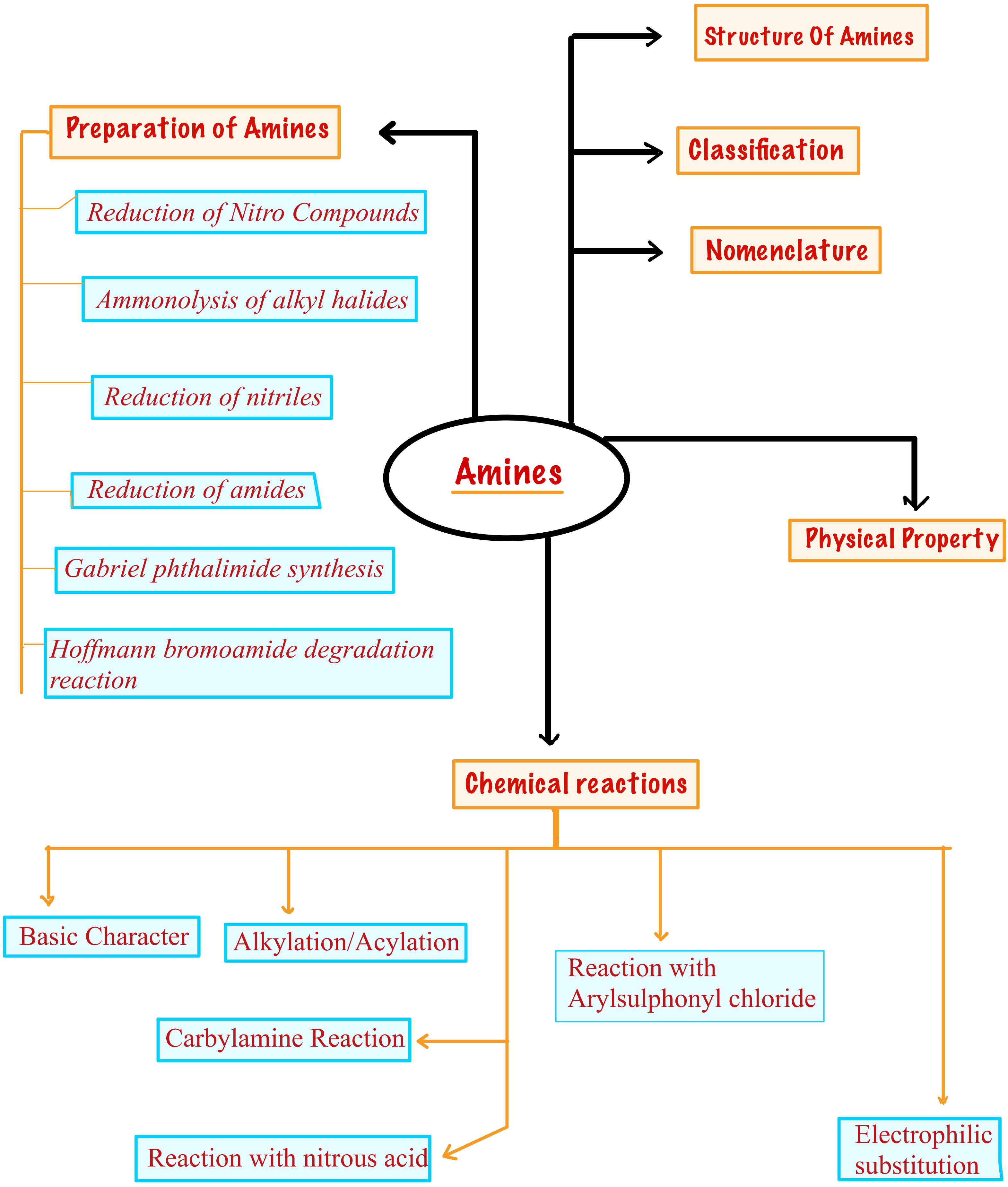
Flow chart



Amines

Structure Of Amines

Classification

Nomenclature

Preparation of Amines

- *Reduction of Nitro Compounds*
- *Ammonolysis of alkyl halides*
- *Reduction of nitriles*
- *Reduction of amides*
- *Gabriel phthalimide synthesis*
- *Hoffmann bromoamide degradation reaction*

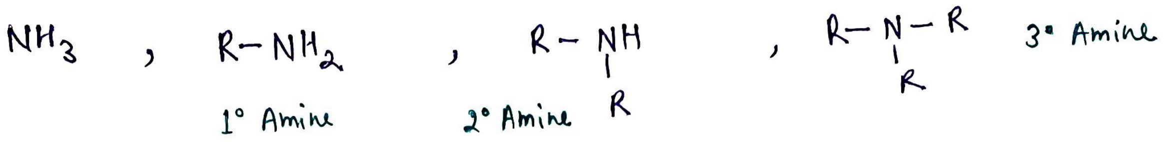
Physical Property

Chemical reactions

- Basic Character
- Alkylation/Acylation
- Carbylamine Reaction
- Reaction with nitrous acid
- Reaction with Arylsulphonyl chloride
- Electrophilic substitution

Amines ($-NH_2$ group)   Prefix: Amino   Suffix: Amine

→ Amines can be considered as derivatives of ammonia.



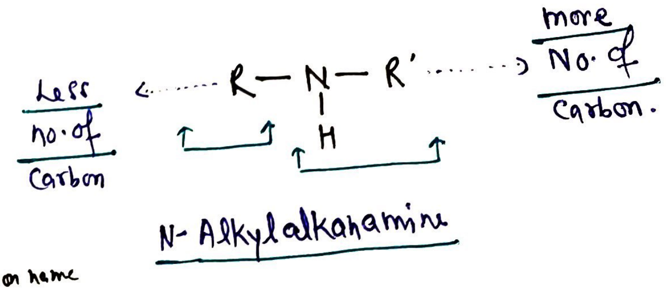
NH_3 , $R-NH_2$, $R-\underset{R}{\underset{|}{N}}H$, $R-\underset{R}{\underset{|}{N}}-R$ 3° Amine

1° Amine   2° Amine

IUPAC Name :— Alkane − e + amine = Alkanamine ($R-NH_2$)

Alkane + diamine → for two amino group.

→ Common Name :- Alkylamine ($R-NH_2$)



$R-\underset{H}{\underset{|}{N}}-R'$

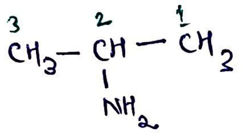
Example :- $CH_3-CH_2-NH_2$ [Ethanamine] → IUPAC

[Ethylamine] → Common name

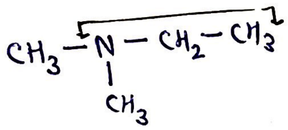
→ $\overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H_2-NH_2$: n-Propylamine [Propan-1-amine]

(Ethylmethylamine) → $CH_3-NH-CH_2-CH_3$

N-Methylethanamine

→ 

$\overset{3}{C}H_3-\underset{NH_2}{\underset{|}{\overset{2}{C}H}}-\overset{1}{C}H_3$: Isopropylamine [Propan-2-amine]

→ 

$CH_3-\underset{CH_3}{\underset{|}{N}}-CH_2-CH_3$: N, N-dimethylethanamine. [Delhi 2017] → {1M}

→  : N-ethyl N-methylethanamine [Delhi 2017] → (1M)

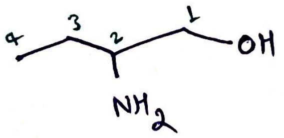
→  : Prop-2-en-1-amine

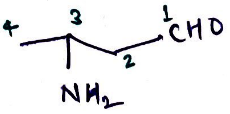
→ N-methylethanamine : $\overset{2}{C}H_3-\overset{1}{C}H_2-NH-CH_3$

→ [CBSE 2013] → $\boxed{2M}$

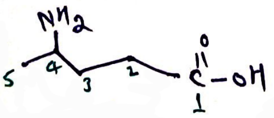
→ $NH_2-\overset{1}{C}H_2-\overset{2}{C}H_2-\overset{3}{C}H=\overset{4}{C}H_2$: But-3-en-1-amine : [Delhi 2010] → (1M)

→ Senior functional group makes as suffix and junior functional groups are treated as substituent. For naming of junior functional group we use Prefix of that group.

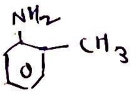
 : 2-Aminobutan-1-ol

 : (CBSE 2014) ↳ (1M)

→ 3-Aminobutanal

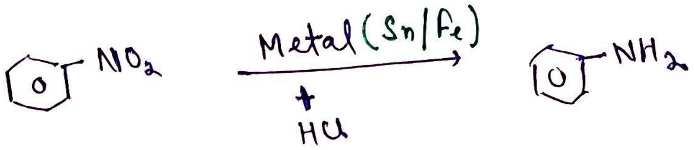
 : 4-Aminopentan-1-oic acid

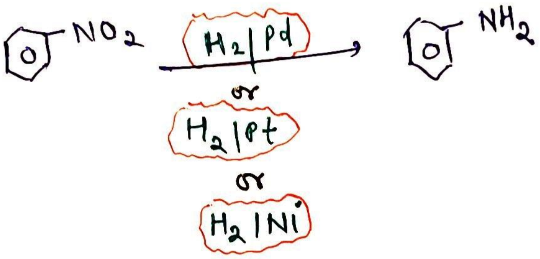
→  : Aniline ;  : 4-Bromoaniline

→  : 2-Aminotoluene [ortho-Toluidine] ;  : N,N-Dimethyl benzenamine

Preparation of amines

① **Reduction of nitro compounds :-**

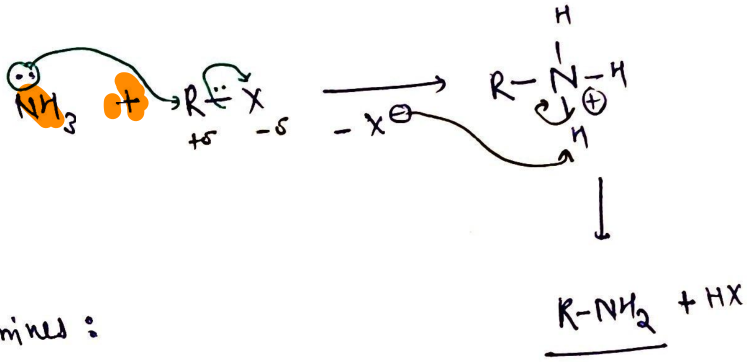


→ 

② **Ammonolysis of alkyl halides :-**

↓

Breaking of bond by ammonia.

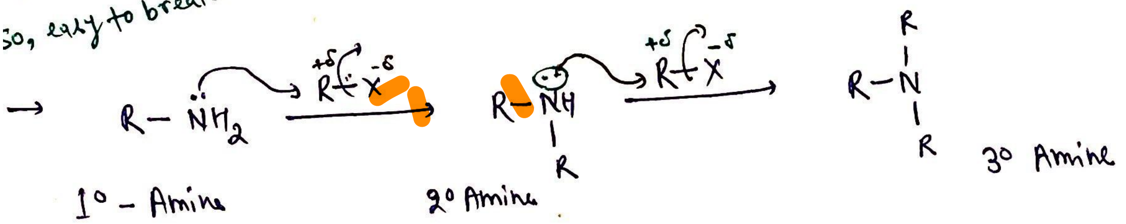


→ Order of reactivity of alkyl halide with amines :

$R-I > R-Br > R-Cl > R-F$

Weak bond so, easy to break.

Strong bond, so tough to break.

→ 

③ **Reduction of nitriles :-**

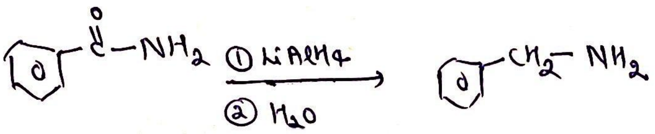
$$R-C\equiv N \xrightarrow[Na(Hg)\,|\,C_2H_5OH]{LiAlH_4\,|\,H_2|Ni} R-CH_2-NH_2$$

④ **Reduction of amides -:**

$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[ii)\,H_2O]{i)\,LiAlH_4} R-CH_2-NH_2$$

Amide Amine

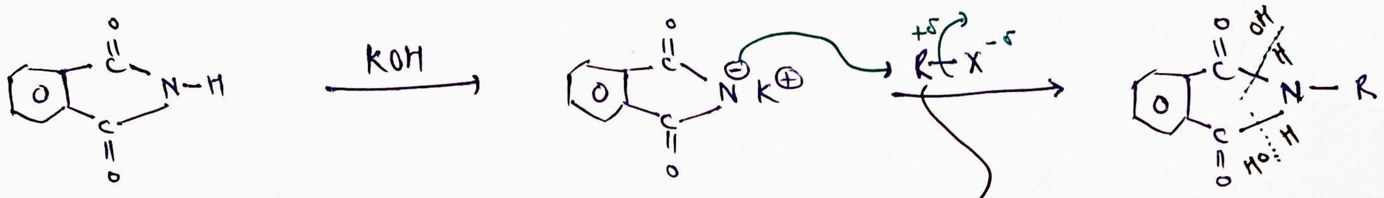
[CBSE 2012/2010] {1M}

→ 

→ $CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[②\,H_2O]{①\,LiAlH_4} CH_3-CH_2-NH_2$ [Delhi 2010 | CBSE 2010] (1M)

⑤ Gabriel Phthalimide Synthesis –: (for preparation of 1° Amines)

[Delhi 2010]

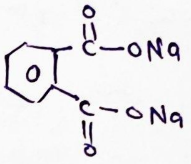


Phthalimide

only aliphatic alkyl groups

because in aromatic (as phenyl) group has double bond character in bond with halogens.

↓ Basic Hydrolysis [NaOH(aq.)]



+ $R-NH_2$

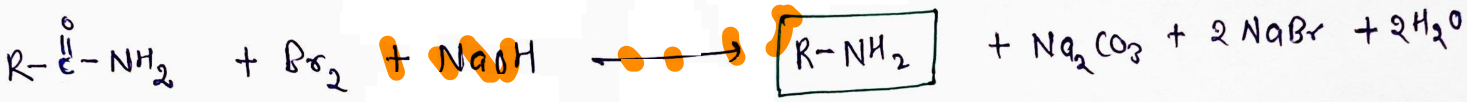
1° Amine

→ (CBSE 2019) → 1M

(Delhi 2012) 2012 CBSE

⑥ Hoffmann bromamide degradation reaction :–

Bromine (Br_2) $R-\overset{O}{\overset{\|}{C}}-NH_2$ Reduction of no. of carbon

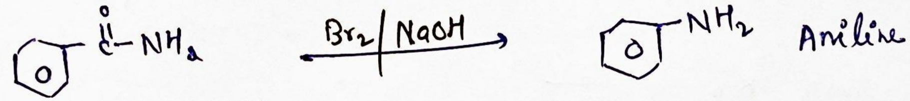


$$R-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + NaOH \longrightarrow \boxed{R-NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

Amide Amine

$$\rightarrow CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{HBDR} CH_3-CH_2-CH_2-NH_2$$

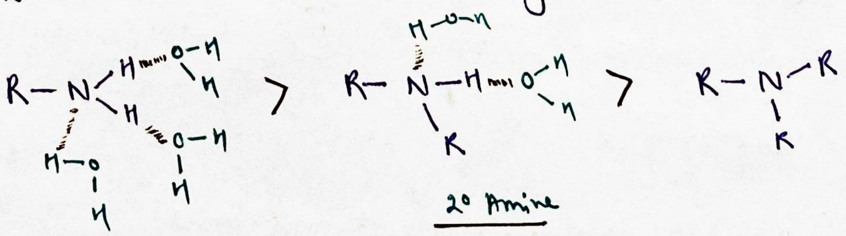
Butanamide Propanamine



→ Benzamide Aniline

Physical properties :–

→ Lower amines are soluble in water because they can form hydrogen bonding with water molecules.



1° Amine 2° Amine

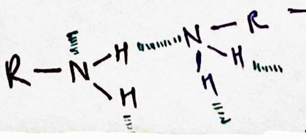
: Extent of H-bonding

: Solubility

→ Aromatic amines (such as aniline) are insoluble in water due to large hydrocarbon part (non-interactive with water). [CBSE 2011] 1M

Boiling Point –: Order of B.P. : 1° Amine > 2° Amine > 3° Amine

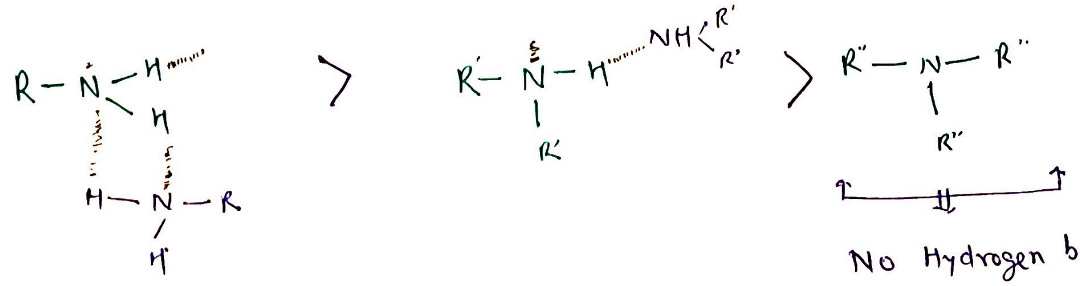
→ This is because of order of extent of H-bonding.



→ Association of molecule

→ This intermolecular association is more in primary amines than in 2° amines as there are two hydrogen atoms are available for hydrogen bond formation in it.

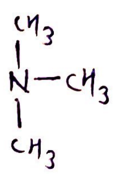
Extent of H-bonding in it :



No Hydrogen bond between itself.

→ Because 3° Amines have no hydrogen bond between itself. So, primary amines have higher B.P. [CBSE 2011] (1M)

For example → B.P. : Propanamine $CH_3-CH_2-CH_2-NH_2$ >



$N(CH_3)_3$ N, N-Dimeth methanamine

(1M) ← [CBSE 2019]

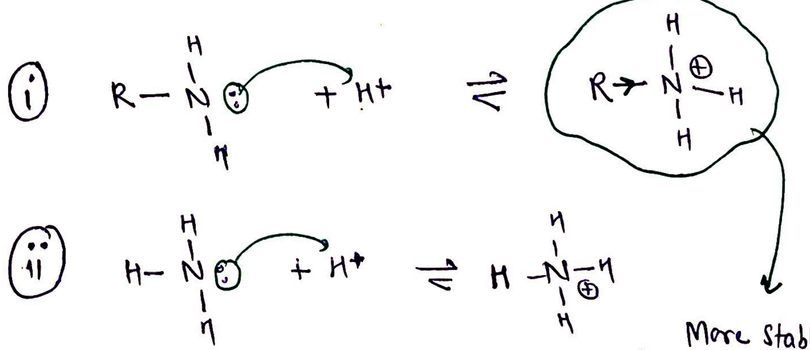
Basicity of amines

→ $R-\ddot{N}H_2 + \overset{+\delta}{H}-\overset{-\delta}{X} \rightleftharpoons R-\overset{\oplus}{N}H_3X^{\ominus}$ (Salt) : Basic Nature of amine is due to its lone pai which attracts H^+ tow itself.

→ Basicity is represented by K_b.

→ $pK_b = -\log K_b$ then $K_b \propto \frac{1}{pK_b}$

→ **Alkanamines Vs. Ammonia** :-

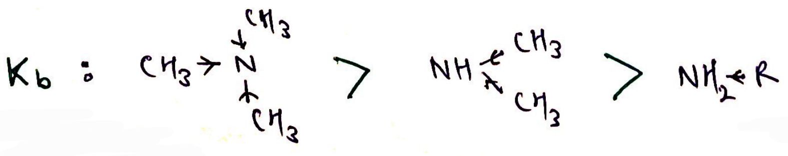


More Stabl than NH_4^+ due to dispersal of ⊕ve charge by +I effect of alkyl group.

Due to stability of $R-\overset{\oplus}{N}H_3$ with respect to NH_4^+, equilibrium constant for reaction ⓘ is more than reaction (ii).

→ Means that. Aliphatic amines are stronger bases than ammonia. $CH_3-\ddot{N}H_2 > \ddot{N}H_3$: K_b

→ order of basicity in gas phase : Explain it by +I effect, as there is no solvent.



K_b : $(CH_3)_3N > (CH_3)_2NH > NH_2R$

→ K_b :

: [Delhi 2019] → (1M)

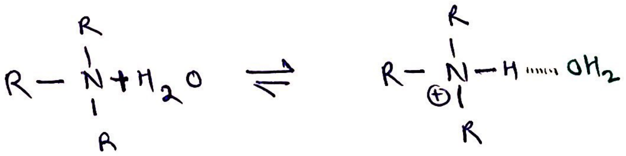
K_b : 3° > 2° > 1° > Ammonia : Gas phase.

→ Basicity of amines in aq. phase :- Above order is not true in aqueous medium. The substituted ammonium cations get stabilised not only by electron releasing effect of alkyl group (+I) but also by solvation with water molecules.

→ The ion having more hydrogen bonds with water molecule, are more stable. So more will be K_b value for that amine.

: 3 H-bonds

: 2 H-bonds



: 1-H bond

→ More solvation ⇒ More stable ion

According to solvation effect K_b : 1° > 2° > 3°

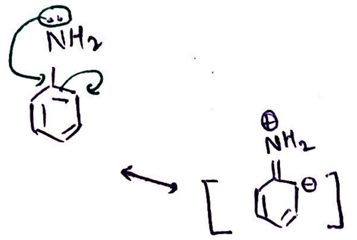
\# K_b : $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$: 2 3 1 NH_3

K_b : $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$: 2 1 3 NH_3

Basic strength in aq. sol^n

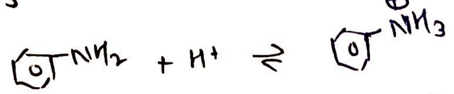
[Delhi 2013 / 2012] (1M)

→ Arylamines Vs. Ammonia :- K_b : $\ddot{N}H_3$ >

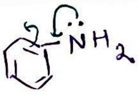


→ Lone pair of nitrogen on ammonia is available for protonation. But in aniline lone pair is not easily available due to resonance with benzene ring.

$NH_3 + H^+ \rightleftharpoons NH_4^+$



→ Basicity Order (K_b) : $CH_3 \rightarrow \ddot{N}H_2$ >

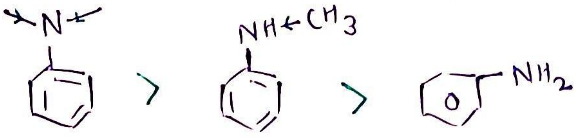


[CBSE 2011] (1M)

Localised lone pair

Delocalised lp, so not available for protonation.

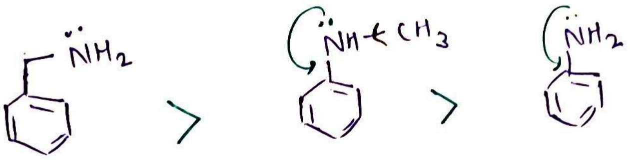
→ K_b :



+I effect of $-CH_3$ group.

[CBSE 2014] (1M)

→ K_b :

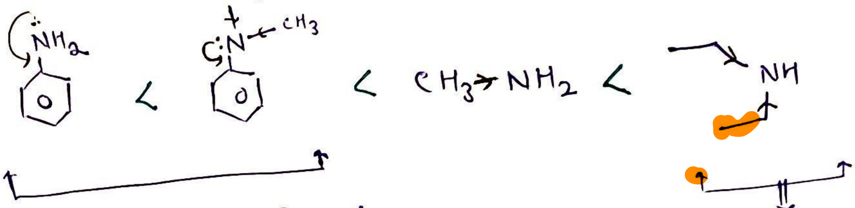


: [CBSE 2014] (1M)

Localised lone pair, free for protonation.

Delocalised Lone pair, So lone pair is not available for protonation.

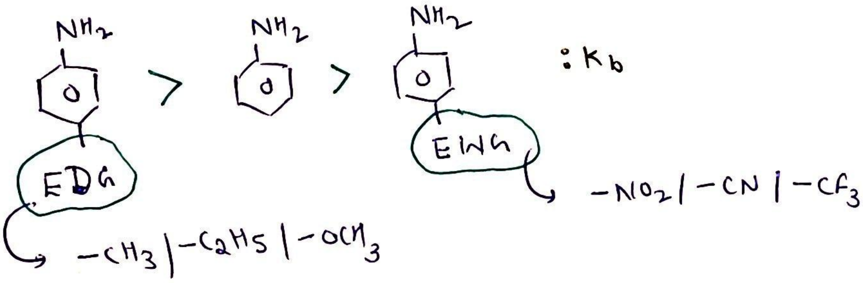
→ K_b :



lone pair is in resonance so not available for protonation.

+I effect of alkyl group.

→



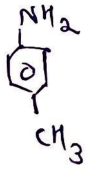
: K_b

$-CH_3 | -C_2H_5 | -OCH_3$

$-NO_2 | -CN | -CF_3$

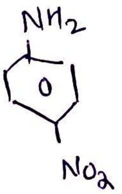
→ Electron donating group increas
electron density at nitrogen of anilin
So, it can easily donate lone pair
to H^+.

→



> p-Toluidine

Aniline >

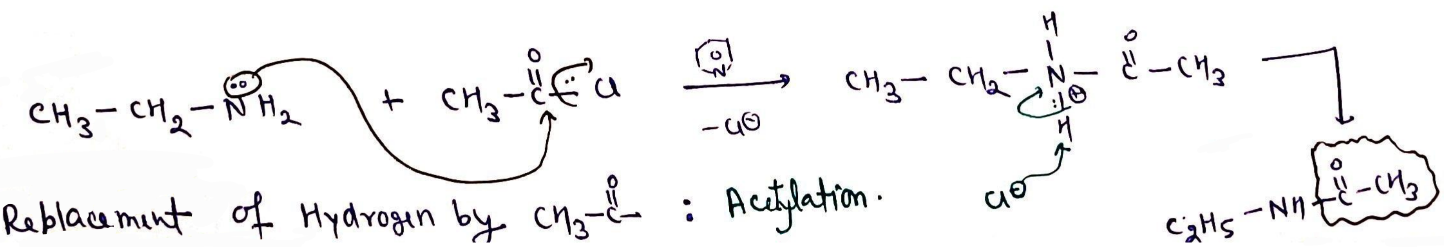


Para-nitroaniline : [CBSE 2015C] (1M)

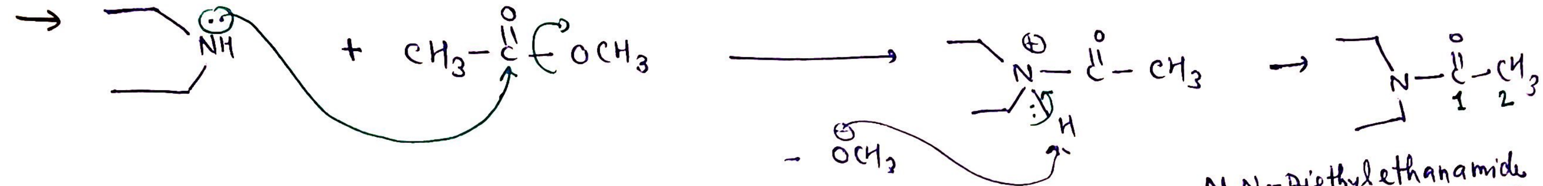
[Delhi 2010] (1M)

Acylation of amines :— (Addition of $-\overset{O}{\overset{||}{C}}-R$ group.)

→ 1° | 2° Amines $\xrightarrow[\text{or } CH_3-\overset{O}{\overset{||}{C}}-OCOCH_3]{CH_3-\overset{O}{\overset{||}{C}}-Cl \;|\; CH_3-\overset{O}{\overset{||}{C}}-OR}$ Acylation of product of 1°/2° Amine

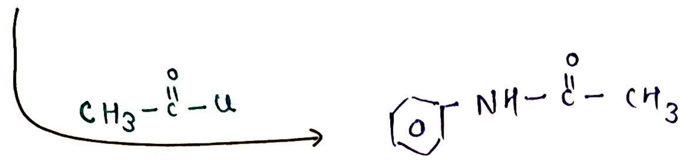


→ Replacement of Hydrogen by $CH_3-\overset{O}{\overset{||}{C}}-$: Acetylation.



N,N-Diethylethanamide

N - Phenylethanamide / Acetanilide



: [CBSE 2013] → 1M

Carbylamine Reaction :- [Test for 1° Amines : Presence of 2 Hydrogen is necessary]

[CBSE 2012 Delhi 2012] → 1M

→ 2° / 3° Amines do not give this reaction.

→ $R-NH_2 + \underline{CHCl_3 + 3KOH} \xrightarrow{\Delta} \boxed{R-NC} + 3KCl + 3H_2O$

Alkyl isocyanide (foul smelling)

1M ← [CBSE 2013]

→ This test is also called Isocyanide test.

$CH_3-CH_2-NH_2 \xrightarrow[KOH]{CHCl_3} CH_3-CH_2-NC$

→ By using this reaction (test) we can distinguish (1° and 2° amines) and (1° and 3° amines.).

→ CH_3-NH_2 , $CH_3-NH-CH_3 \xrightarrow[KOH]{CHCl_3}$ No reaction

(1° Amine) (2° Amine)

$\xrightarrow[KOH]{CHCl_3}$ Foul smelling (CH_3-NC)

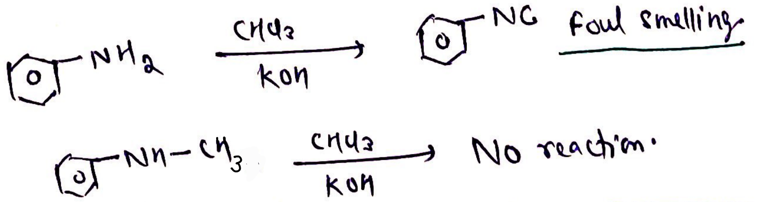
1M ← [CBSE 2019]

→ Similarly Ethylamine (⌒NH$_2$) and Diethylamine (⌒NH⌒) can be distinguished by carbylamine test. 1° Amine (⌒NH$_2$) gives foul smelling with $CHCl_3$ and KOH.

[Delhi 2013C] → 1M

→ Aniline & N - methylaniline :-

[CBSE - 2010] 1M

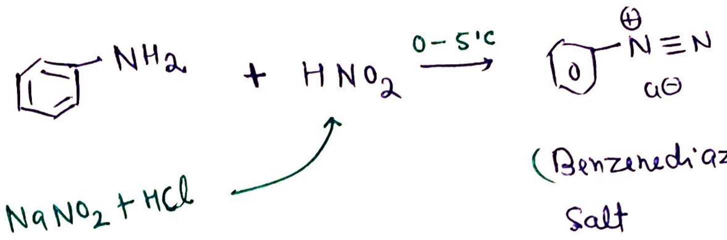


→ Reaction with HNO_2 [Nitrous Acid] –:

① Primary aliphatic amines :- $R-NH_2 + HNO_2 \longrightarrow R-\overset{\oplus}{N}\equiv N\ Cl^- \xrightarrow{H_2O} R-OH + N_2\uparrow + HCl$

→ Evolution of nitrogen.

② Aromatic Amines –:

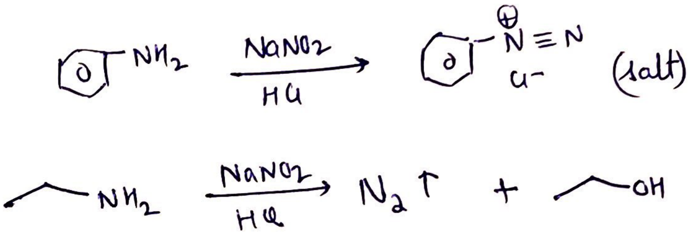


(Benzenediazonium chloride)
Salt

→ Aromatic and aliphatic amines can be distinguished by above reaction.

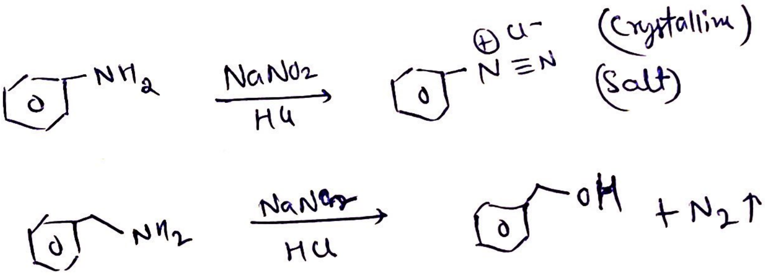
For example –: Aniline and Ethylamine

[CBSE 2014C | 2019
Delhi 2013C] → 1M



Aniline and Benzylamine

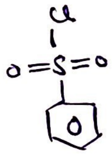
(CBSE 2014C) → 1M



(1° Amine) Benzylamine.

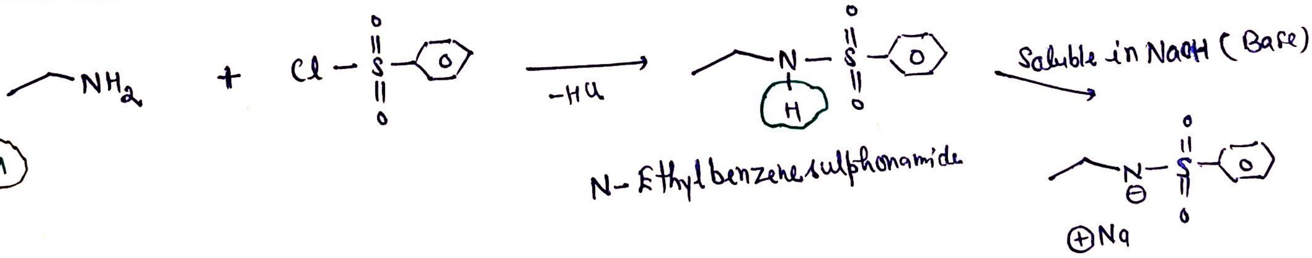
→ Reaction with Hinsberg Reagent –:

Hinsberg Reagent –:



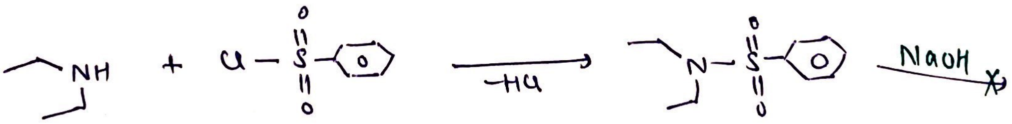
Benzenesulphonyl Chloride.

→ 1° Amine



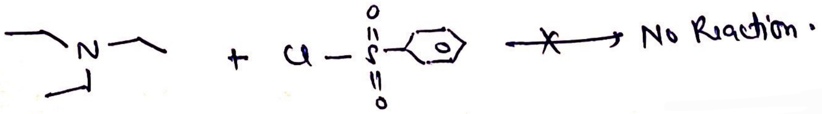
[CBSE 2013] 1M

→ 2° Amine



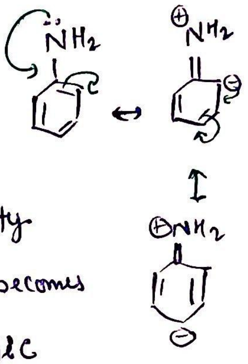
Not soluble in alkali because there is no acidic hydrogen.

→ 3° Amine



→ This reagent can be used to distinguish 1°/2°/3° Amines.

Electrophilic Substitution Reaction :-



→ $-NH_2$ group is ortho-para directing and powerful activating group.

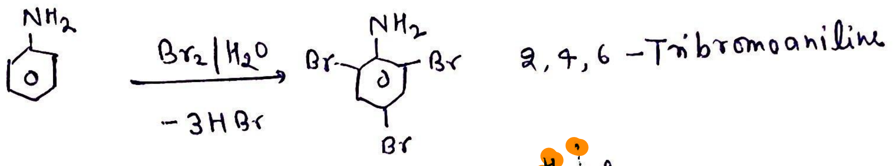
In resonating structure, ⊖ve charge is present at ortho and para position.

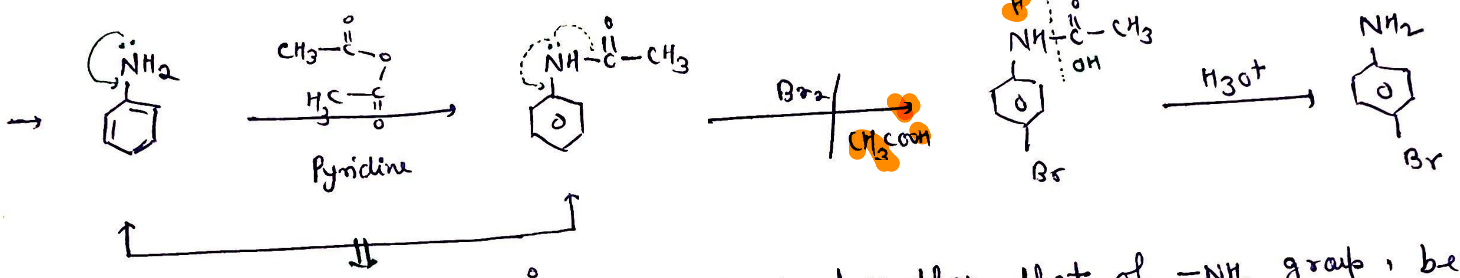
It donates electron density to benzene ring & ring becomes more active for electrophilic reaction.

→ That's why electrophilic substitution takes place more readily in aromatic amines than benzene. [Delhi 2010C] (1M)

[2013] (1M)

① **Bromination :-**



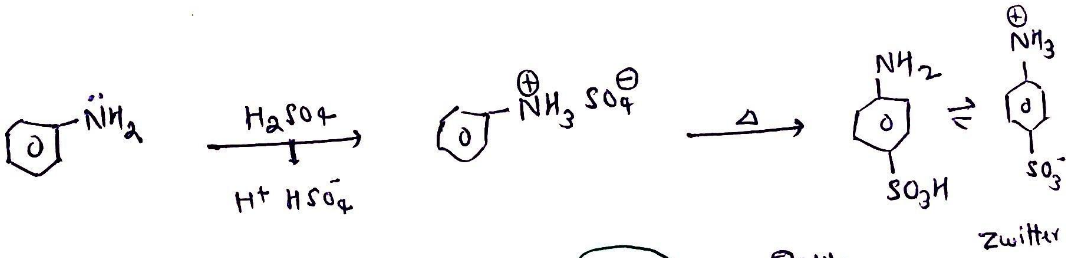


→ Activating effect of $-NH-\overset{O}{\overset{||}{C}}-CH_3$ group is less than that of $-NH_2$ group, because

in

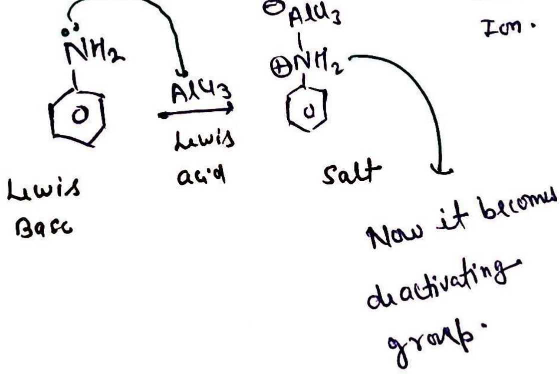
lone pair of nitrogen is shared also with $-\overset{O}{\overset{||}{C}}-$ group. So it can not activate benzene ring as much as $-NH_2$ group.

(ii) **Sulphonation :-**



→ Aniline does not undergo Friedel Crafts Reaction due to salt formation with $AlCl_3$. Hence acts as a strong deactivating group for further reaction.

[Delhi 2014C] → (1M)



Complete the following reaction ?

ⓐ $CH_3-\overset{+\delta}{CH_2}-\overset{-\delta}{Cl} \xrightarrow{NaCN} CH_3-CH_2-C\equiv N \xrightarrow{Ni/H_2} CH_3-CH_2-CH_2-NH_2$

$^{\ominus}:C\equiv N$

(1M) [All india 2010]

[b] $CH_3-\overset{O}{\overset{\parallel}{C}}-OH \xrightarrow{NH_3/\Delta} \underset{Ⓐ}{CH_3-\overset{O}{\overset{\parallel}{C}}-NH_2} \xrightarrow[KOH]{Br_2} \underset{Ⓑ}{CH_3-NH_2} \xrightarrow[KOH]{CHCl_3} \underset{Ⓒ}{CH_3-NC}$

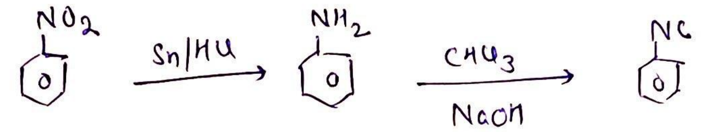
[CBSE 2017] (1.5 M)

[c] $CH_3-Cl \xrightarrow{KCN} CH_3-CN \xrightarrow{LiAlH_4} CH_3-CH_2-NH_2$

$CH_3-CH_2-NH_2 \xrightarrow{CHCl_3/KOH} CH_3-CH_2-NC$

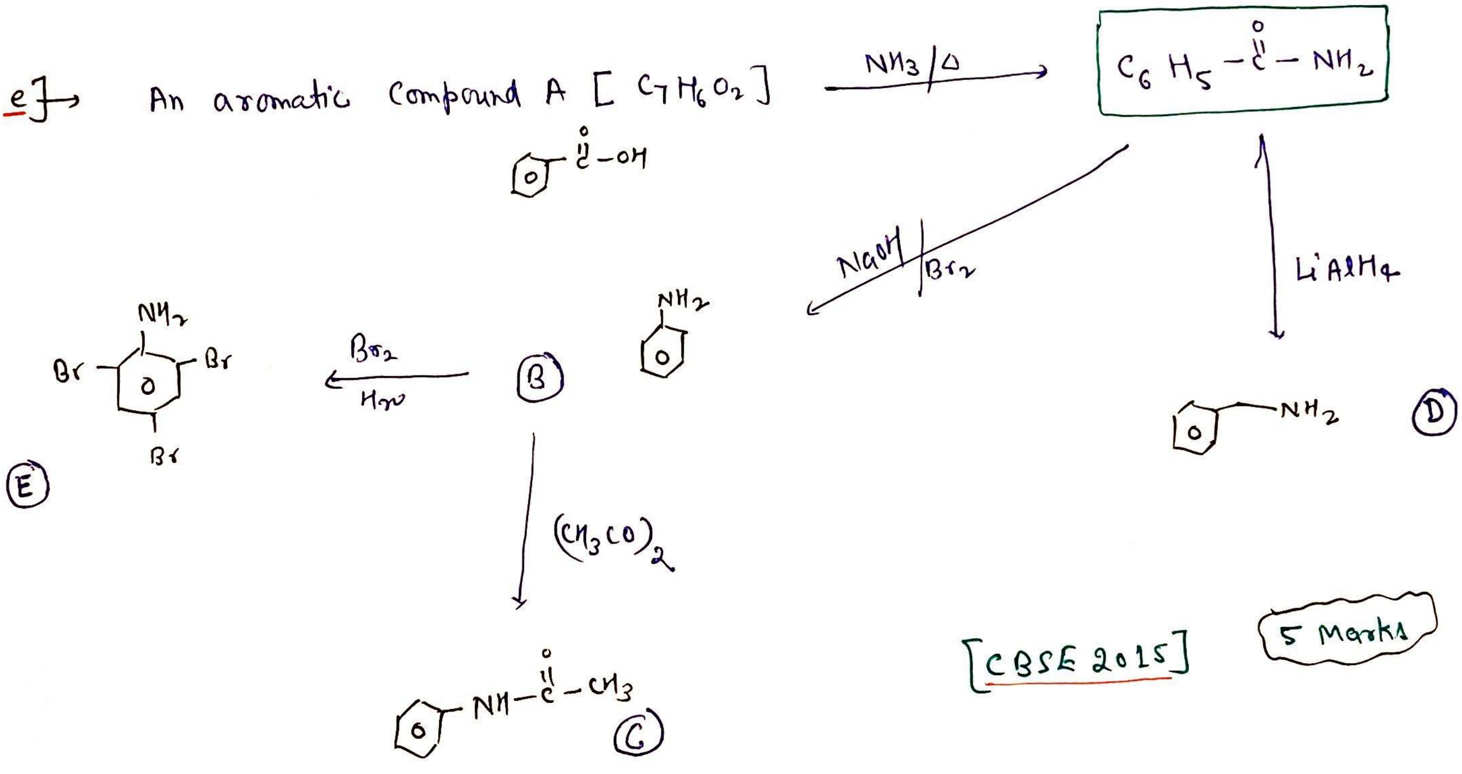
[Delhi 2016] (1.5 M)

d]



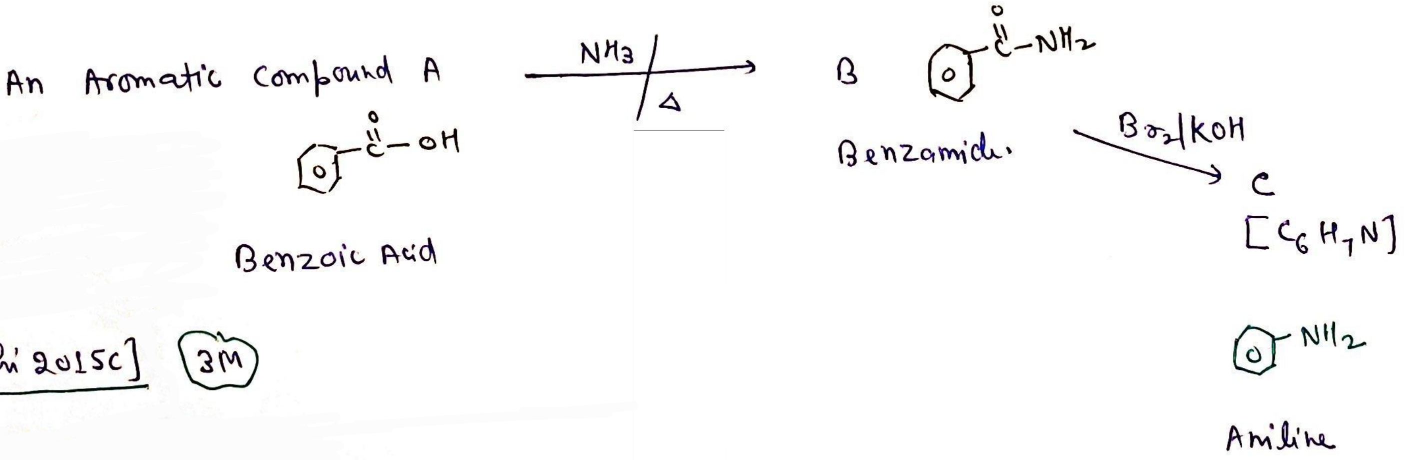
— (1M) [CBSE 2016C]

e]



[CBSE 2015] (5 Marks)

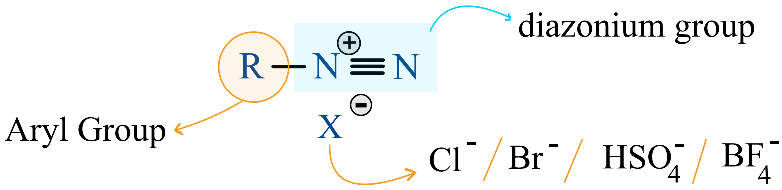
f.]

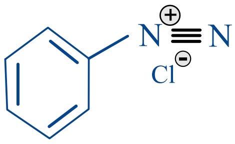


[Delhi 2015C] (3M)

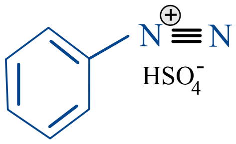
Diazonium Salts

General formula :





(Benzenediazonium Chloride)



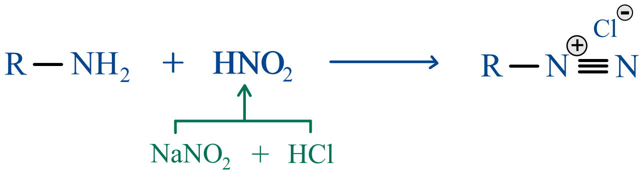
(Benzenediazonium hydrogensulphate)

Methods of Preparation :

Diazotisation :

The conversion of primary aromatic amines into diazonium salts is known as diazotisation.

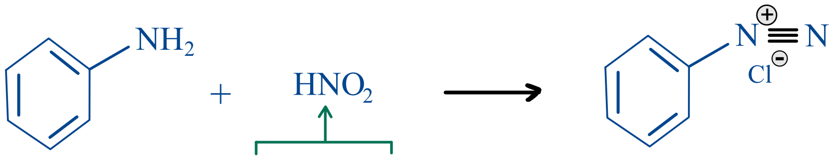
1) Primary aliphatic amines :-



$$R-NH_2 + \underset{NaNO_2\ +\ HCl}{\underset{\uparrow}{\mathbf{HNO_2}}} \longrightarrow R-\overset{\oplus}{N}\equiv N\ Cl^{\ominus}$$

Primary aliphatic amines form highly unstable alkyldiazonium salts.

2) Aromatic Amines :-

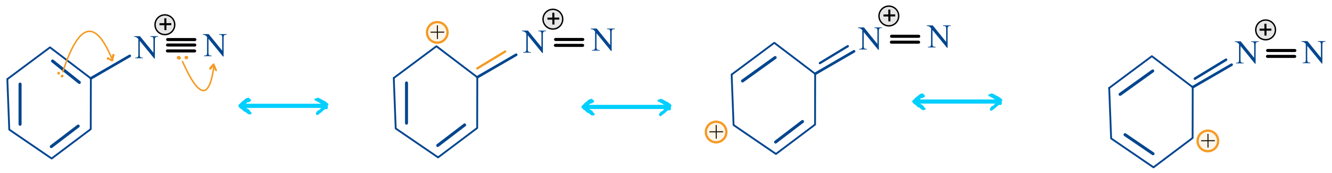


Aromatic Amines
(Aniline)

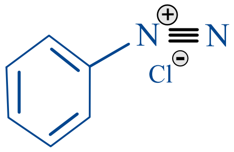
(Benzenediazonium Chloride)
Salt

Primary aromatic amines form arenediazonium salts which are stable for a short time in solution at low temperatures (0-5 ℃).

Reason for stability of arenediazonium : Resonance phenomenon

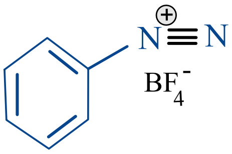


Physical Properties :



(Benzenediazonium Chloride)

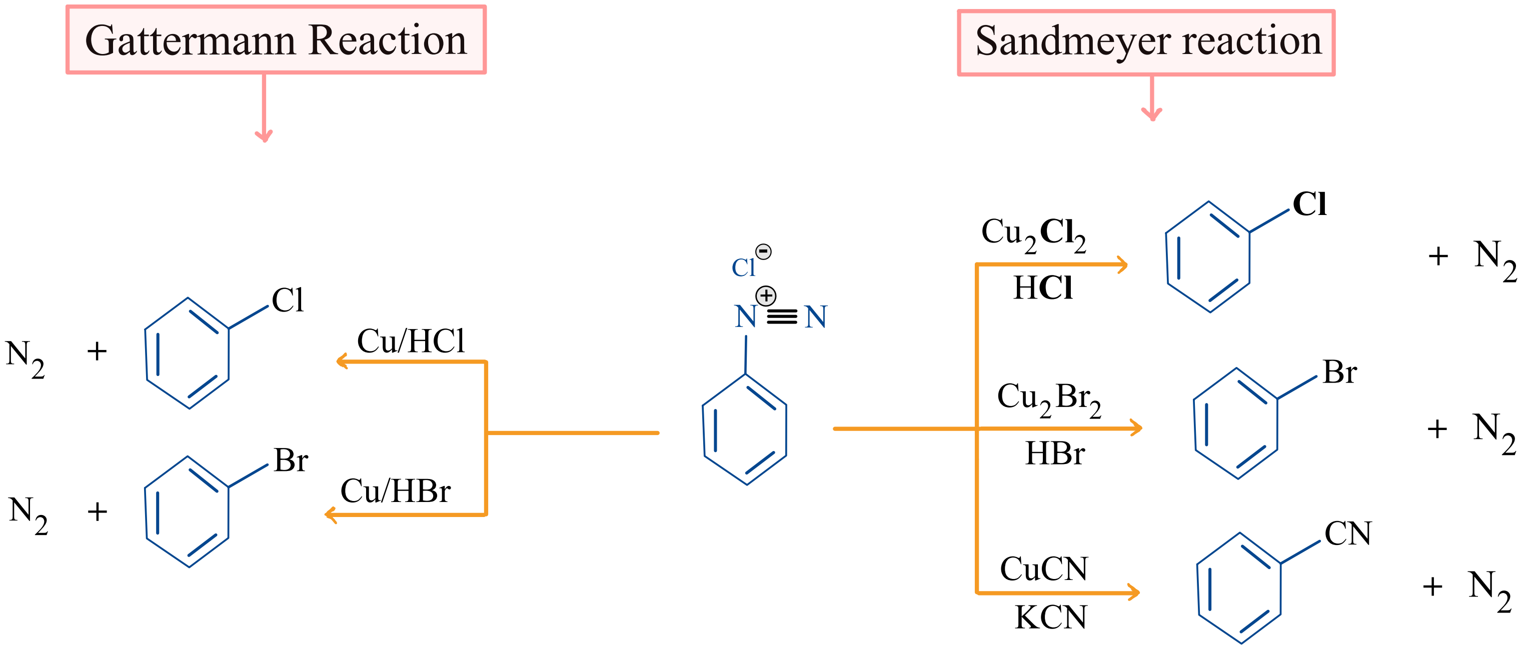
- Colourless crystalline solid
- It is readily soluble in water and is stable in cold but reacts with water when warmed. It decomposes easily in the dry state.



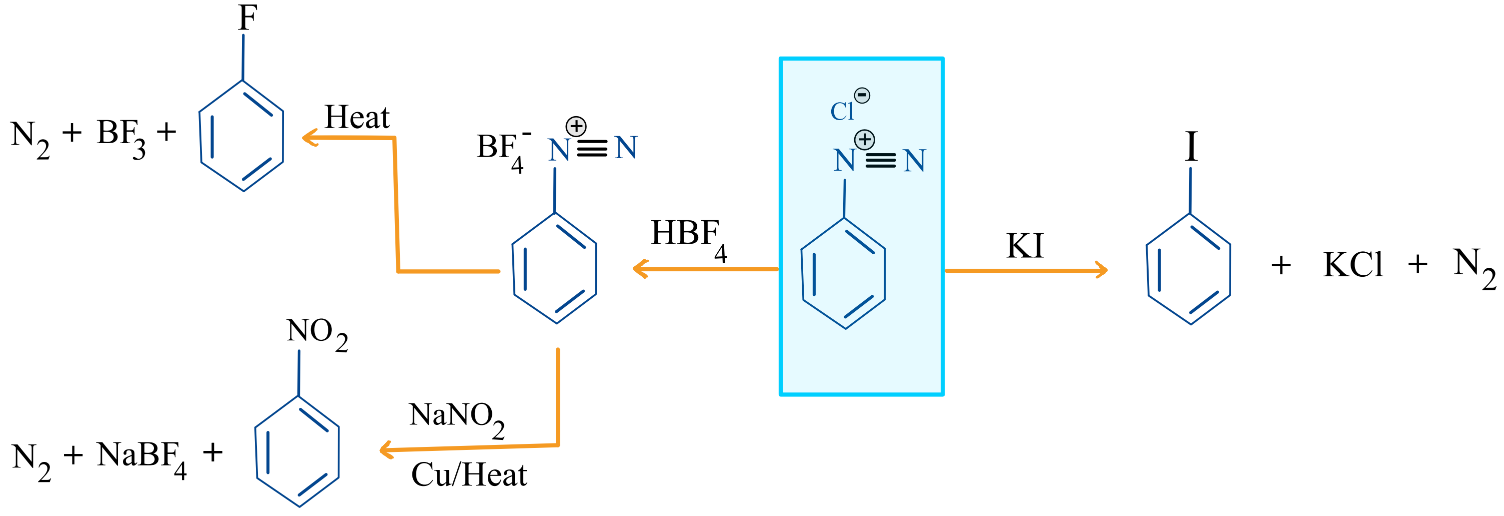
Benzenediazonium fluoroborate is water insoluble and stable at room temperature.

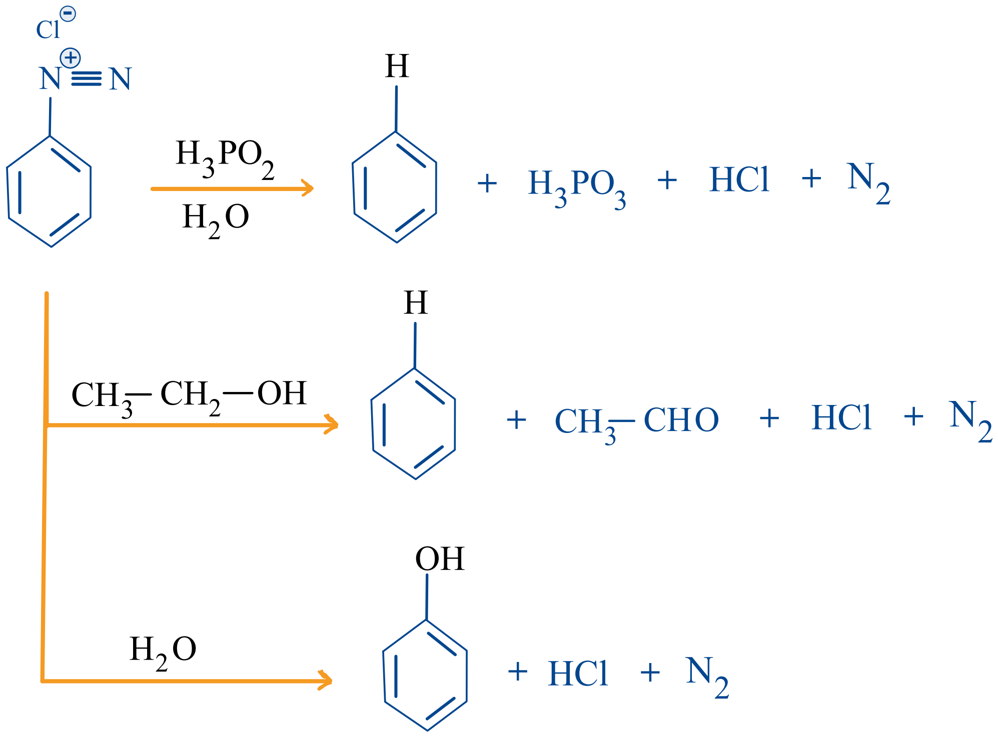
Chemical Reactions

Reactions involving displacement of nitrogen

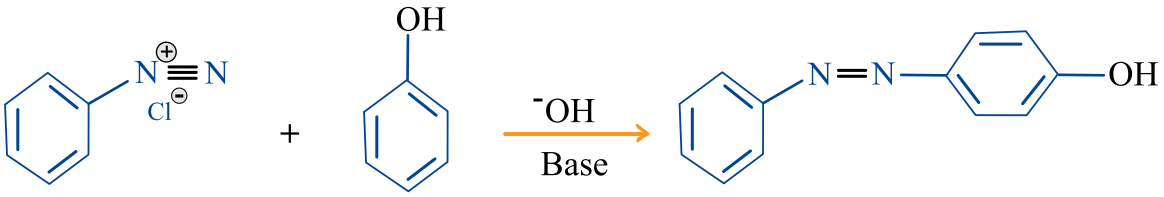


Other important reactions :



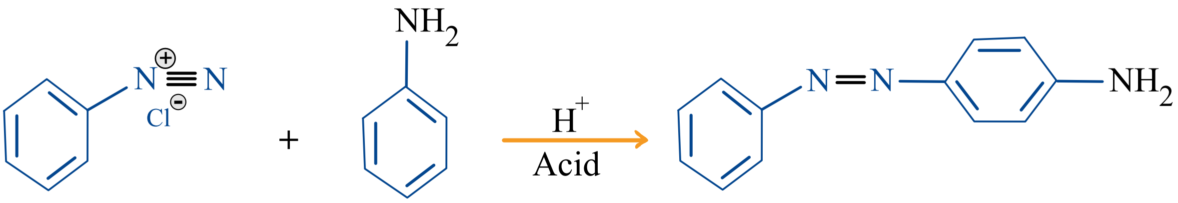


Coupling Reaction :



Phenol

p-Hydroxyazobenzne (Orange Dye)



Aniline

p-Aminoazobenzne (Yellow Dye)

The azo products obtained have an extended conjugate system having both the aromatic rings joined through the –N=N– bond. These compounds are often coloured and are used as dyes.