

# Amines

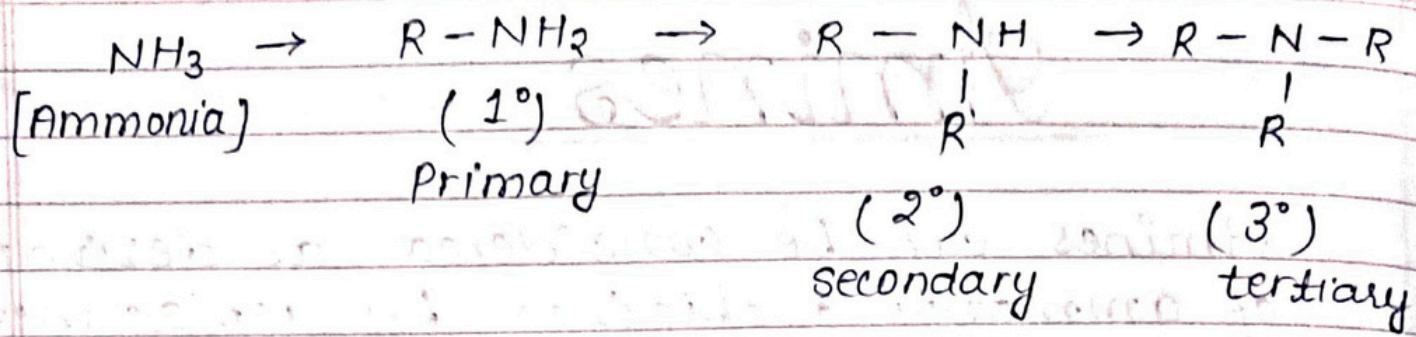
[7 mark]

Amines can be considered as derivatives of ammonia, obtained by replacement of one, two or all the three hydrogen atoms by alkyl and / or aryl groups.

- Nitrogen orbitals in amines are  $sp^3$  hybridised.
- Geometry of amines is Tetrahedral.
- Shape of amines is Pyramidal.
- The fourth orbitals of nitrogen in all amines contain an unshared pair of electron.
- Due to the presence of unshared pair of electron, the angle is less than  $109.5^\circ$  (It is  $108^\circ$  in case of trimethylamine).

## Classification of Amines

$\downarrow$ $1^\circ$ amines (primary)	$\downarrow$ $2^\circ$ amine (secondary)	$\downarrow$ $3^\circ$ amine (tertiary)
when only one H-atom is replaced by alkyl or aryl group in ammonia.	when two H-atom are replaced by alkyl or aryl group in the ammonia.	when 3 H atom are replaced by alkyl or aryl group in the ammonia.
eg. $R-NH_2$	eg. $R-NH-R'$	eg. $R-N(R')_2$

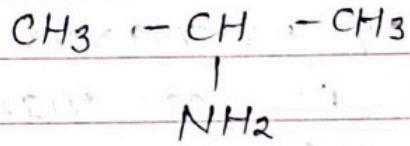


### Nomenclature :-

→ for primary amines ;

Common name →	alkylamines
IUPAC name →	alkanamines

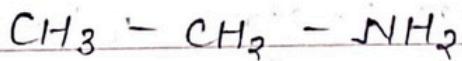
eg.



Common name →	Propylamine
IUPAC name →	Propan - 2 - amine



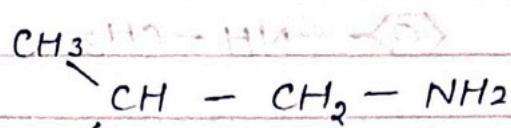
Common name →	methylamine
IUPAC →	methanamine



Common name →	ethylamine
IUPAC name →	ethaneamine



Common name →	aniline
IUPAC name →	Benzylamine or Aniline



anilized  $\text{CH}_3\text{CH}_2\text{NH}_2$  to amino ethane

unringed diphenyl-am to amino benzene

IUPAC: 2-methylpropan-1-amine.

For secondary amine:

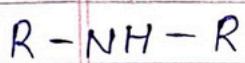


Simple 2° amine

secondary amine IUPAC → R-NH-R'

simple 2° amine

mixed 2° amine



common → dialkylamine

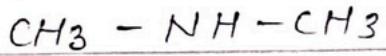
common → alkylalkyl amine

IUPAC → N-alkyl alkanamine

IUPAC → N-alkyl alkanamine

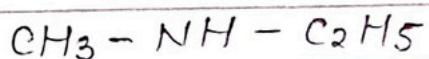
less number of C atoms

Eg.



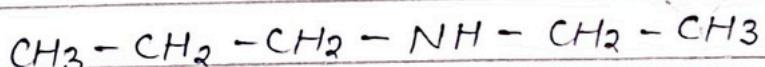
Common name → dimethylamine

IUPAC name → N-methylmethanamine.



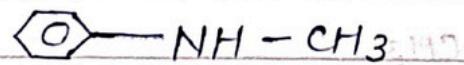
Common name → ethylmethylamine

IUPAC name → N-methylethanamine



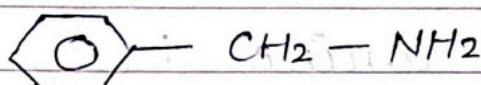
Common name → ethylpropyl amine

IUPAC name → N-ethylpropanamine



Common name  $\rightarrow$  methyl aniline

IUPAC name  $\rightarrow$  N-methyl benzenamine



IUPAC  $\rightarrow$  1-Phenyl methanamine

Common  $\rightarrow$  Phenyl methyl amine

For tertiary amines :

Common name  $\rightarrow$  N,N,N-trialkyl amine

IUPAC name  $\rightarrow$  N,N-dialkyl alkyl amine



Common name  $\rightarrow$  N,N,N-trimethyl amine

IUPAC name  $\rightarrow$  N,N-dimethylmethanamine



Common name  $\rightarrow$  N-p-bromo aniline

IUPAC name  $\rightarrow$  4-bromobenzene amine

or

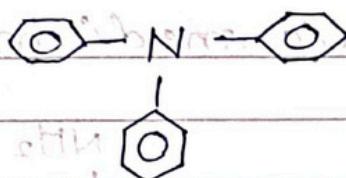
4-bromoaniline

$N(CH_3)_2$



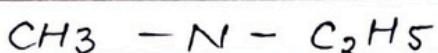
Common name -  $N, N$ -dimethylaniline

IUPAC name -  $N, N$ -dimethylaniline



Common name -  $N, N, N$ -triphenylamine

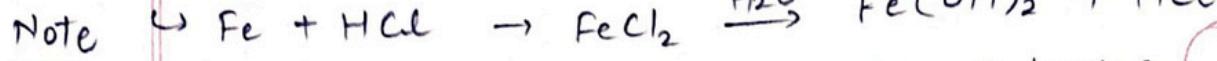
IUPAC name -  $N, N$ -diphenylbenzenamine



common name -  $N$ -ethyl- $N$ -methylaniline.

IUPAC name -  $N$ -ethyl- $N$ -methylbenzenamine

Preferred because-



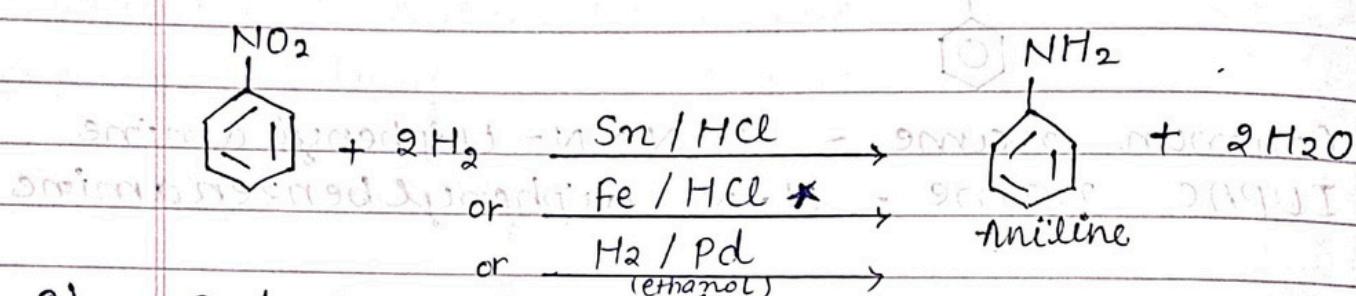
more HCl is getting produced during reaction

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## Methods of Preparation :-

### 1). Reduction of Nitro-compounds

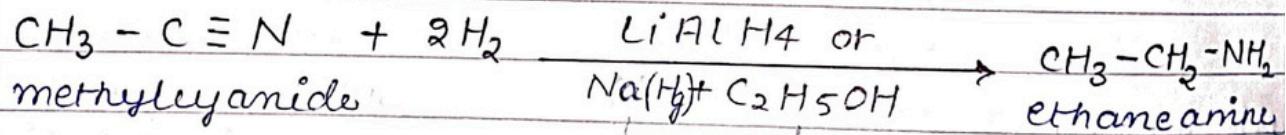
Nitro compounds are reduced to amines by passing Hydrogen gas in the presence of Ni, Pd or Pt and also by reduction with metal in acidic medium.



### 2). Reduction of Nitrile

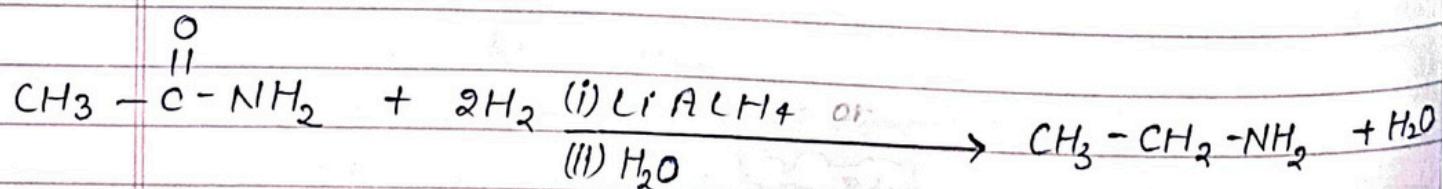
Nitriles are reduced to amines with  $\text{LiAlH}_4$  or  $\text{Na/C}_2\text{H}_5\text{OH}$  (ethanolic sodium) or  $\text{H}_2/\text{Ni}$  (catalytic hydrogenation).

Note: This reaction increase no. of C in parent chain by one.



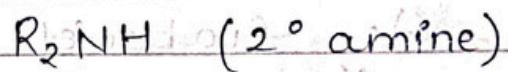
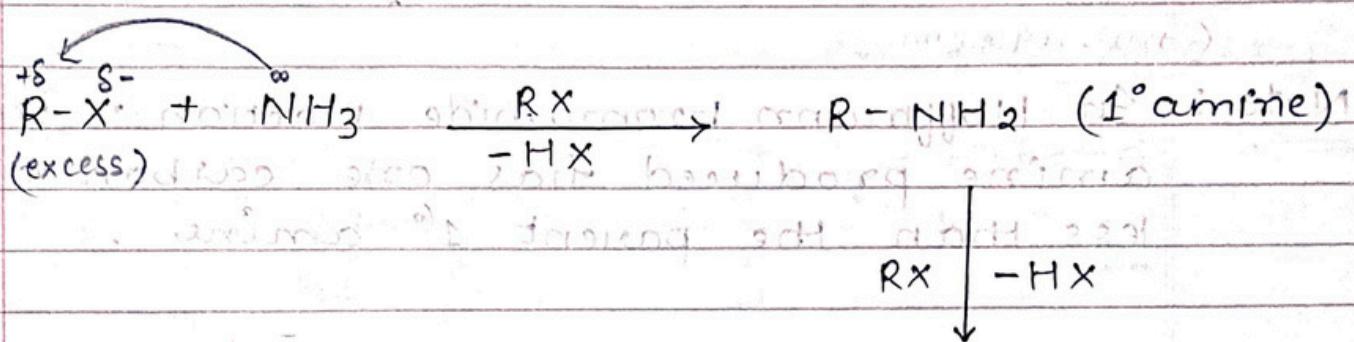
### ③ Reduction of amides

Amides are reduced to amines with  $\text{LiAlH}_4$  or  $\text{Na/C}_2\text{H}_5\text{OH}$ .



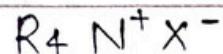
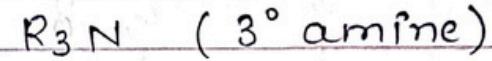
## (Hoffmann's Ammonolysis).

④. Ammonolysis is the process when alkyl halide ( $R-X$ ) reacts with alcoholic solution of ammonia, halogen atom of alkyl halide is replaced by  $NH_2$  group of ammonia. This process of cleavage of  $R-X$  by ammonia is known as ammonolysis.



$$RI > RBr > RCl$$

→ For  $RNH_2$  as major product take ammonia in excess.

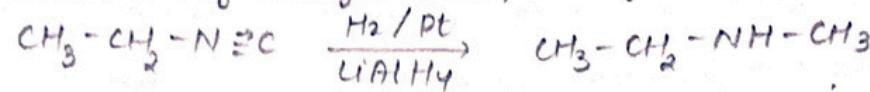


(quaternary salt)

Drawback :

→ By this reaction, a mixture of 1°, 2° and 3° and quaternary salts are obtained.

#### 7. Reduction of isocyanide / carbonyl amine

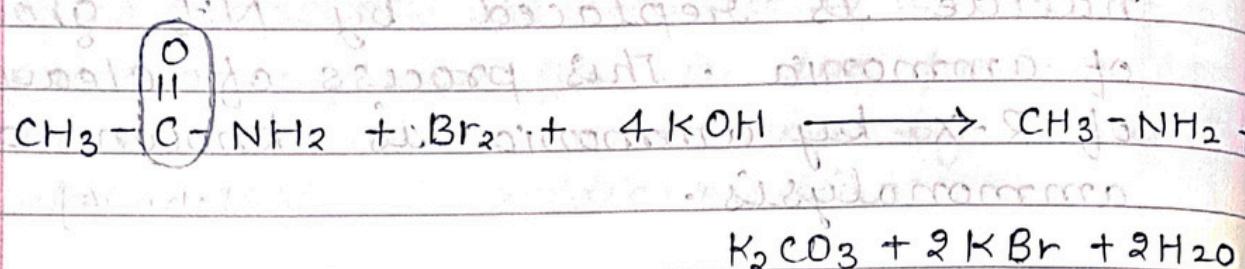


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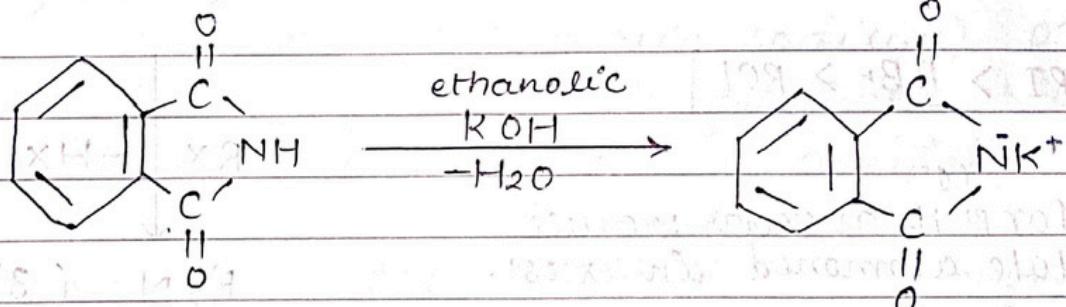
### 5). ~~Group~~ Hoffmann Bromamide Reaction -

Primary amines are prepared by treating an amide with  $\text{Br}_2$  and  $\text{KOH}$  or  $\text{NaOH}$ .



Note: In Hoffmann bromamide reaction, the amine produced has one carbon atom less than the parent  $1^\circ$  amine.

### (contd) 6. Gabriel Phthalimide Reaction -

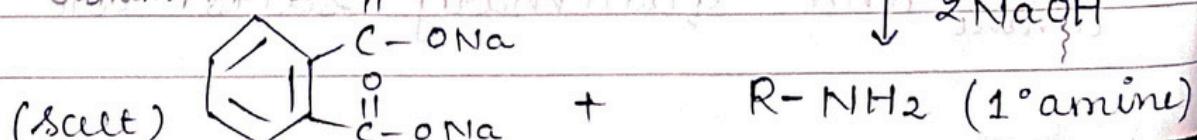
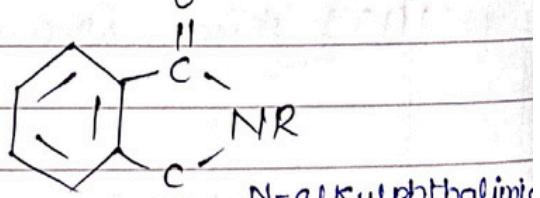


Note. \* Used for preparation of  
1° amine

\* aliphatic amines only.

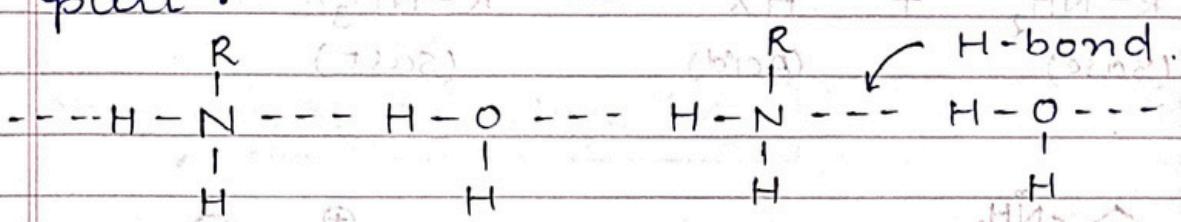
because nucleophilic substitution

is not feasible in Aromatic amine

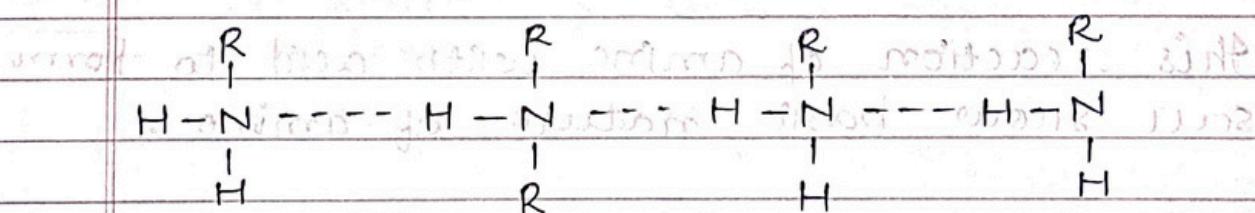


## Physical Properties :-

- i). lower amines are colourless gases with fishy odour whereas higher amines are colourless liquid or solid.
- but occupies colour due to oxidation.
- ii). Lower amines are soluble in water because of forming Hydrogen bond with water molecules. Higher amines are insoluble in  $H_2O$  due to increase in size of alkyl part.



- iii) Boiling point of amines are comparable high due to the formation of the intermolecular Hydrogen bonding.



$1^\circ$  amine  $>$   $2^\circ$  amine  $>$   $3^\circ$  amine

decreasing order of boiling points of amines.

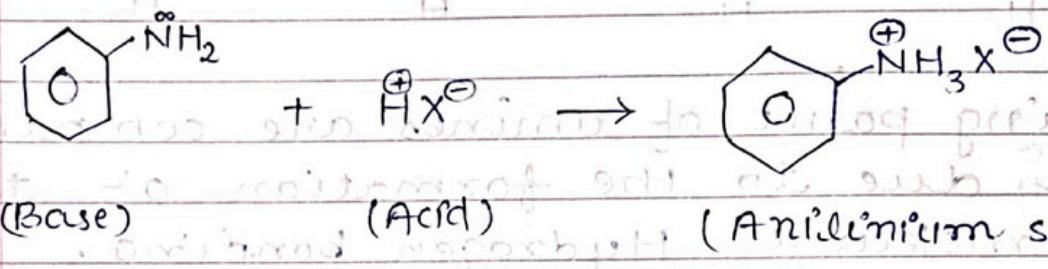
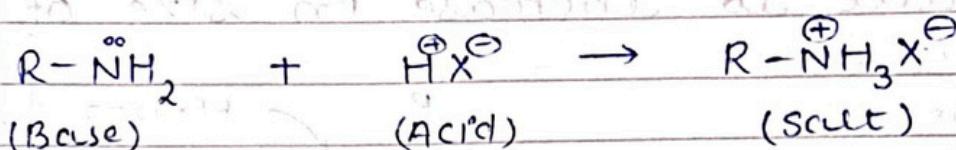
this is because tertiary amines cannot form intermolecular  $H^-$  bonding due to the absence of  $NH^+$  bond.

Amines less soluble than alcohol but more than water due to its more electronegativity.

## Chemical Properties

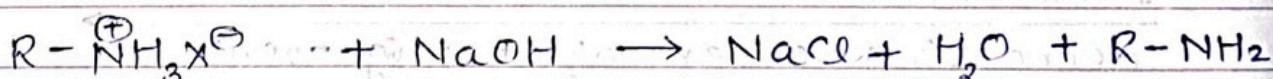
## 1) Basic Nature of Amines

Due to the presence of lone pair of electrons on nitrogen atom, amines show basic nature. Therefore behave as LEWIS BASE. (Lone pair donor).



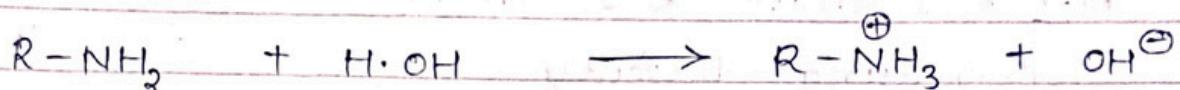
This reaction of amine with acid to form salt shows basic nature of amine.

→ If these salt are treated with a base we will regain our amine.



→ Amines are basic in nature and therefore they are soluble in water but not much in organic solvent like ether. But other non-basic organic solvents are water insoluble. ∴ Amines can be separated easily.

Basic strength character of amine can be understood in term of their  $K_b$  and  $pK_b$  values as explained below -



$$K_b = \frac{[RNH_3^+][OH^-]}{[RNH_2][H_2O]}$$

where,  $K_b$  is equal to the dissociation constant of base.

Also ;  $pK_b = -\log_{10}[K_b]$

$\because$  Larger the value of  $K_b$   
Smaller the value of  $pK_b$   
STRONGER is the BASE.

Note:- Aliphatic amines  $>$   $NH_3$   $>$  Aromatic amines

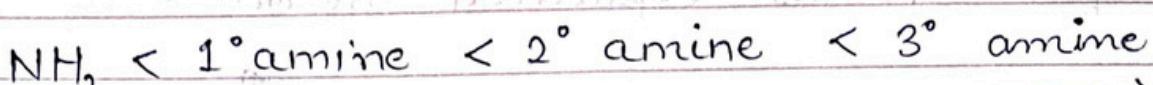
in terms of basicity .

### Alkyl amines vs Ammonia :

Basic strength of amines are affected by + I effect (gas phase) , solvation effect (aqueous phase) and steric hindrance .

$\rightarrow$  In gaseous phase : In amines the presence of e- releasing group (-R) increases the e- density on N making it a good e- pair

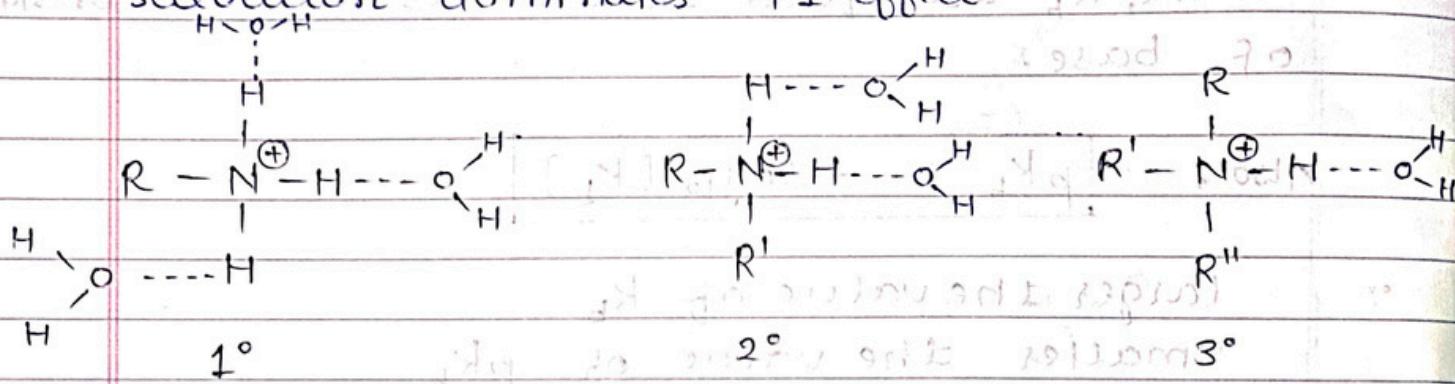
donor hence the basicity increases so it is because of +I effect.



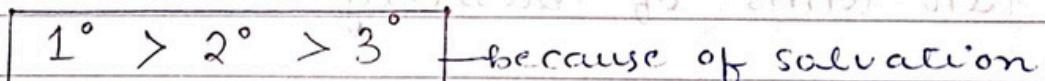
increasing basicity

no. of alkyl group ↑

But in aqueous medium along with +I effect solvation also contributes its basicity and solvation dominates +I effect.



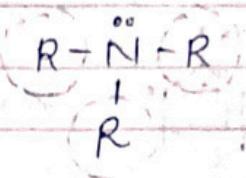
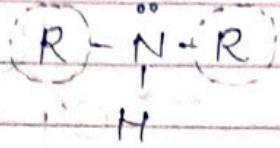
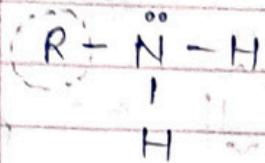
Because of 3 - Hydrogen are present on  $1^\circ$  amine it forms 3 , hydrogen bonding and hence make it more stable.



because of salvation

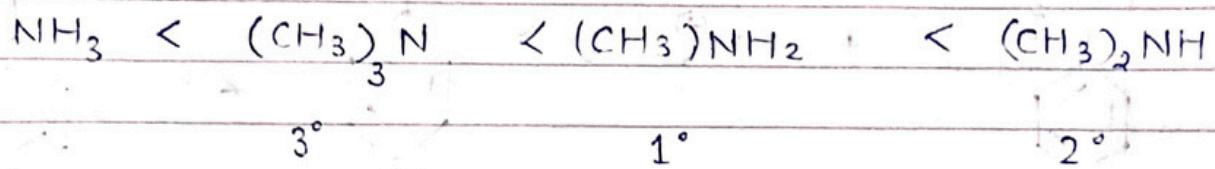
Greater the size of ion, lesser will be solvation and less stabilise is the ion hence basicity decreases.

→ presence of alkyl group also affect the basicity along with +I effect and solvation effect. **STERIC HINDERANCE**



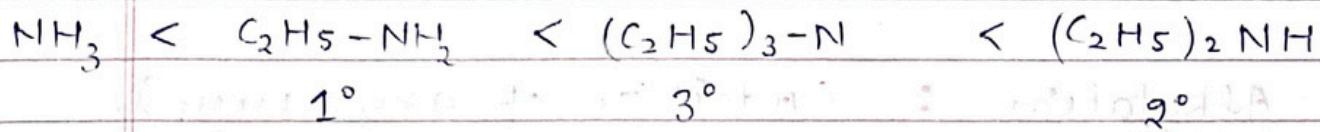
$$1^\circ > 2^\circ > 3^\circ$$

→ Basic strength of methyl amine :



$$2^\circ > 1^\circ > 3^\circ > \text{NH}_3$$

→ Basic strength of ethyl amine or above :



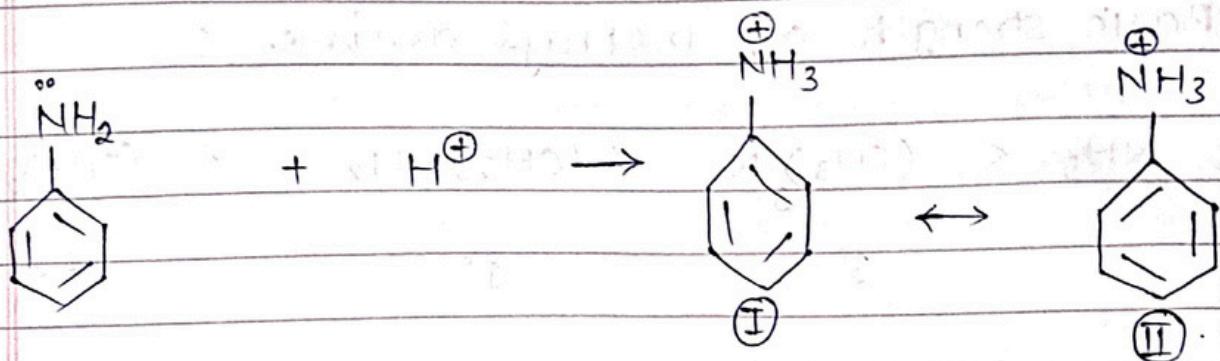
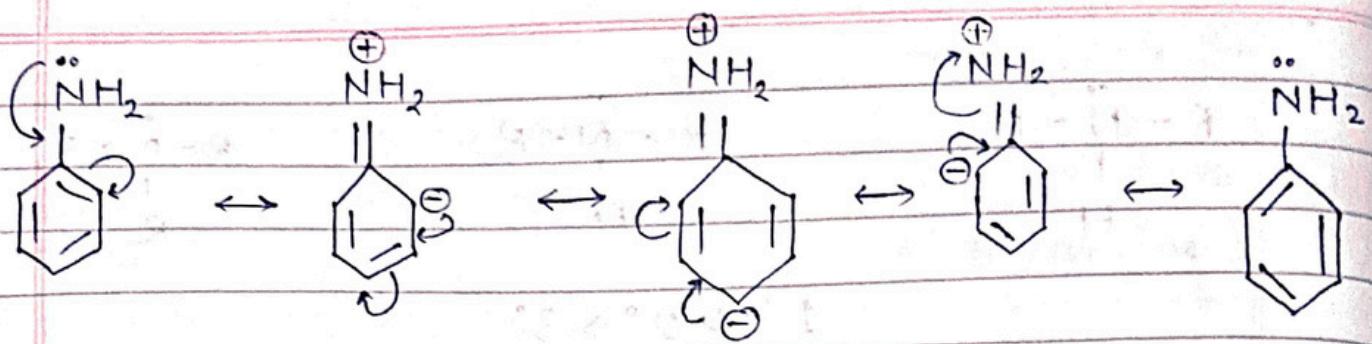
$$2^\circ > 3^\circ > 1^\circ > \text{NH}_3$$

Aryl Amine v/s Ammonia :-

$(\text{NH}_3 > \text{Aniline})$

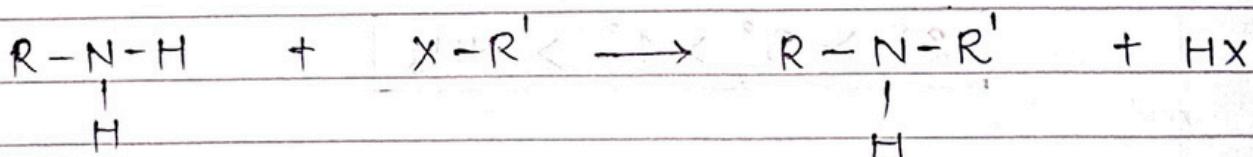
Because of electron withdrawing nature of aryl amine  $\text{NH}_2$  it's not available to release  $e^-$  pair towards proton ( $\text{H}^+$ ).

Hence, less basic nature.

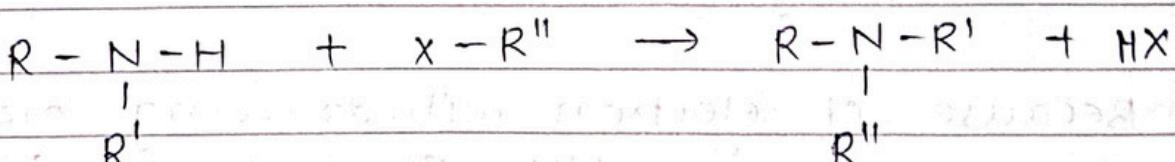


Also, if it donates e-pair to form Anilinium ion, only two resonating structure form making it highly unstable. Hence less Basic.

### (3) Alkylation : (Addition of alkyl group).

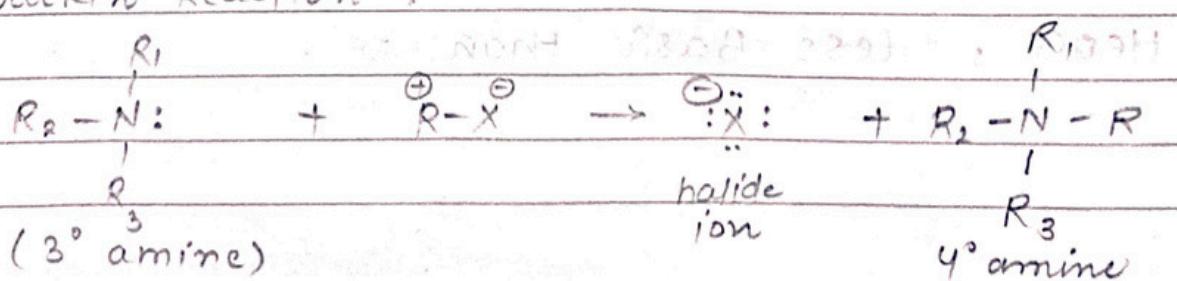


1° amine



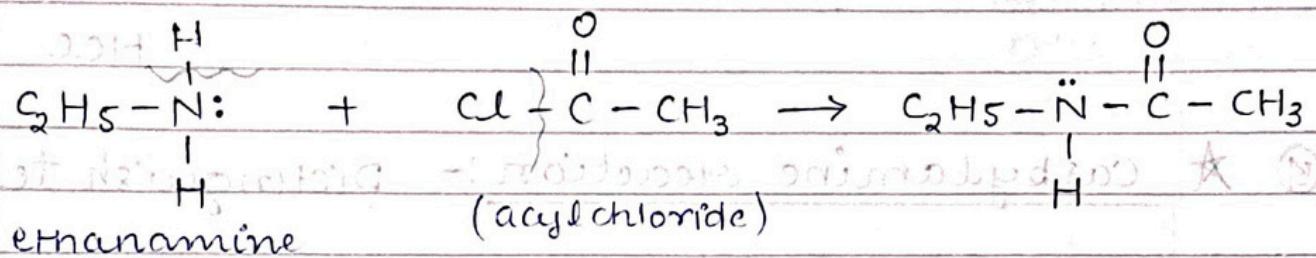
2° amine

Menschutkin reaction :

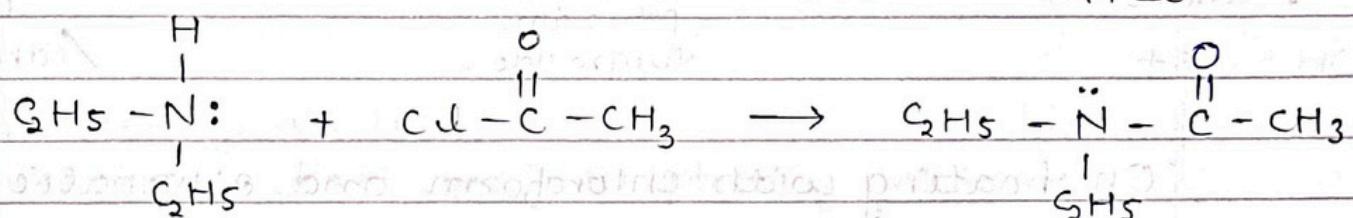


### ③ Acylation : Distinguish test

Being reacted with acyl chloride, anhydride and ester, amine form amide. This reaction is known as acylation.

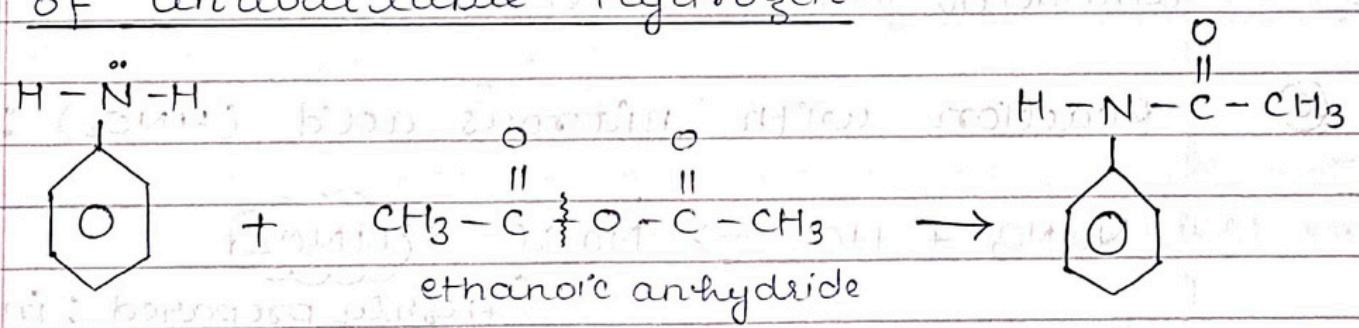


N-ethyl ethanamide

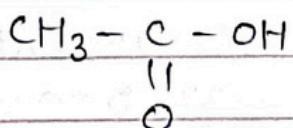


N-ethyl ethanamine      N,N-diethyl ethanamide

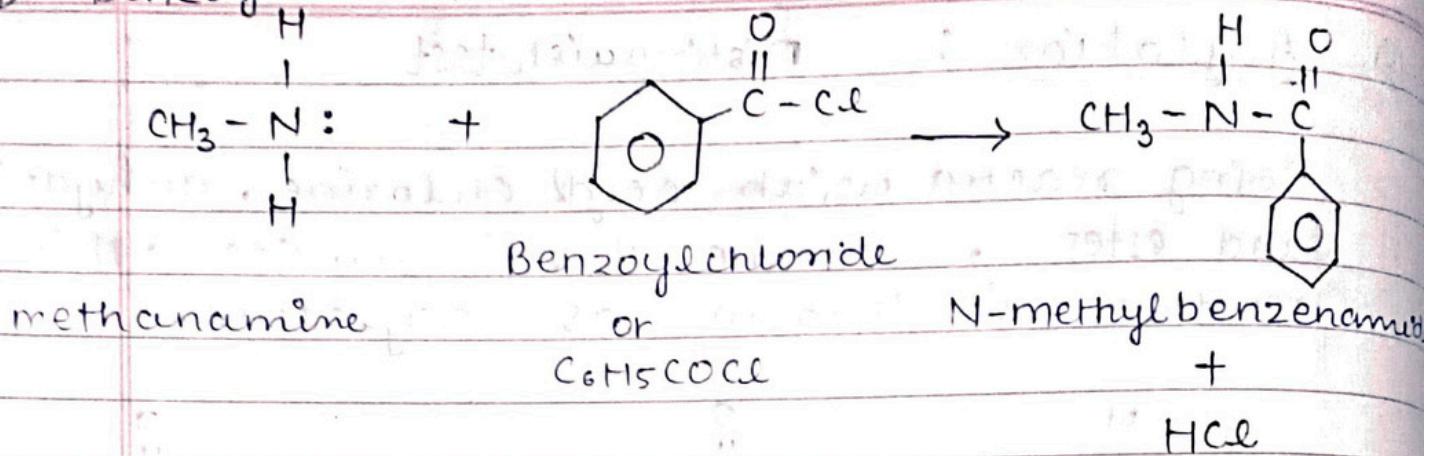
$\Rightarrow$  3° amine do not show this reaction because of unavailable hydrogen.



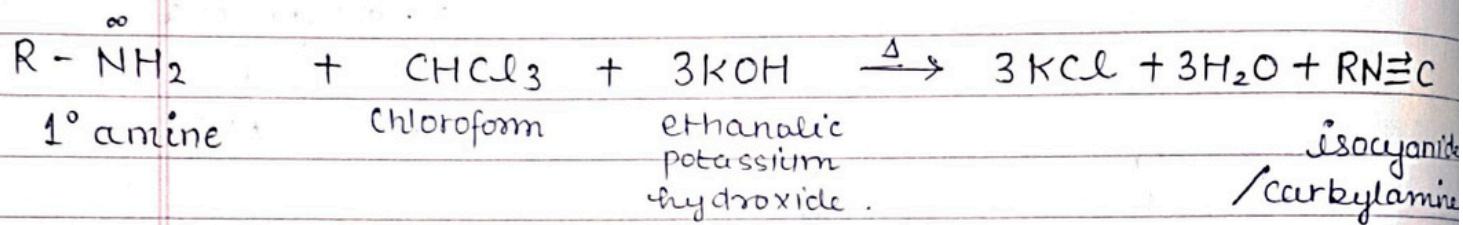
N-phenylethanamide



#### ④ Benzoylation :-

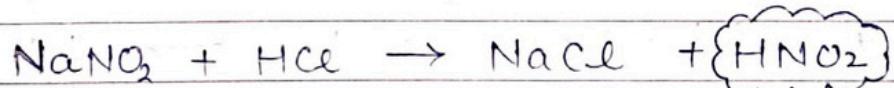


⑤ **Carbylamine reaction** :- Distinguish test



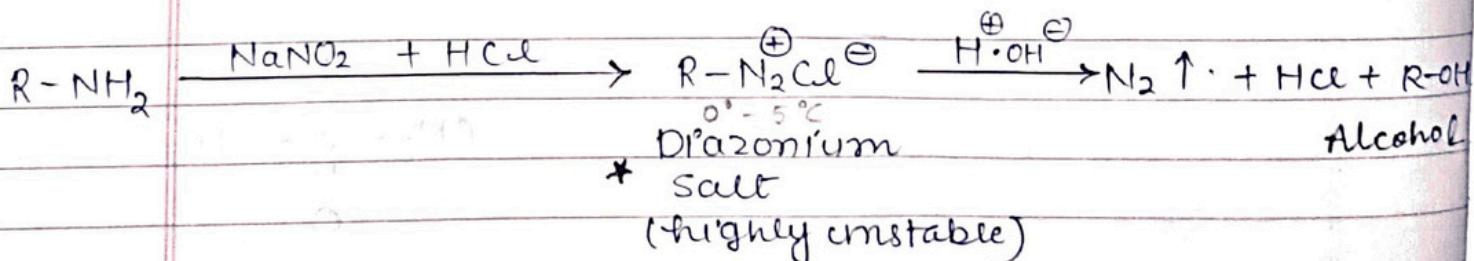
On heating with chloroform and ethanolic KOH  
 amine forms 'isocyanide' or carbylamine  
 having foetid smell. This reaction is known  
 as carbylamine reaction or isocynide test  
 used as test for primary amine, because  
 $1^\circ$  amine show this reaction while  $2^\circ$  and  $3^\circ$   
 amine do not show this.

⑥ Reaction with nitrous acid ( $\text{HNO}_2$ ) :-

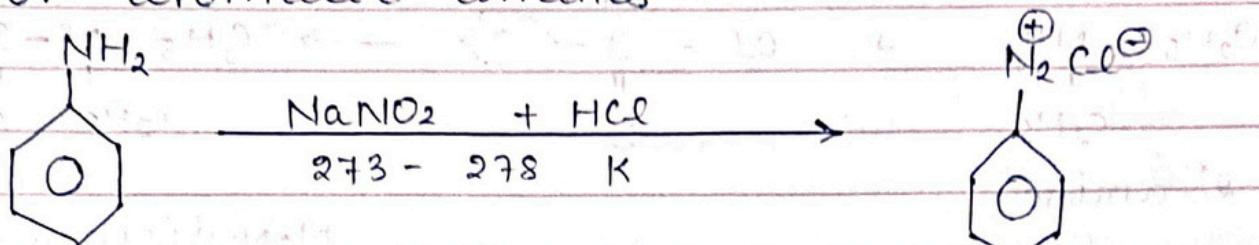


[ freshly prepared : in situ ]

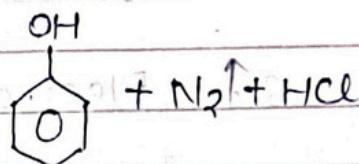
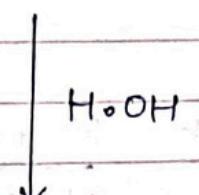
i) for aliphatic amines -



ii) for aromatic amines -

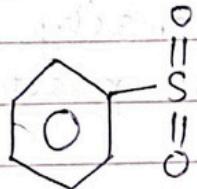


Benzene  
Diazonium  
Chloride.



\* (Distinguish test)

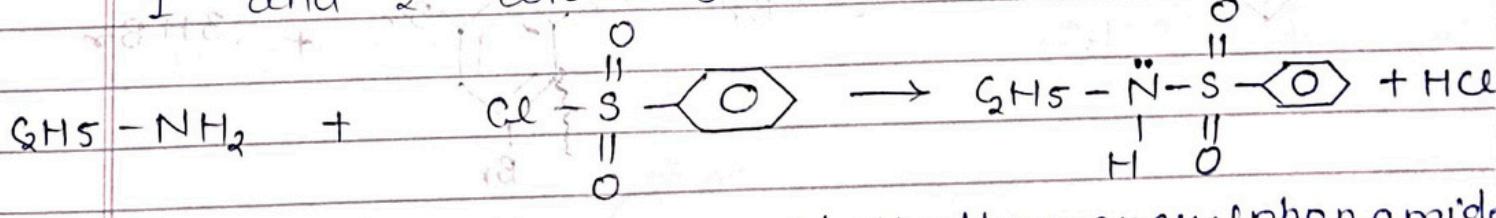
(7) Reaction with acyl sulphonyl chloride :-



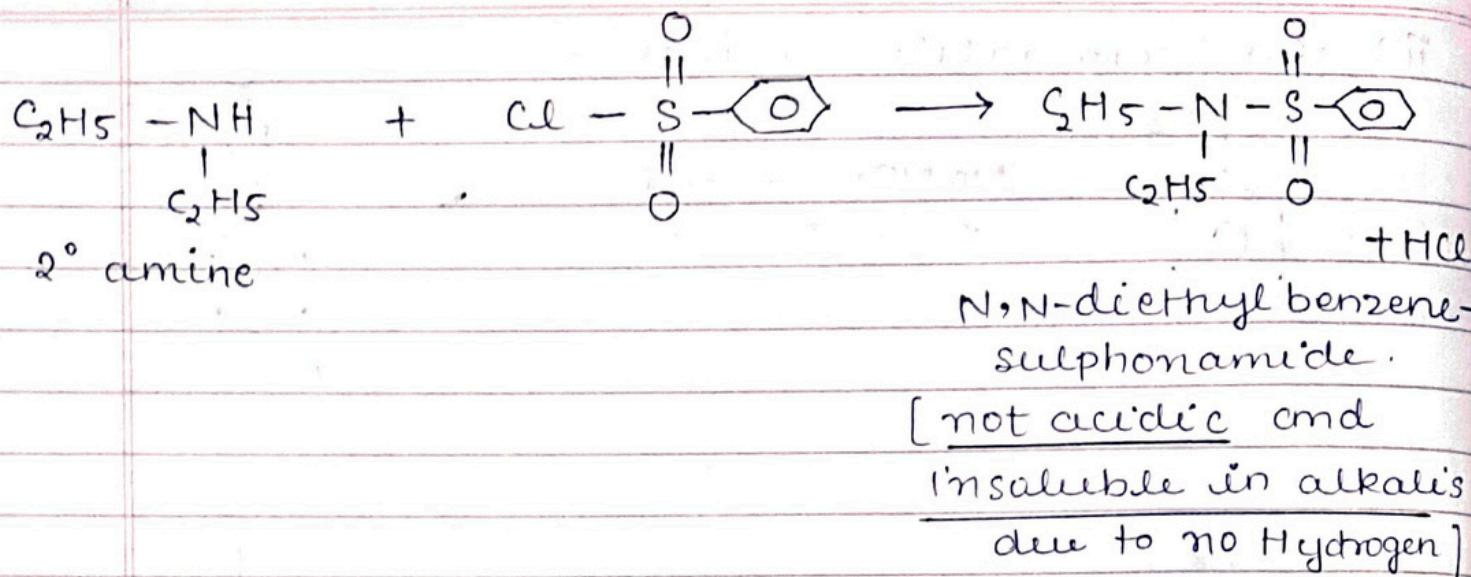
\* Hinsberg reagent or  
Benzenesulphonyl chloride.

$\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$  is also known as Hinsberg's reagent  
this reaction is used for distinction of  $1^\circ$ ,  
 $2^\circ$  and  $3^\circ$  amines.

$3^\circ$  amines because of unavailable  $\text{H}$  do not show this reaction, hence distinguish test for  $1^\circ$  and  $2^\circ$  with  $3^\circ$  amine.



N-ethylbenzenesulphonamide  
[acidic and soluble in alkali].



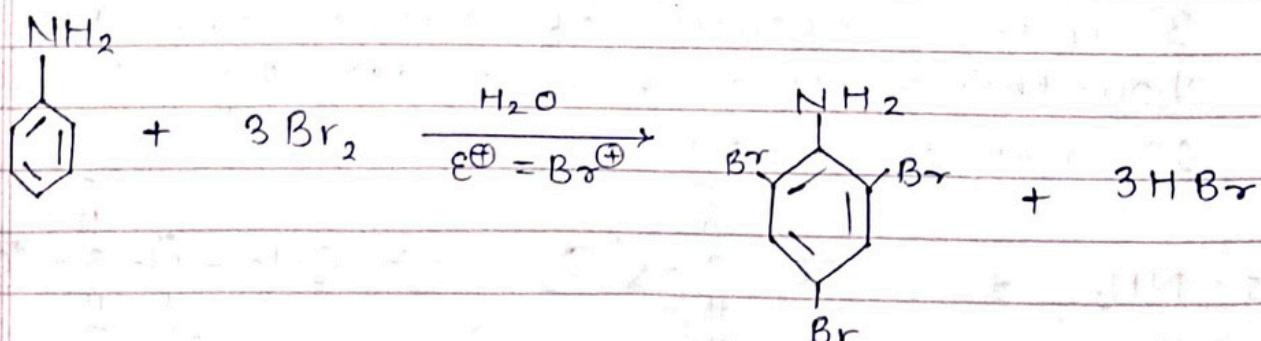
→ 3° amine do not show this reaction because of absence of Hydrogen.

### B. Electrophilic Substitution reaction :-

Amiline is ortho and para directing group compound because electron density is increased on ortho and para position of benzene ring.

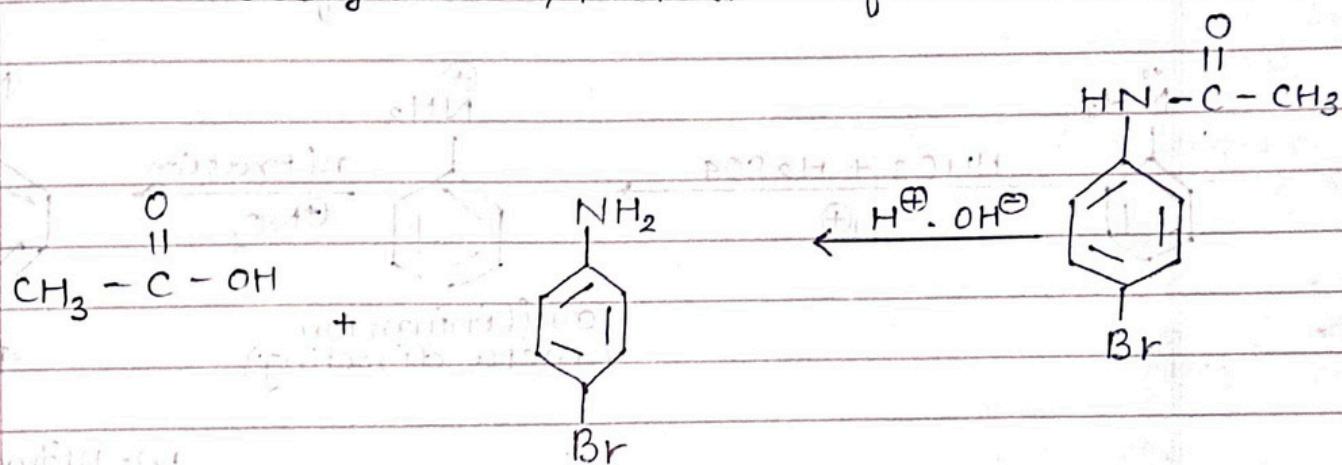
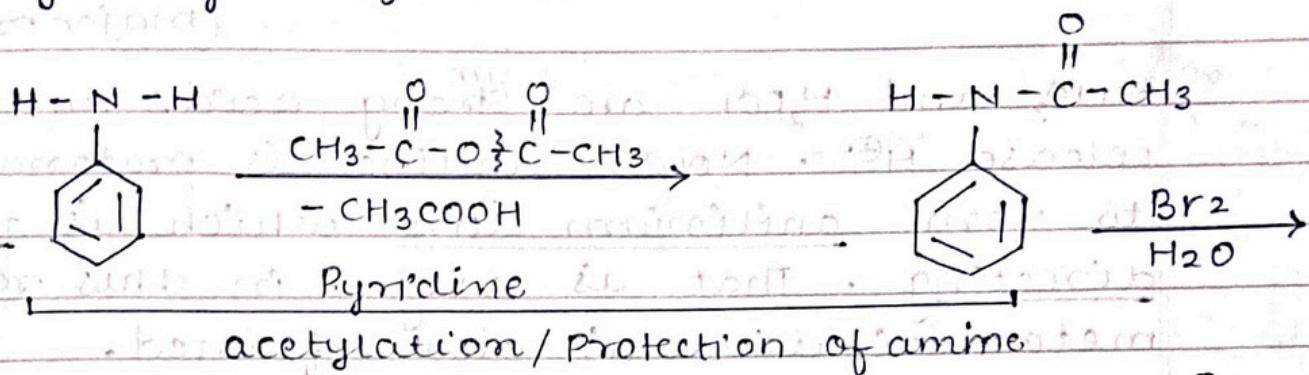
### i) Bromination :-

Aniline reacts with bromine water to give white ppt of 2,4,6-tribromomili



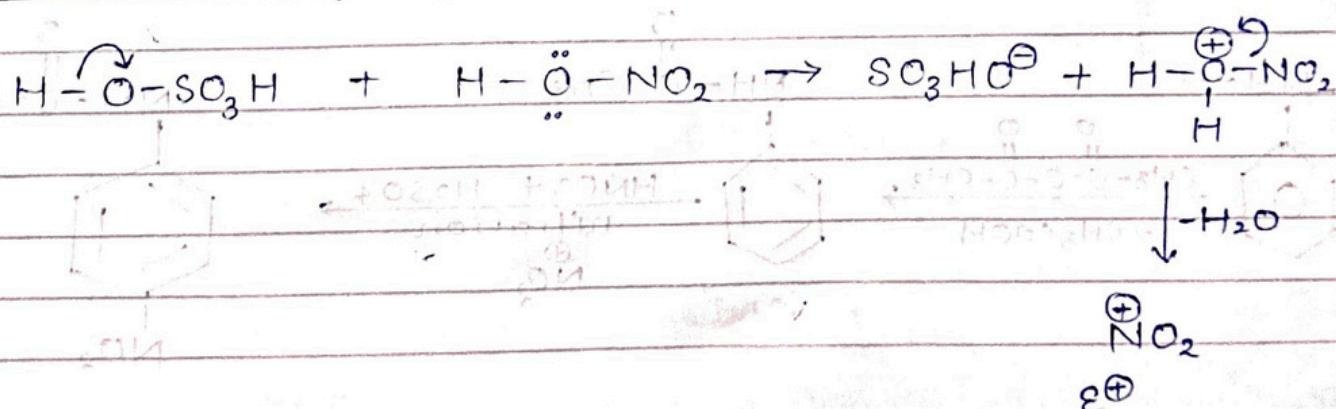
white ppt.  
2,4,6-tribromoaniline

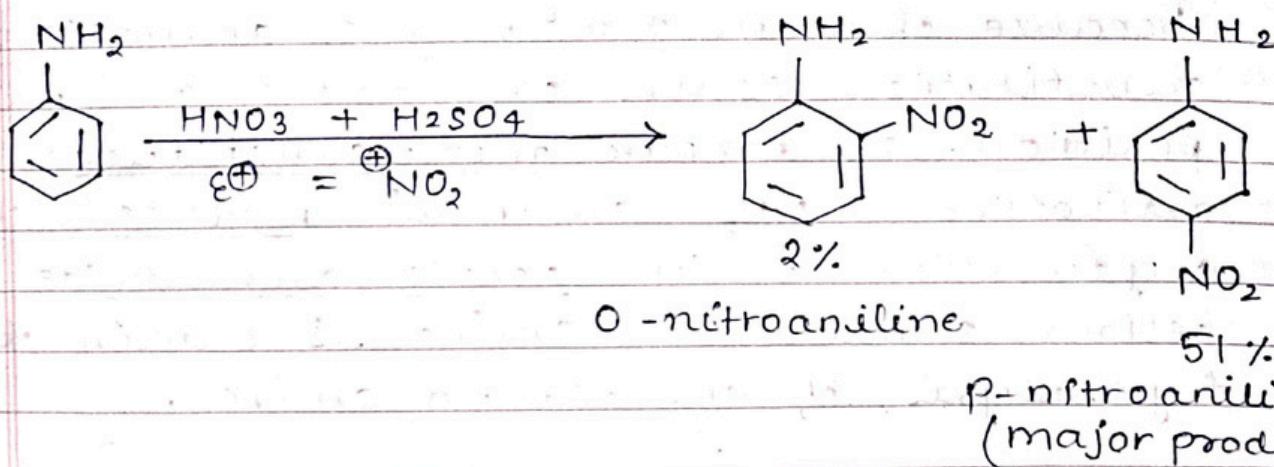
because of high reactivity of aromatic amine substitution occurs on ortho and para position. To prepare monosubstituted aniline derivative  $-\ddot{\text{N}}\text{H}_2$  group is protected by acetylation with acetic anhydride, then desired substituted amine is obtain by hydrolysis of substituted amine.



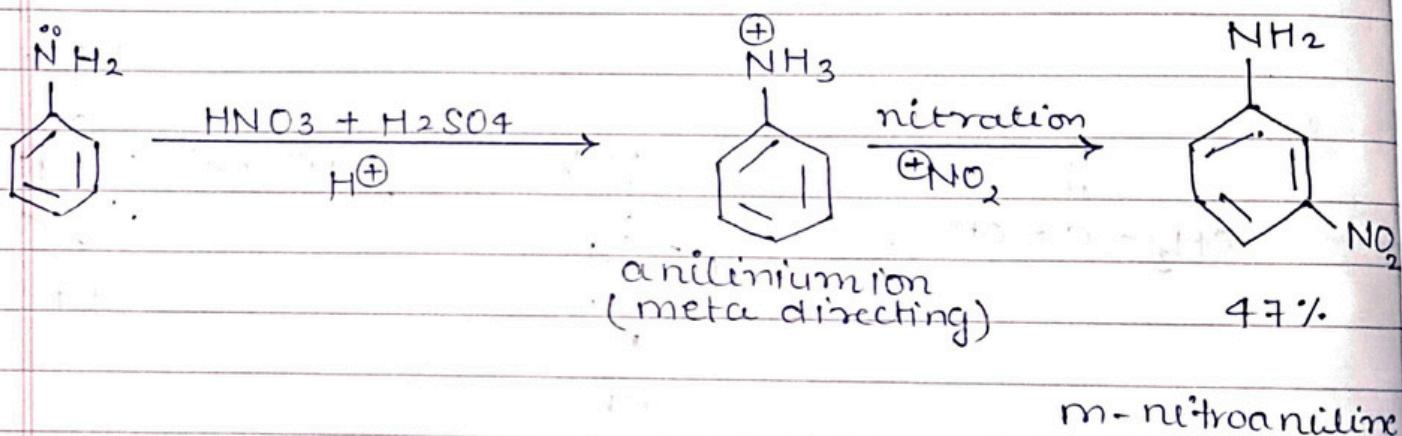
## ii) Nitration

Generation of electrophiles:

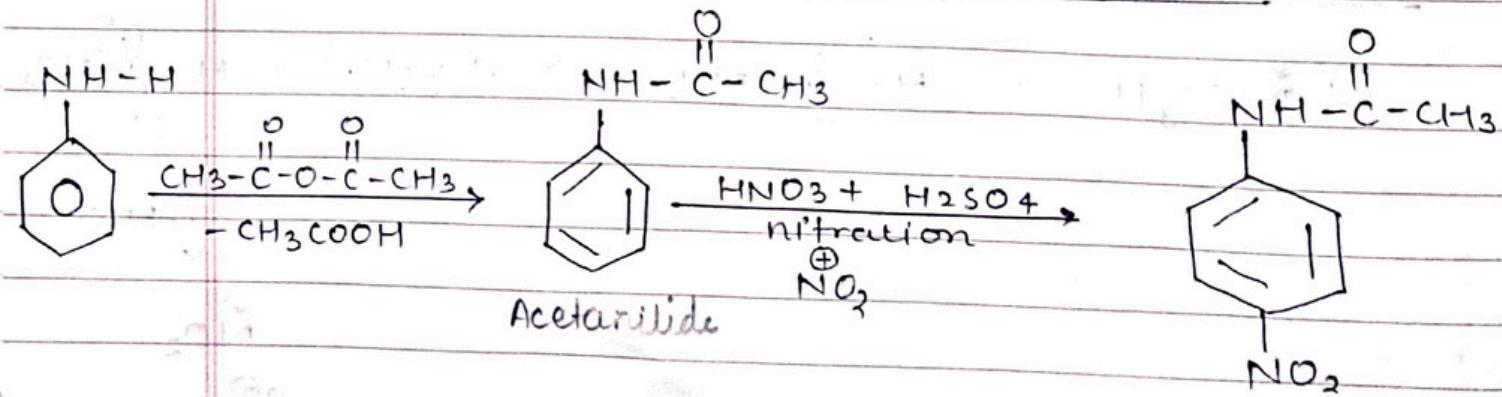


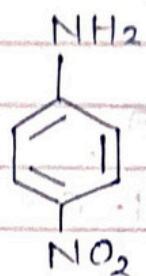


~~HNO<sub>3</sub>~~ and H<sub>2</sub>SO<sub>4</sub> are strong acids and they release H<sup>+</sup>. Now, aniline is protonated to form anilinium ion which is meta-directing. That is why, in this reaction, meta derivative is also formed.

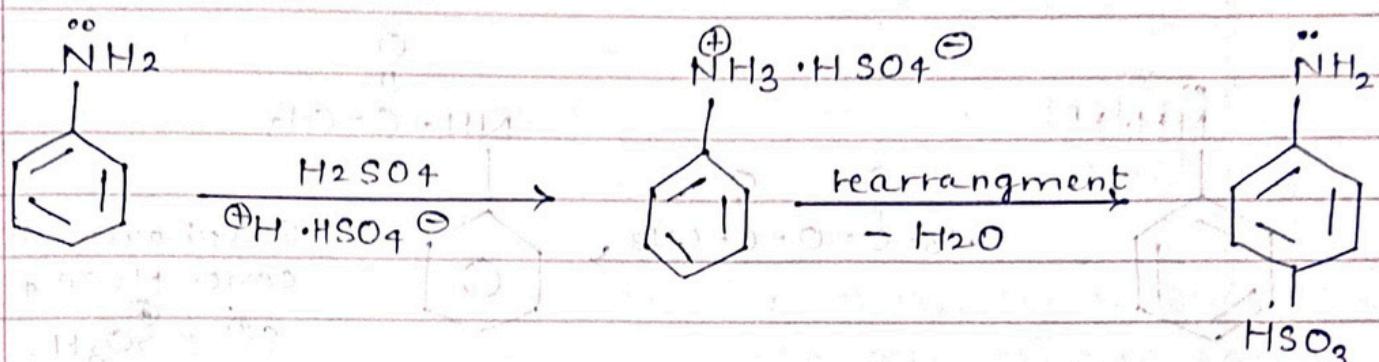


However, by protecting the NH<sub>2</sub> group by acetylation with acetic anhydride, nitration can be controlled and only p-nitro derivative can be obtained as a major product.

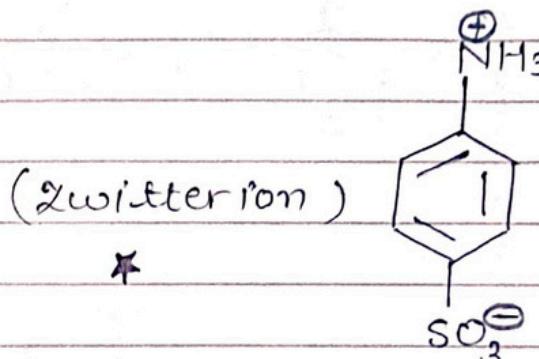


Puroncation $H^+ / OH^-$ 

P-nitroaniline

iii). Sulphonation :P-aminobenzene  
sulphonic acid

11

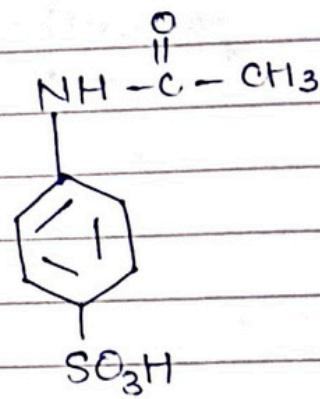
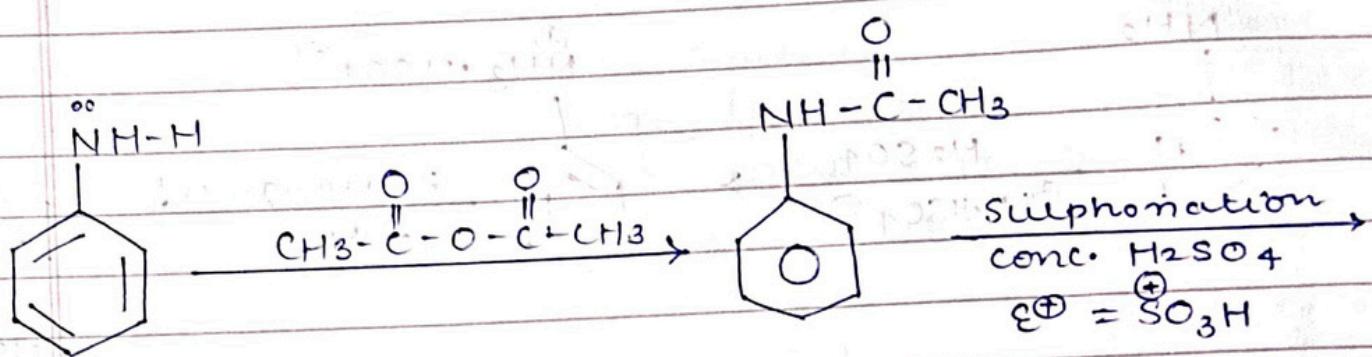
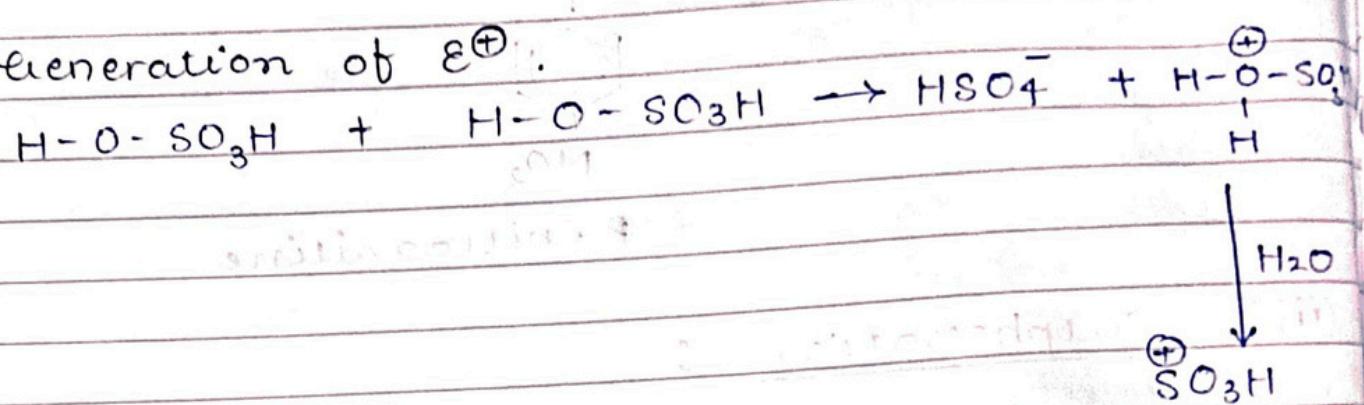


is o-&amp;p directing.

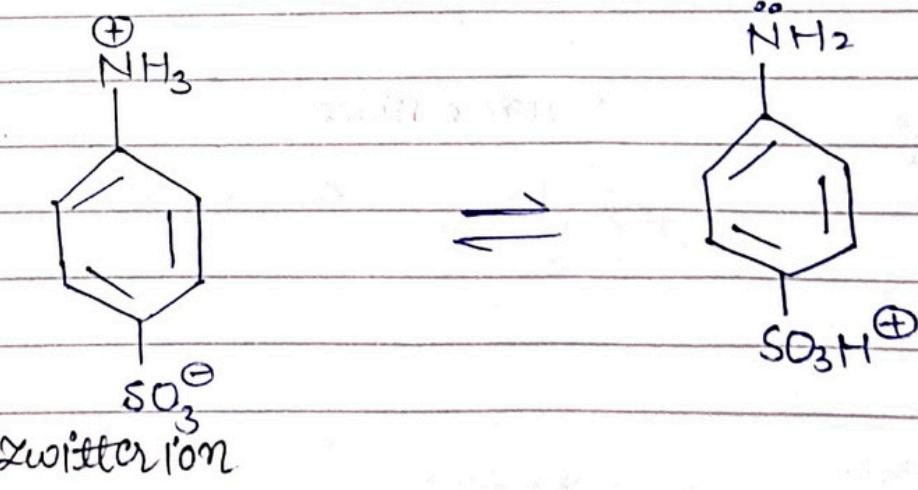
is m-directing.

Mechanism :-

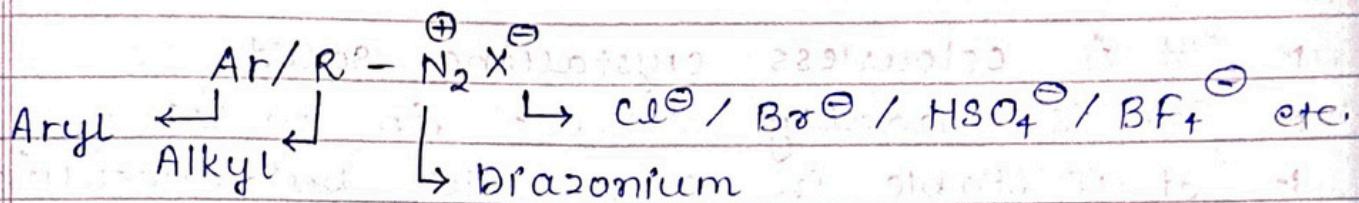
Generation of  $\delta^+$ .



$\text{H}^+ / \text{OH}^-$   
Protonation



## Diazonium Salt:

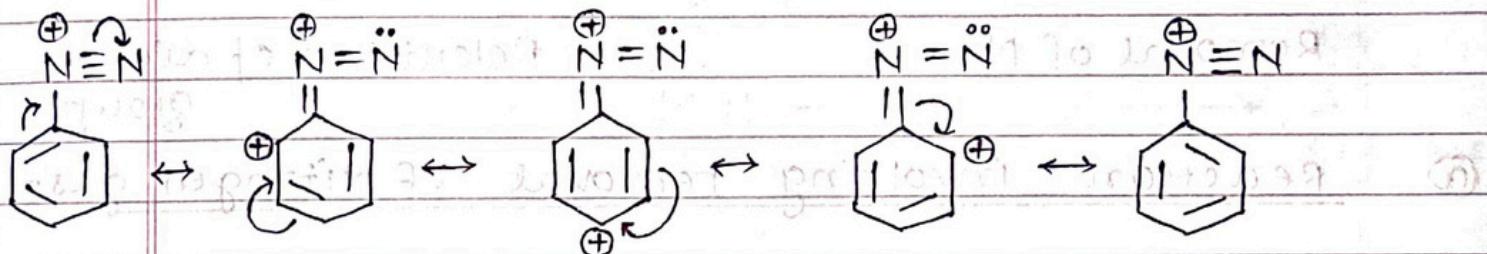


Diazonium salt have general formula  $\text{RN}_2^{\oplus}\text{X}^{\ominus}$  where R stands for an aryl group and  $\text{X}^{\ominus}$  may be  $\text{Cl}^{\ominus}$ ,  $\text{Br}^{\ominus}$ ,  $\text{HSO}_4^{\ominus}$ ,  $\text{BF}_4^{\ominus}$  etc.

e.g. Benzenediazonium chloride,  $\text{C}_6\text{H}_5\text{N}_2^{\oplus}\text{Cl}^{\ominus}$

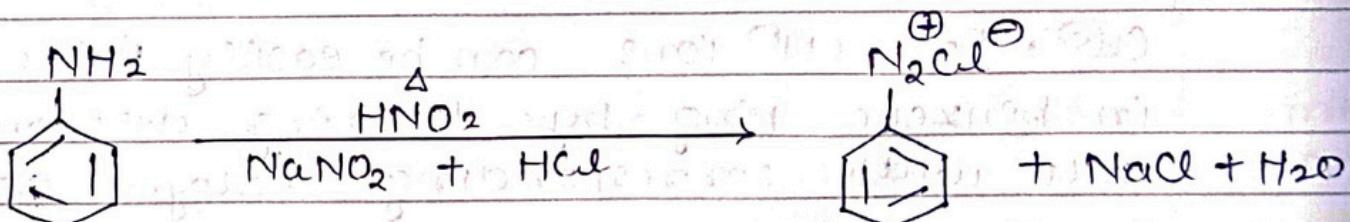
Benzenediazonium Hydrogensulphate,  $\text{C}_6\text{H}_5\text{N}_2^{\oplus}\text{HSO}_4^{\ominus}$

Alkyl diazonium salts are highly unstable but aryl diazonium salts are stable for a short time at low temperature due to resonance.



## Methods of Preparation :-

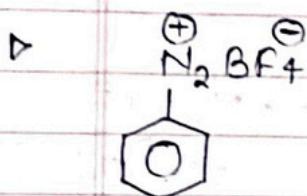
Benzenediazonium chloride is prepared by the reaction of aniline with  $(\text{HNO}_2)$  Nitrous acid at low temperature.



This reaction is known as Diazotisation.

## Physical properties :-

- It is colourless crystalline solid.
- It is readily soluble in water.
- It is stable in cold water but react with hot water.
- It decomposes easily in dry state, because  $N_2^{\ominus}$  is a strong leaving group.



Benzenediazonium fluoroborate is insoluble in  $H_2O$  and stable at 100m temperature.

## Chemical Properties :-



Removal of  $N_2$

Retention of diazo group

### ② Reaction involving removal of Nitrogen gas

Being a good living group, diazonium group is substituted by  $\text{Cl}^{\ominus}$ ,  $\text{Br}^{\ominus}$ ,  $\text{I}^{\ominus}$ ,  $\text{OH}^{\ominus}$ ,  $\text{CN}^{\ominus}$  which displace Nitrogen from the aromatic ring and nitrogen escapes as a gas.

### i) Sandmeyer Reaction :

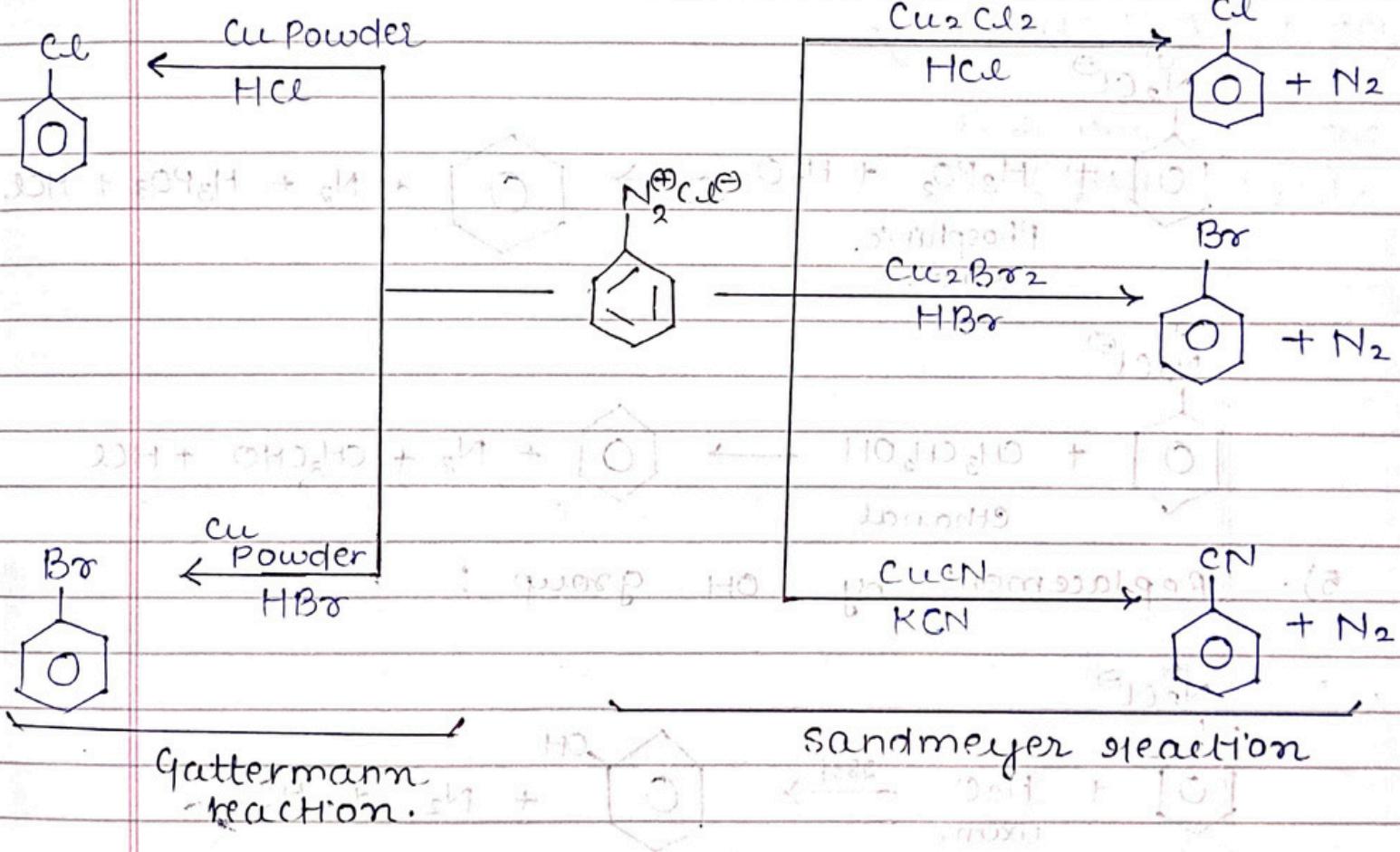
$\text{Cu}^{\ominus}$ ,  $\text{Ba}^{\ominus}$ ,  $\text{CN}^{\ominus}$  ions can be easily introduced in benzene ring by treating diazonium salt with corresponding halogen acid in presence

### i) Sandmeyer Reaction:

$\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{CN}^-$  ions can be easily introduced in benzene ring in the presence of Cu (I). This reaction is called \* Sandmeyer reaction.

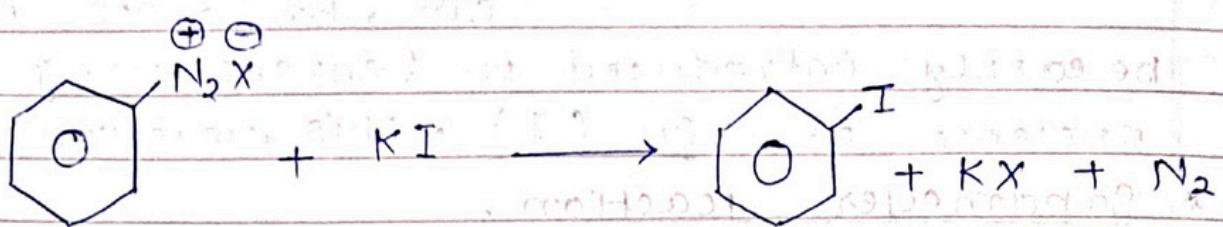
### ii) Gattermann Reaction:

$\text{Cl}^-$  and  $\text{Br}^-$  ions can be introduced in benzene ring by treating diazonium salt with corresponding halogen acid in the presence of copper powder. This reaction is called Gattermann reaction.

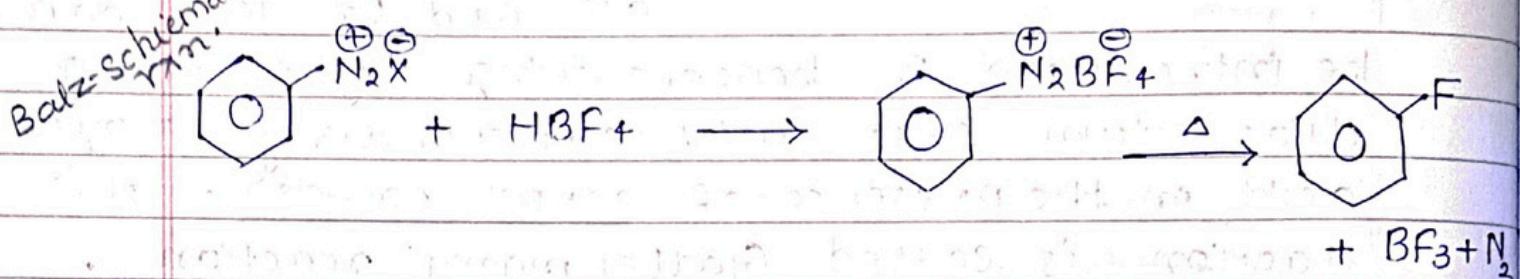


- Sandmeyer reactions have better yield than Gattermann reaction.

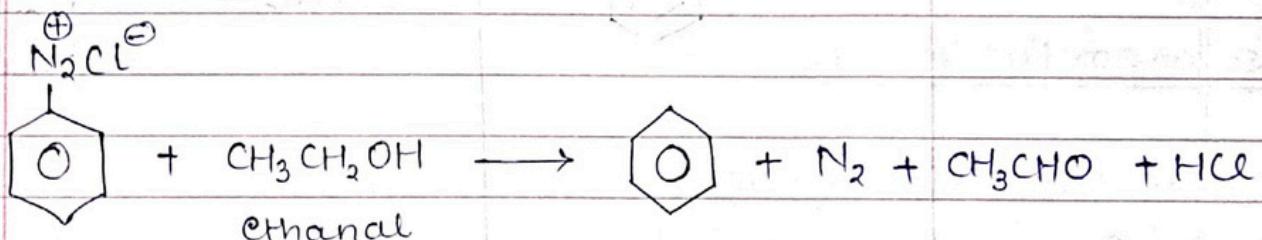
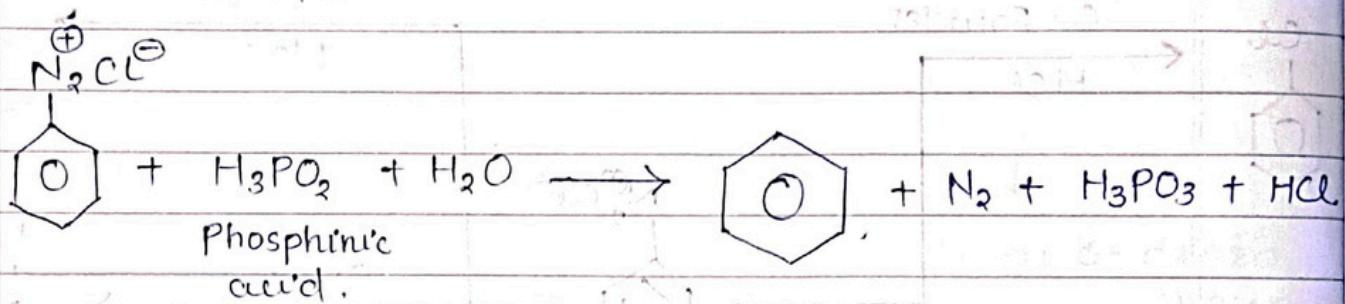
2). Replacement by Iodide Ion:



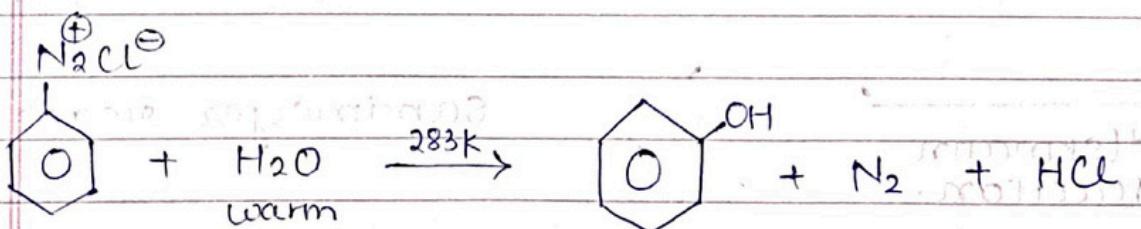
3) Replacement by Fluoride Ion:



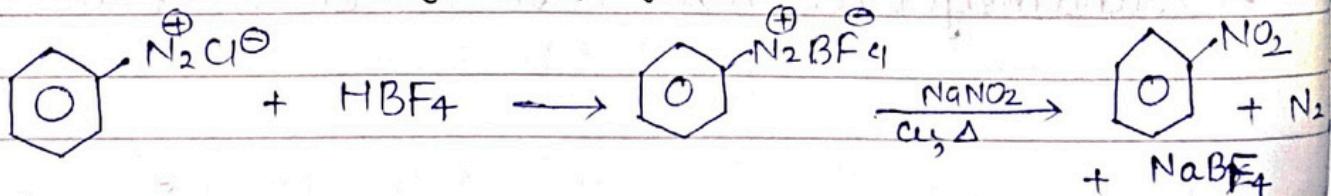
4). Replacement by H :



5). Replacement by -OH group :



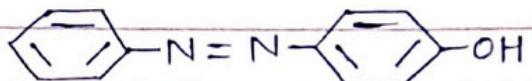
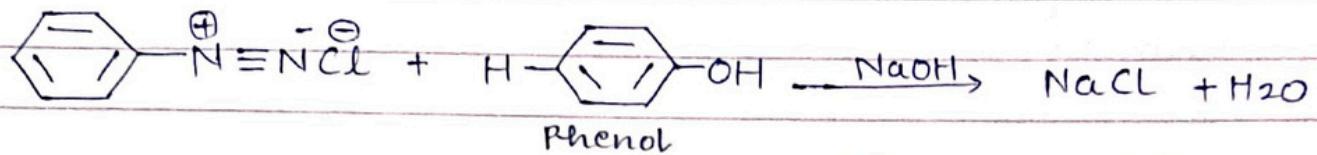
6). Replacement by  $-\text{NO}_2$  group :



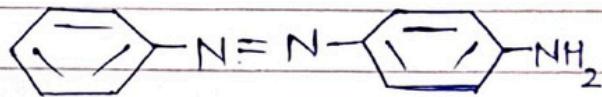
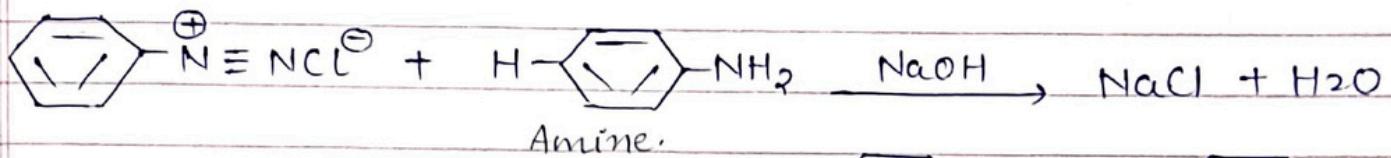
## Dye test for 1° aromatic amines

(b). Reaction involving of retention of Diazo-group:

\* Coupling Reaction:



P-Hydroxyazobenzene  
(orange dye)



P-Aminoazobenzene  
(yellow dye).