



-X	O	P
-I	12	88
-Cl	30	69
-Br	32	62
-F	38	60



Other methods for acylation:

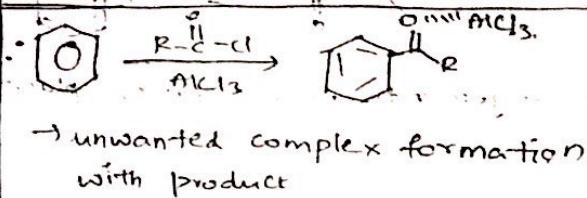


### Alkylation

- Rearrangements are possible
- Poly alkylation takes place  
(Reason: Product is more reactive than reactant)
- No need of extra catalyst

### Acylation

- No Rearrangements
- Poly acylation never occurs.  
(Reason: Reactant is more reactive than product)
- Excess of Lewis acid is required.

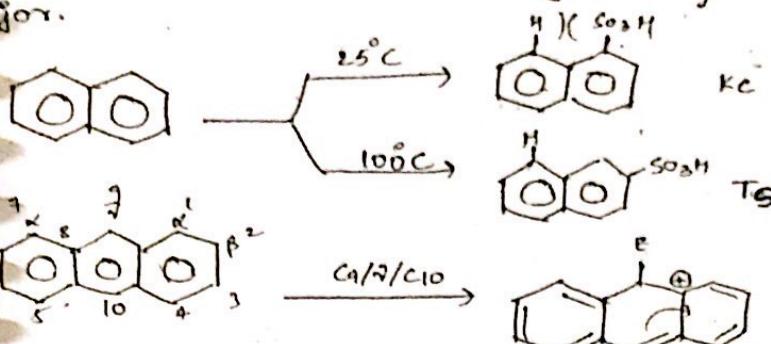




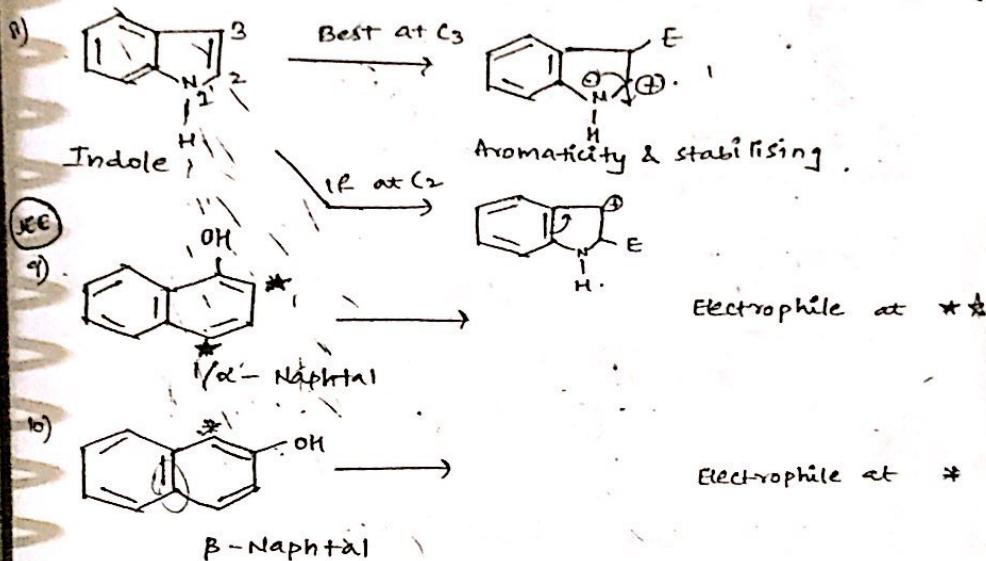
→ Best at C<sub>1</sub>, since it has 2 R.S. (12)  
out of which 4 will have benzoid character.

→ If at C<sub>2</sub>, 6 Resonating structures; 2 of them will have benzoide character.

NOTE :- But for bulky electro-ophile (like sulphonation), at low temperature, kinetically controlled product is major, whereas at high temperature, thermodynamically stable product is major.

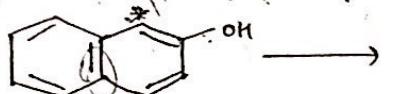


Both benzene are gaining aromaticity.



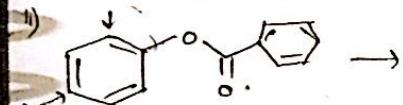
JEE  
10)

Electrophile at \*

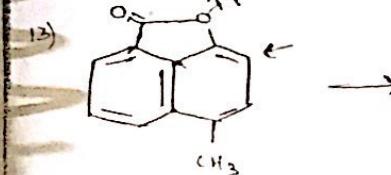
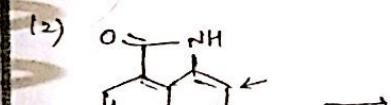
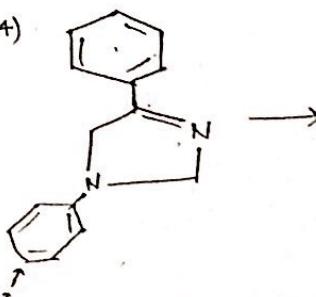


Electrophile at \*

Beta-Naphthal

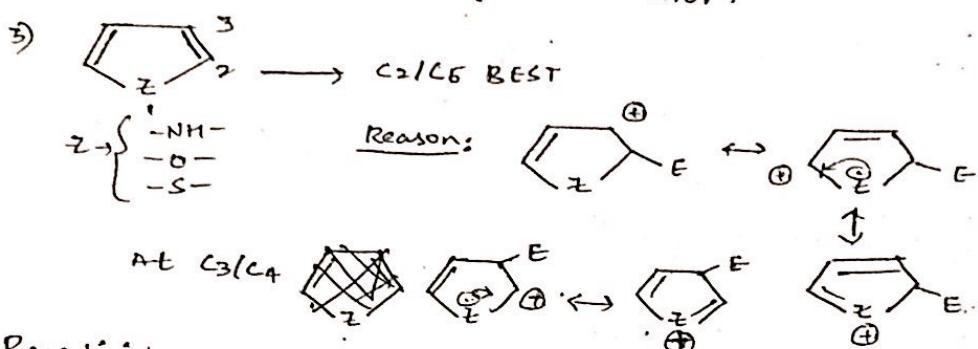
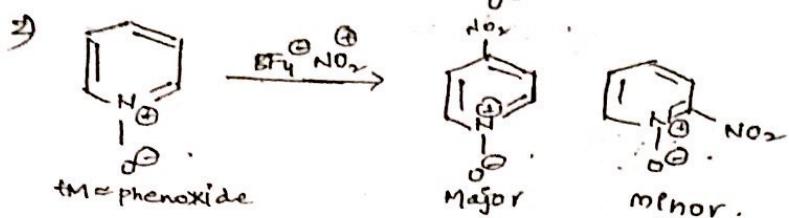
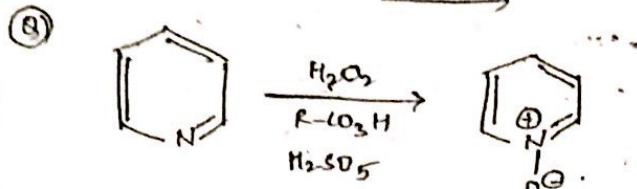
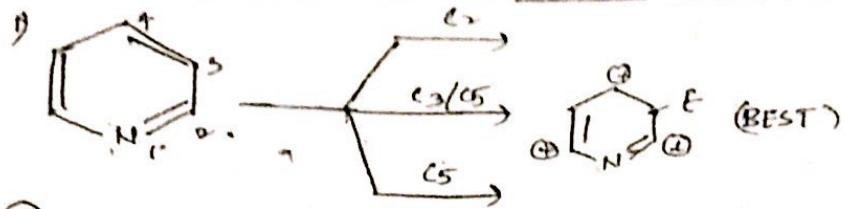


(14)

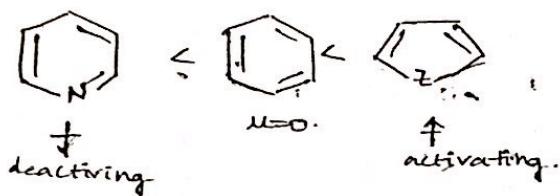


## ORIENTATION OF $E^+$ IN OTHER SYSTEMS:

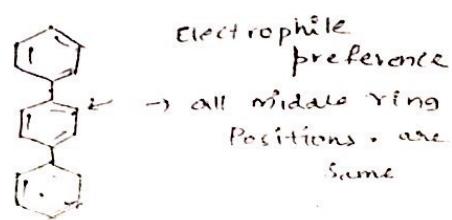
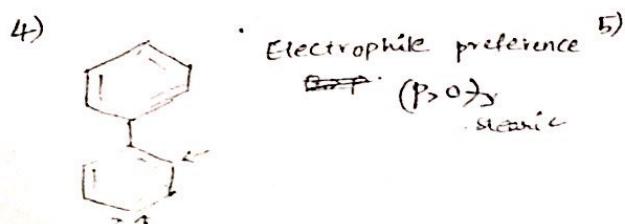
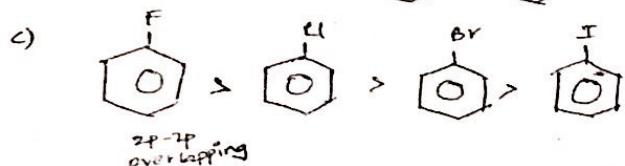
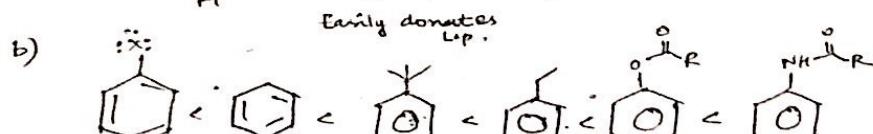
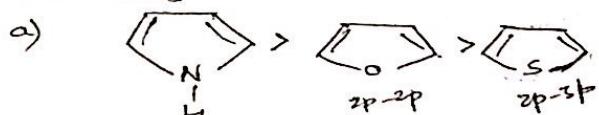
(1)



### Reactivity:-



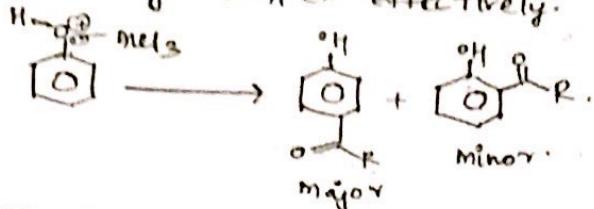
### Reactivity:



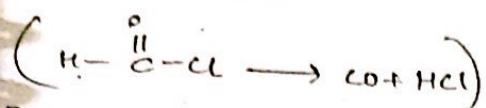
Lewis acid [catalyst].

111

Strongly activating group like phenol gives poor yield since not forming complex effectively.

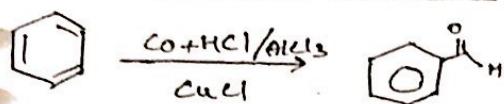


Benzaldehyde is not obtained in Friedel-Crafts since  $H-C(=O)-Cl$  (Formyl chloride) doesn't exist at experimental condn's. Exist at  $-58^{\circ}C$ .

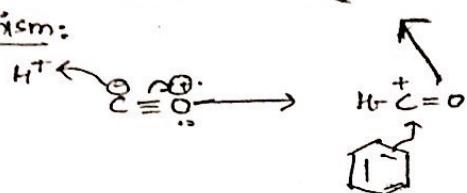


### PREPARATION OF BENZAL DEHYDRE:

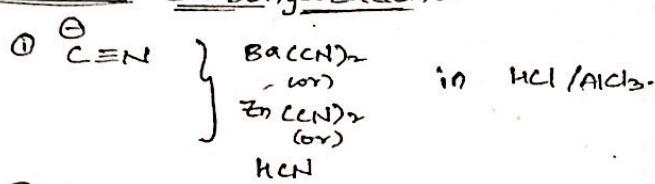
#### Gattermann-Koch Reaction:-



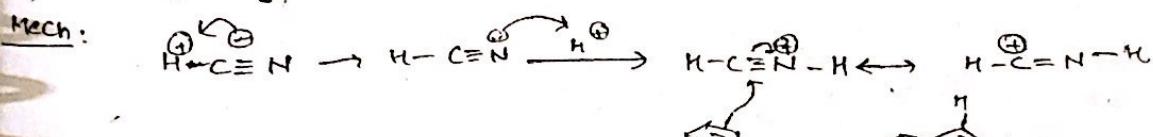
Mechanism:



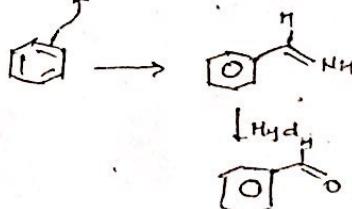
#### Gattermann-Carbonylization:-



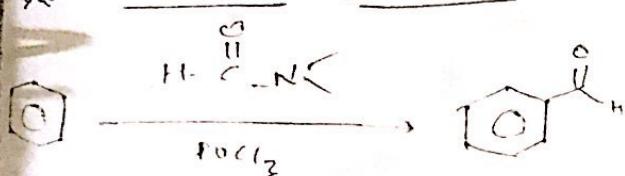
#### ② Hydrolysis.



Hint:



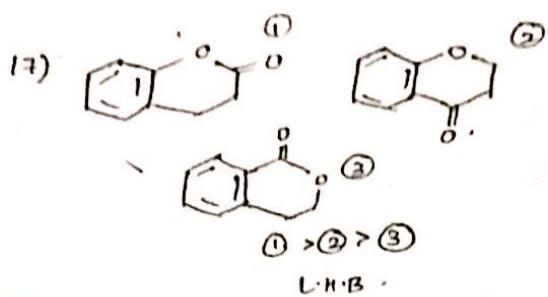
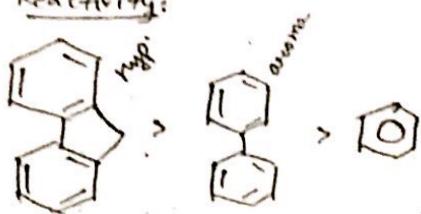
#### Vilsmeier Reaktion:



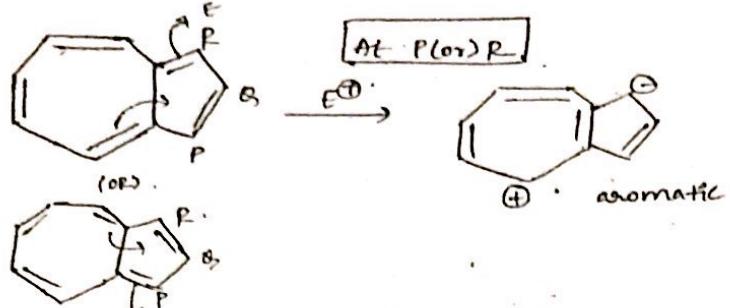
15)



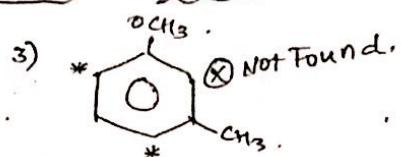
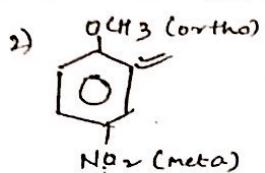
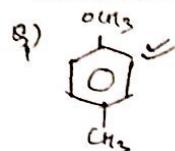
16) Reactivity:



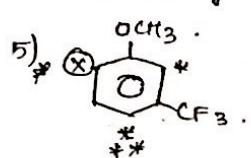
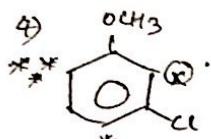
17)



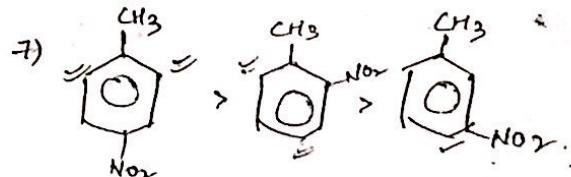
### ORIENTATION OF E<sup>+</sup> IN DISUBSTITUTED BENZENES:-



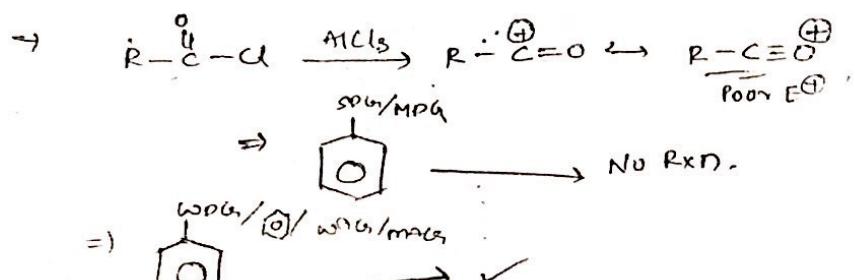
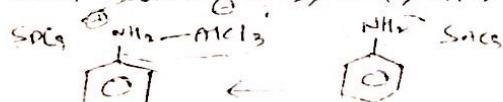
Both are directing same position



6) Reactivity:



### LIMITATIONS OF FRIEDEL-CRAFT REACTIONS:-

→ SAG like  $\text{NH}_2^-, \text{NHR}^-, \text{NR}_2^- \rightarrow \text{No Rxn}$ . Since,

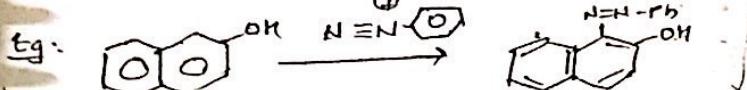
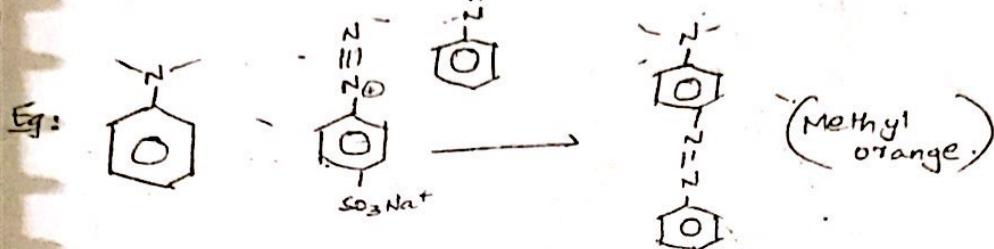
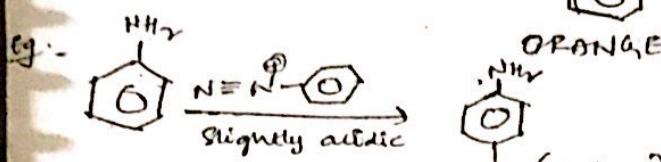
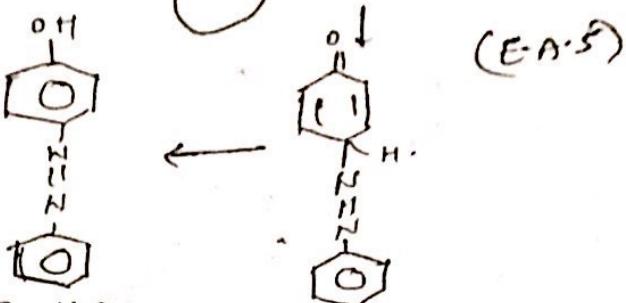
→ Since, SAG become stable by donating lone pair forming complex with

Used as a electrophile in preparation of dyes.

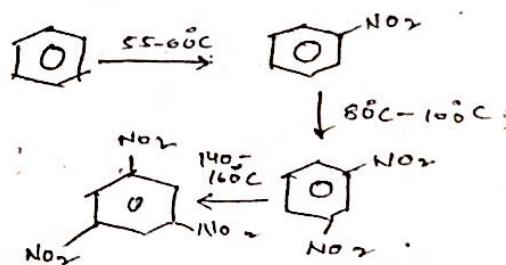
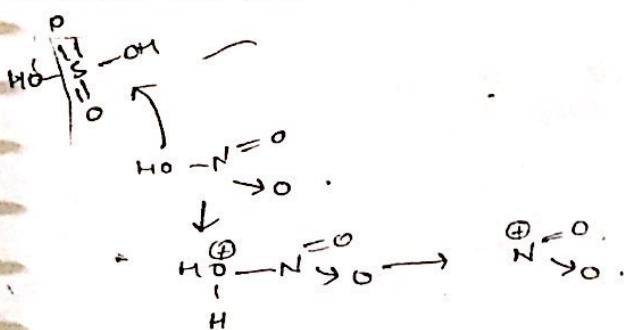
Reacts only with S.A.G.



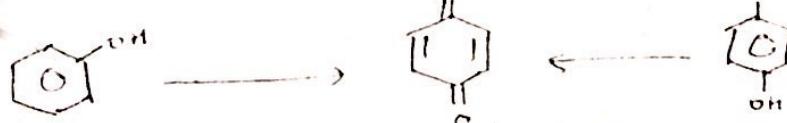
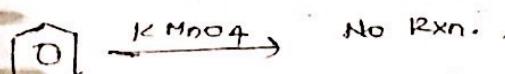
→ "Coupling Reaction"  
EAS.

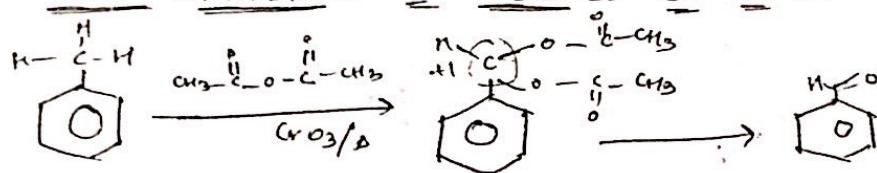
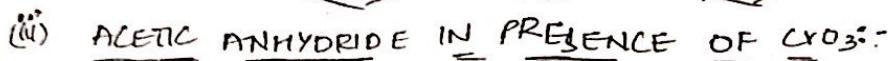
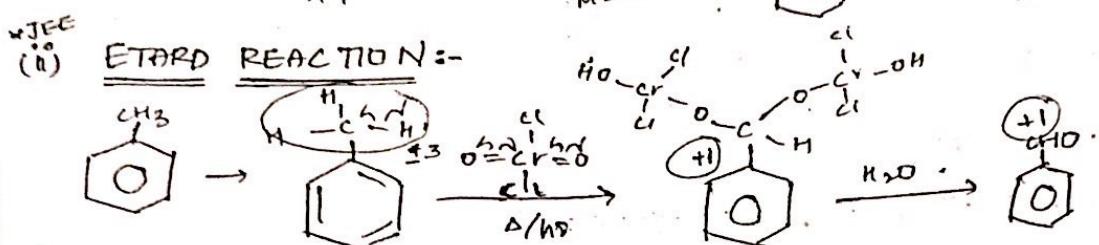
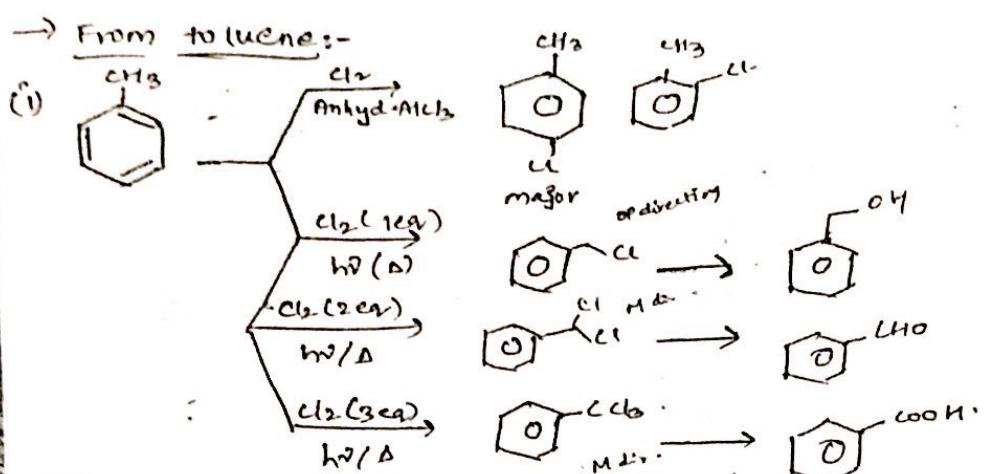


### VERY GOOD ELECTRO-PHILE:



### KMnO4 Reactions:-



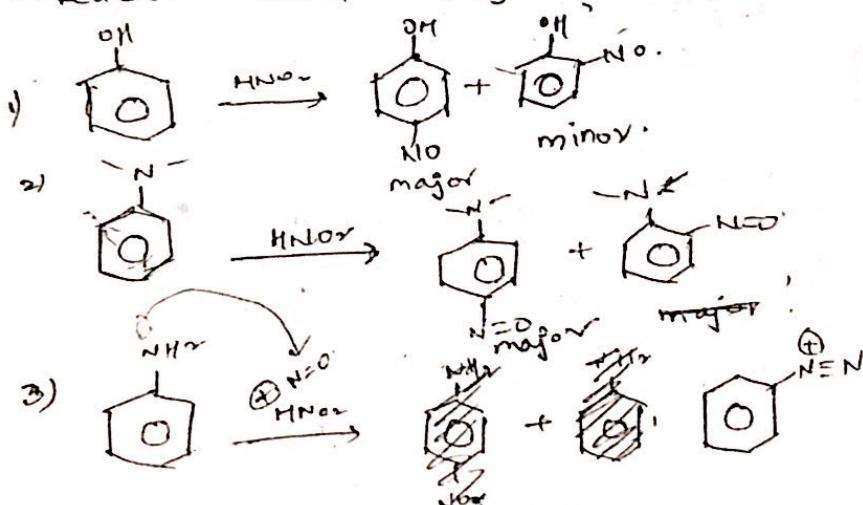


### NITROSATION:

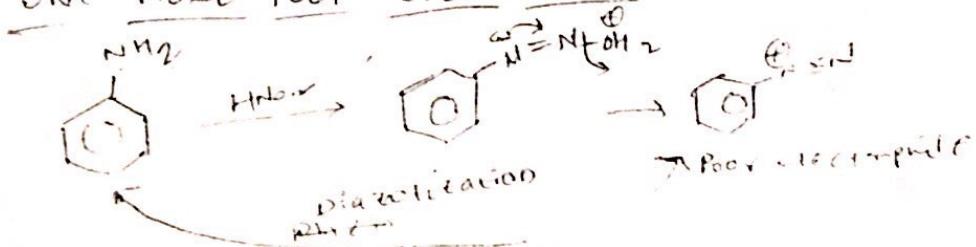
Electrophile is Nitronium:-

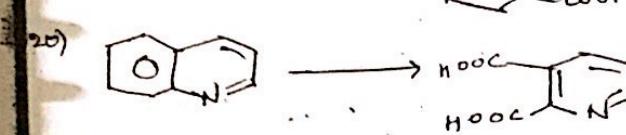
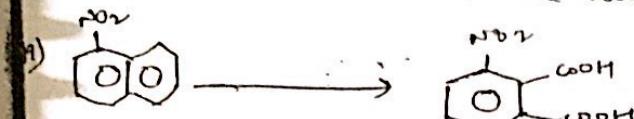
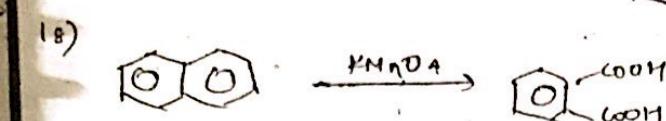
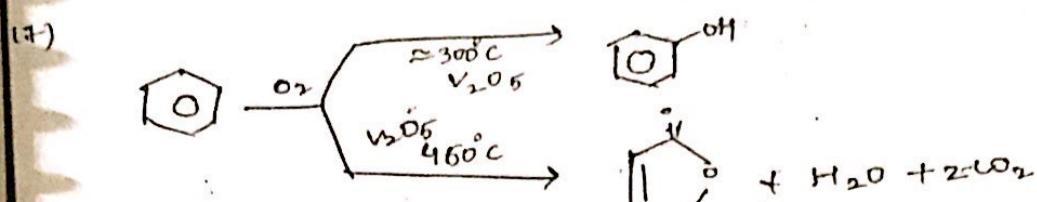
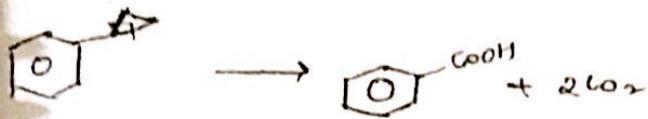
$\text{H}-\overset{\oplus}{\text{O}}\text{N}=\text{O} \rightarrow \text{N}=\text{O}^+ \rightarrow \text{N}=\text{O}^+$  groups.

→ Reacts with only strongly activating groups.

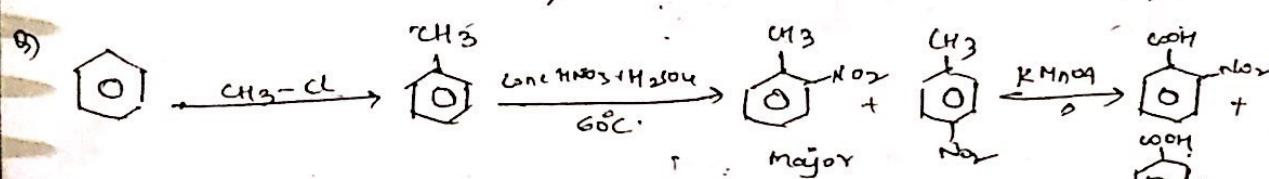
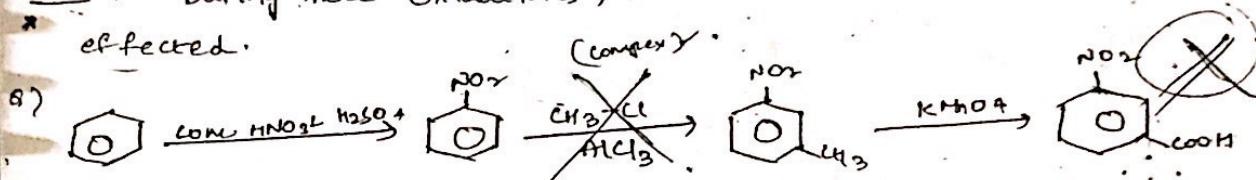


### ONE MORE POOR ELECTROPHILE:-

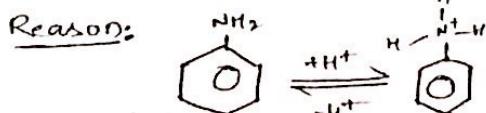
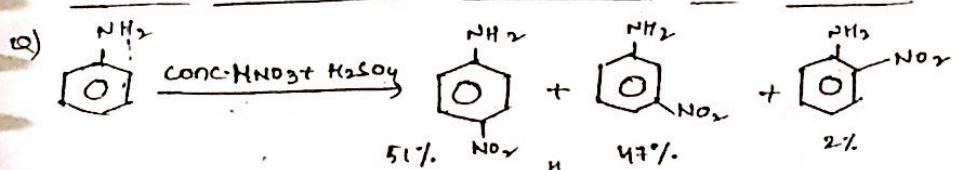




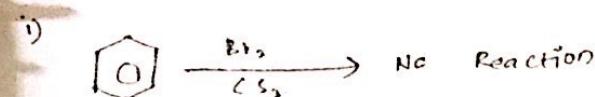
Note: During these oxidations,  $-NO_2$ ,  $-SO_3N^-$ ,  $-X$  does not get effected.



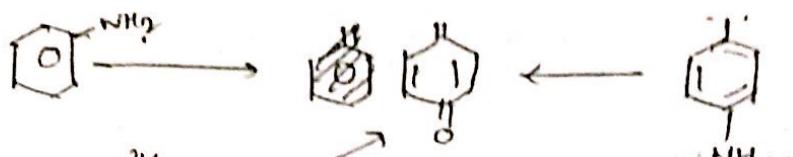
### 1 MORE ANAMALOUS BEHAVIOUR OF ANILINE:-



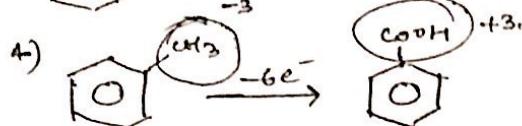
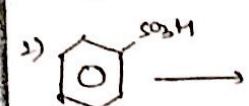
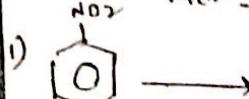
### OTHER EXAMPLES:



(17)

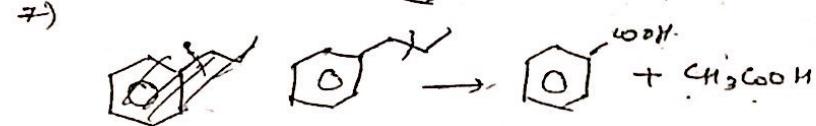
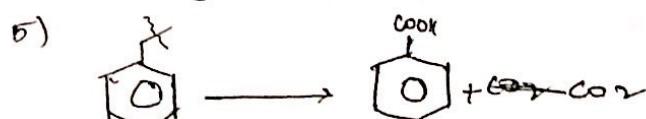


Reagent:  $\text{KMnO}_4 / \text{K}_2\text{Cr}_2\text{O}_7$  (acidic) /  $\text{HNO}_3$

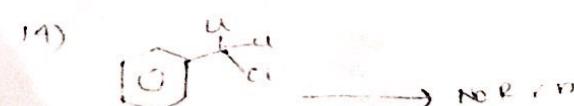
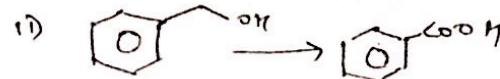
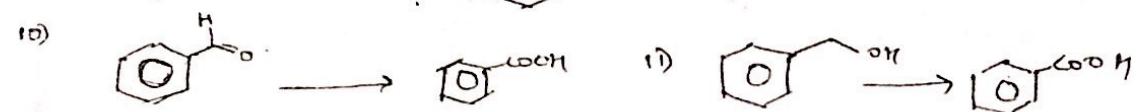


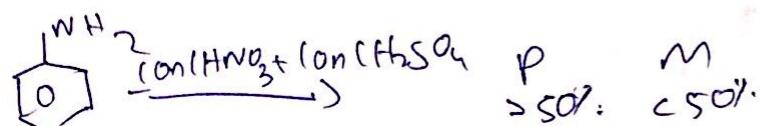
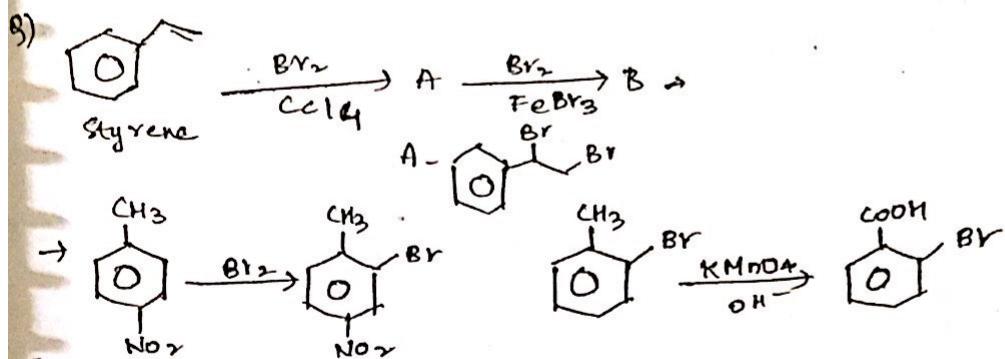
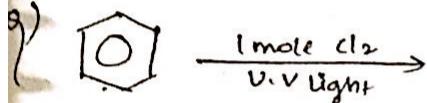
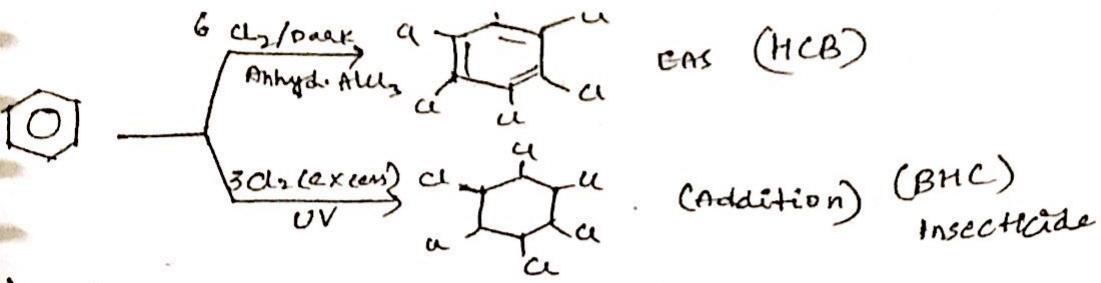
No Reaction  
(deactivating -  
Ring is not oxidised)

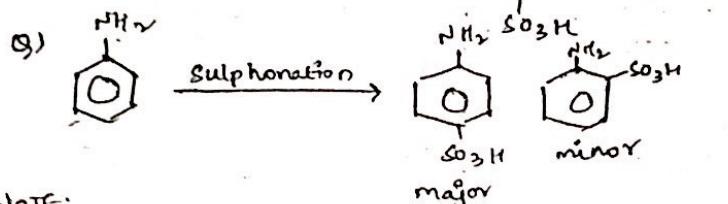
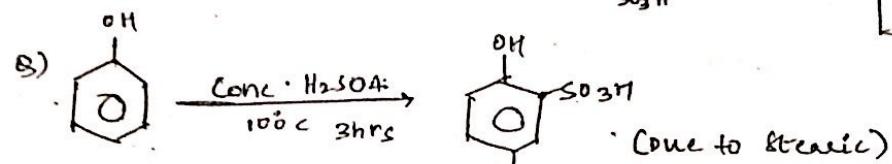
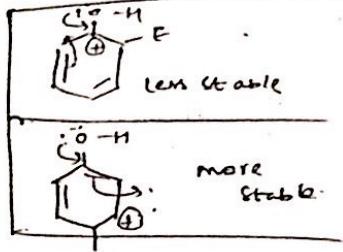
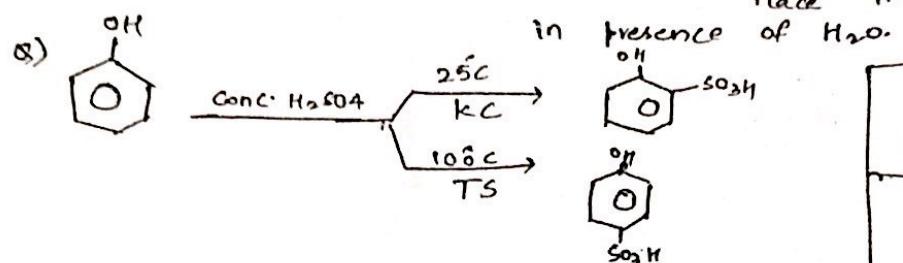
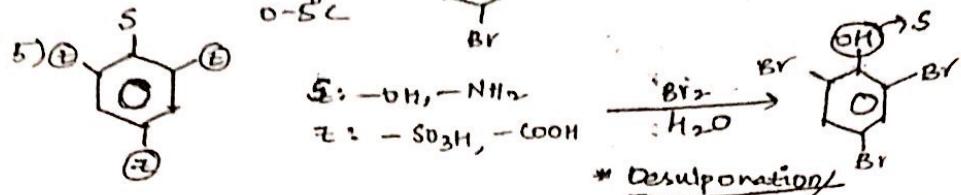
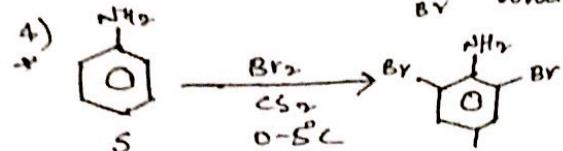
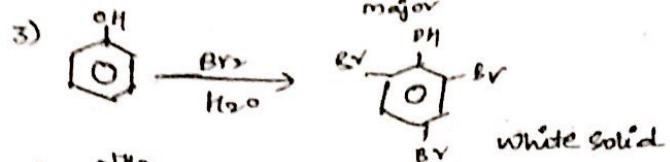
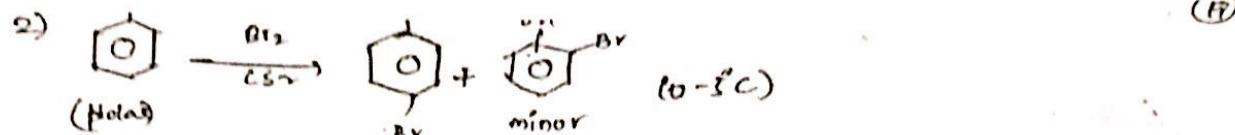
→ Benzene possess alkyl groups, atleast with 1 Benzylic hydrogen. becomes  $\text{COOH}$ .



No Rxn (IEE)  
May be no rxn /  $\text{+ COOH}$

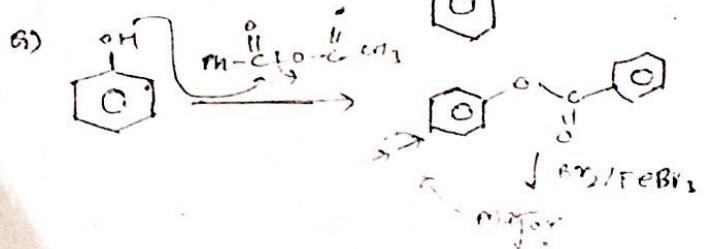
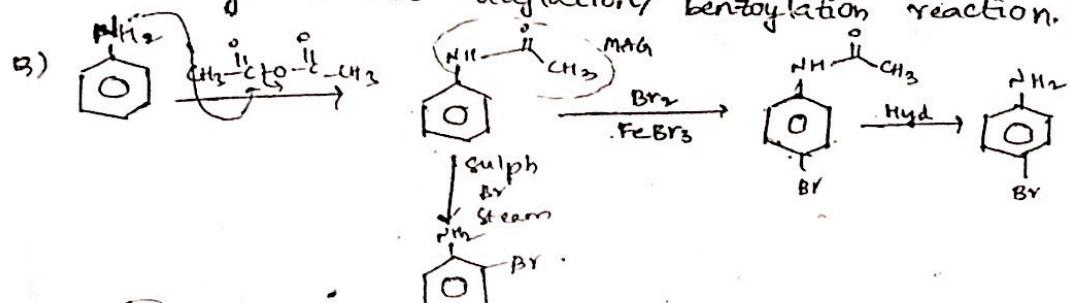






NOTE:

→ To control the anomalous behaviour of Nitrogen, to decrease its reactivity. conduct acylation/ benzoylation reaction. [Schotten-Baumann]



## GRAHAM'S LAW OF DIFFUSION:-

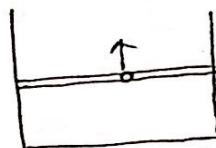
DIFFUSION: The process of intermixing of gases from higher conc. to lower conc.

→ It is multi-directional.

→ It is a spontaneous process:



EFFUSION: The process of the movement of gas through a small hole into vacuum is called Effusion.



→ According to Graham's law of diffusion at constant 'P' for any given mass of a gas rate of diffusion is inversely proportional to molecular mass.

$$\text{Rate of Effusion} = \frac{PA_NA}{\sqrt{2\pi M RT}}$$

$$r \propto \frac{P}{\sqrt{M}}$$

P - Pressure

A - Area of cross section

N - Avagadro no.

m - mol.mass

R - Universal gas const.

T - Temp. in 'K'.

### Case - I:

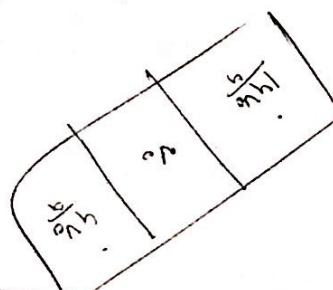
$$\frac{r_1}{r_2} = \frac{P_1}{P_2} \times \sqrt{\frac{M_2}{M_1}}$$

If P is const.

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

i.e.

$$r \propto \frac{1}{\sqrt{M}}$$



∴ r1 is highest for H2 gas.

Case - II :

$$P \propto n$$

$$\frac{P_1}{P_2} = \frac{n_1}{n_2}$$

$$\Rightarrow \frac{r_1}{r_2} = \frac{n_1}{n_2} \sqrt{\frac{M_2}{M_1}}$$

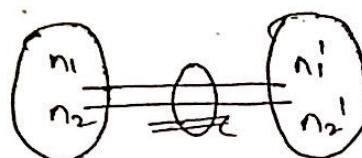
$\therefore n_1$  and  $n_2$  are no-of moles initially present.

Case - III :

$$\text{Mol. mass} = 2 \times V \cdot D$$

$$\frac{r_1}{r_2} = \sqrt{\frac{V D_1}{V D_2}} \quad (\text{Const. } P)$$

Case - IV :

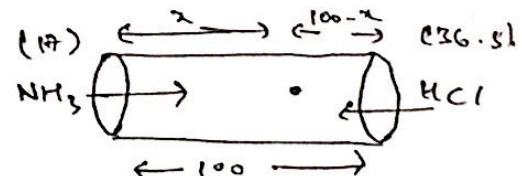


$$\text{rate of diffusion} = \frac{\text{dist. travelled by gas}(e)}{\text{Time}}$$

$$\frac{r_1}{r_2} = \frac{l \sqrt{t_1}}{l_2 / t_2} = \sqrt{\frac{M_2}{M_1}} \quad (\text{Const. } P)$$

Eg.:

$$\frac{r_{NH_3}}{r_{HCl}} = \frac{l_{NH_3}}{l_{HCl}} = \sqrt{\frac{M_{HCl}}{M_{NH_3}}}$$



$$\frac{x}{100-x} = \sqrt{\frac{M_{HCl}}{M_{NH_3}}}$$

$$\frac{x}{100-x} = \sqrt{\frac{36.5}{17}}$$

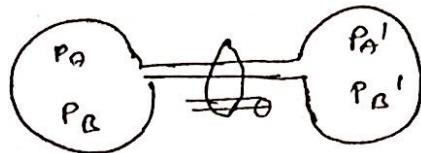
case-VI:

Rate of diffusion =  $\frac{\text{Volume}}{\text{Time}}$

$$\frac{r_1}{r_2} = \frac{V_1/t_1}{V_2/t_2} = \sqrt{\frac{M_2}{M_1}}$$

case-VII:

$$\frac{r_1}{r_2} = \frac{P_A - P_A'}{P_B - P_B'} \left( \sqrt{\frac{M_B}{M_A}} \right)$$



case-VIII:

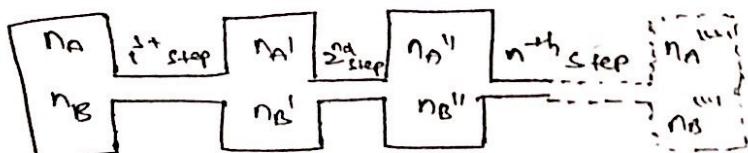
Mixture of gases were ~~not~~ taken

$$M_{\text{avg}} = \frac{\sum n_i M_i}{\sum n_i}$$

$$\frac{r_{\text{gas}}}{r_{\text{mix}}} = \sqrt{\frac{M_{\text{mix}}}{M_{\text{gas}}}}$$

### ENRICHMENT FACTOR:-

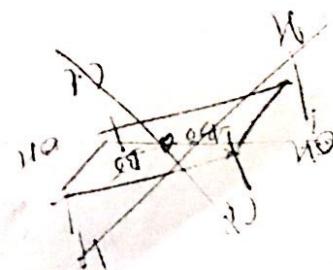
→ This is application of Graham's law of diffusion.



$$\frac{n_A'}{n_B'} = \frac{n_A}{n_B} \sqrt{\frac{M_B}{M_A}}$$

$$\frac{n_A''}{n_B''} = \frac{n_A'}{n_B'} \sqrt{\frac{M_B}{M_A}} = \frac{n_A}{n_B} \left( \sqrt{\frac{M_B}{M_A}} \right)^2$$

$$\frac{n_A''''}{n_B''''} = \frac{n_A}{n_B} \left( \sqrt{\frac{M_B}{M_A}} \right)^{n/2}$$



→ From Graham's law of diffusion, if mix. of heavier gas B and lighter gas A is placed in a container. Then the gas will be enriched with lighter component i.e. A.

→ Therefore, light component in each step is enriched by a factor of " $\sqrt{\frac{M_B}{M_A}}$ ".

$$\left( \sqrt{\frac{M_B}{M_A}} \right)^n = \frac{\text{desired mole ratio}}{\text{initial mole ratio.}}$$

$n \rightarrow$  no. of steps to get desired ratio.

$$t = \frac{v_x}{v_x} \text{ sec.}$$

$$\Rightarrow \frac{1x1}{\frac{2}{v_x}} = \frac{v_x}{l} \text{ collisions.}$$

1 collision  $\Rightarrow$  total change in momentum =  $2mv_x$

$$\frac{v_x}{l} \text{ " } \Rightarrow ?$$

$$= 2mv_x \times \frac{v_x}{l} = \frac{2mv_x^2}{l}$$

$$\text{Tot. change in momentum along } x, y, z = \frac{2m}{l} (v_x^2 + v_y^2 + v_z^2)$$

Multiply and divide by 'N'.

$N \rightarrow$  no-of molecules.

$$\Rightarrow = \frac{2mN}{l} \left( \frac{v_x^2 + v_y^2 + v_z^2}{N} \right).$$

$$c = \sqrt{\left( \frac{v_x^2 + v_y^2 + v_z^2}{N} \right)}$$

$\rightarrow$  Root mean square velocity (RMS)

$$c^2 = \frac{v_x^2 + v_y^2 + v_z^2}{N}$$

$$\text{Tot. change in momentum along } x, y, z = \frac{2mN}{l} c^2$$

$$P = \frac{F}{A} = \frac{2mN(c^2)}{\frac{l}{(6e^2)}} = \frac{1}{3} \frac{mNc^2}{l^3} = \frac{1}{3} \frac{mnc^2}{V}$$

$$Pr = \frac{1}{3} mnc^2$$

P - pressure

V - volume

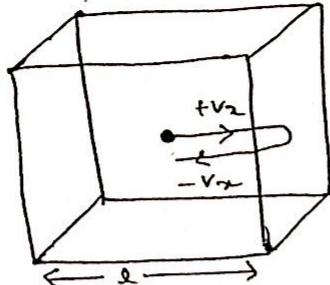
m - mass of 1 gas molecule.

N - no-of molecules

## KINETIC GAS EQUATION:-

### CONCLUSION OF KINETIC THEORY OF GASES: (KTG)

- Gases always moves in st. line.
- Volume occupied by gas molecule is negligible when compared to total volume of the container.
- There will be no forces of attraction, (or) repulsion b/w gas molecules.
- Pressure is due to collision b/w gas molecules and walls of the container.
- Collisions are considered as perfectly ~~elastic~~ elastic. i.e Energy and momentum are conserved.
- Avg. K.E is directly proportional to absolute temperature.



$v_x$  → Velocity along  $x$ -direction.

Change in momentum before collision =  $+mv_x$

" " " after collision =  $-mv_x$

$$\begin{aligned} \text{tot. } " & " & " & = mv_x - (-mv_x) \\ & & & = 2mv_x \end{aligned}$$

$$v_x = \frac{l}{t} \Rightarrow t = \frac{l}{v_x}$$

For one collision time required is  $\frac{l}{v_x}$  sec

The For one second, no. of collision = ?

$\therefore PV = RT$  when  $n=1$

$$\boxed{\text{Avg. KE} = \frac{3}{2} RT}$$

Avg. K.E FOR 1 GAS MOLECULE:

$$PV = \frac{1}{3} m N c^2$$

multiply and div. by 2.

$$PV = \frac{2}{3} \times \frac{1}{2} m N c^2 = \frac{2N}{3} \times \frac{1}{2} m c^2$$

↳ Avg. KE of a gas molecule.

$$\text{Avg. KE} = \frac{3PV}{2N}$$

$$PV = RT \text{ if } n=1$$

$$\boxed{\text{Avg. KE} = \frac{3}{2} \times \frac{RT}{N_A}}$$

$$\text{Boltzmann constant (K)} = \frac{R}{N_A}$$

$$\therefore \text{Avg. KE} = \frac{3}{2} K T$$

# CALCULATION OF RMS VELOCITY FROM KINETIC GAS EQUATION:

$$PV = \frac{1}{3} m N_A C^2$$

$$\therefore m N_A = M$$

$$PV = \frac{1}{3} M C^2$$

$$C = \sqrt{\frac{3PV}{M}}$$

$$d = \frac{M}{V} \Rightarrow$$

$$C = \sqrt{\frac{3P}{d}}$$

For 1 mole of gas,

$$PV = RT$$

$\Rightarrow$

$$C = \sqrt{\frac{3RT}{M}}$$

Case-1: For same gas,

$$\frac{C_1}{C_2} = \sqrt{\frac{T_1}{T_2}}$$

Case-2: For same temp

$$\frac{C_1}{C_2} = \sqrt{\frac{M_2}{M_1}}$$

Case-3: For  $C_1 = C_2$  Temp relation

$$\frac{T_1}{M_1} = \frac{T_2}{M_2}$$

AVERAGE KINETIC ENERGY OF 1 MOLE OF GAS  
FROM M      KGE:

$$PV = \frac{1}{3} M C^2$$

Multiply and div. by  $2$

$$PV = \frac{2}{3} \times \left( \frac{1}{2} M C^2 \right)$$

$\hookrightarrow$  Avg. K.E of 1 mole of gas

$$\text{Avg. KE} = \frac{3PV}{2}$$

no. of molecules.

- Increase in Temp. incre. the K.E. of molecule. by which fraction of molecules having lower speed range ↓. whereas fraction of molecules in higher speed range ↑ on ↑ temperature.
- on ↑ Temp., most probable velocity also gets shifted towards higher value.
- As T ↑, fraction of molecules ↓.
- Speed distribution also depends on molar mass for the 2 gases having different molar masses at same temperature.
$$\left( \frac{1}{N} \cdot \frac{dN_u}{du} \right) \propto 4\pi \left( \frac{M}{2\pi RT} \right)^{3/2}$$
- The fraction of molecules moving with most prob. velocity ↑ with ↑ in molecular mass.

### TYPES OF MOLECULAR VELOCITIES:-

## MAXWELL DISTRIBUTION VELOCITIES:-

$$dN_u = \frac{4\pi N}{2\pi RT} \left( \frac{M}{2\pi RT} \right)^{3/2} u^2 \cdot e^{-\frac{Mu^2}{2kT}} \cdot du$$

$dN_u \rightarrow$  Total no-of molecules in velocity Range  $U$  to  $U+du$

$N \rightarrow$  Total no-of particles

$M \rightarrow$  Molar mass in kg/mole

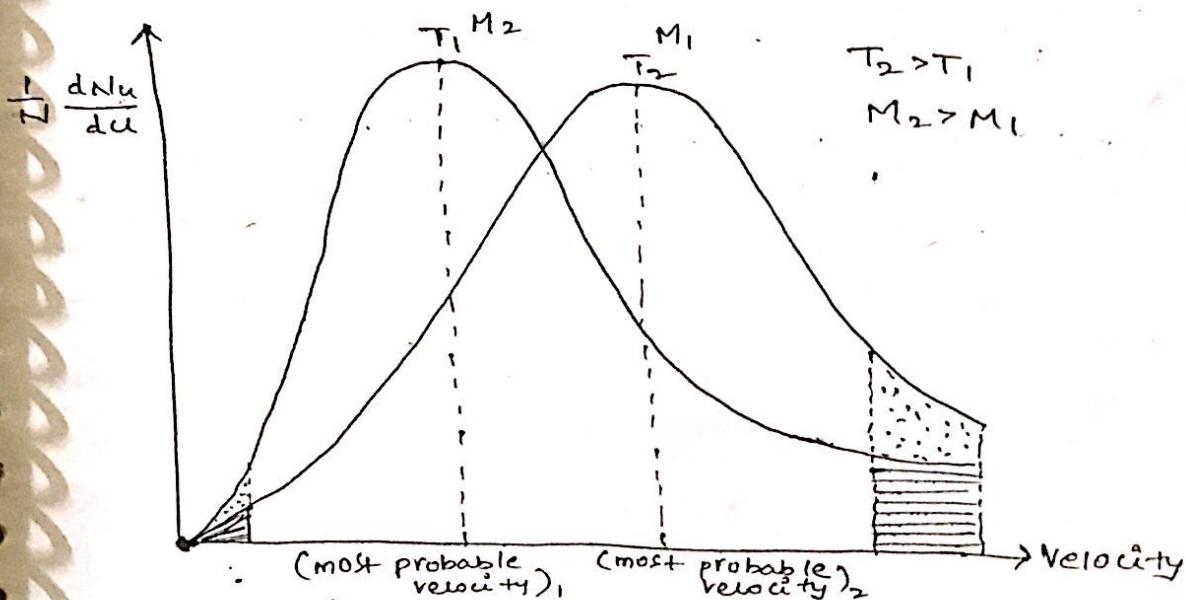
$T \rightarrow$  Absolute temperature

$u \rightarrow$  Starting velocity

$du \rightarrow$  difference in velocity

$R \rightarrow$  Universal constant.

$\frac{dN_u}{N} \rightarrow$  Fraction of molecules having velocities in the range of  $U$  and  $U+du$ .



- The Fraction of molecules having very low Speed (or) very high speed is very less.
- Majority of the molecules have speed near most probable velocity
- Total area under curve is measure of total