Nomenclature

1. **Common system →** 1° - amines are named by adding the suffix amine to the name of alkyl groups.

$CH_3 - NH_2 \rightarrow$ Methylamine.

For simple 2° & 3° amines the prefix di and tri is added to the name of alkyl group.

→ In case of mixed 2° & 3° amines the name of alkyl group is written in alphabetical order.

→ phenyl amines are named as derivatives of aniline. ($C_6H_5NH_2$)

→ other aryl amines are named as derivatives of aniline.

2. **IUPAC System →**

→ In this system 1° amines are named as amino alkane or alkaneamine, 2° or 3° amines are named as N- alkyl derivatives of alkanamine (amino alkane). In this case smaller alkyl group is taken as substituent group.

→ The aniline is named as benzamide (aminobenzene other aryl are derivatives of benzamine

Formula	Common name	IUPAC Name.
$CH_3 - NH_2$	Methyl amine	Methane amine.
$CH_3 - CH_2NH_2$	ethyl amine	ethanamine.
$CH_3 - CH_2CH_2 - NH_2$	n-propyl amine	1-propanamine.
$CH_3 - \underset{NH_2}{CH} - CH_3$	Iso propyl amine	2- propanamine.
$CH_3 - \overset{H}{N} - CH_3$	Dimethylamine	N-methyl methanamine
$CH_3 - CH_2 - \underset{CH_3}{N} - CH_2 - CH_2 - CH_3$	ethyl methyl	n-propyl amine.

↳ I/N N-ethyl, N - methyl propanamine

Amino Compounds
Amines and Aniline

[A] **Amines** ⇝ Compounds which are formed by ~~NH3 by alkyl or aryl groups are called~~ replacement of one or more H-atoms of NH_3 by alkyl or aryl groups are called amines. Amine may be classified as 1°, 2° and 3° depending upon the number of H-atom displaced.

$$NH_3 \longrightarrow \begin{cases} \xrightarrow[+R]{-H} R-NH_2 \quad 1^\circ \text{ amine } -NH_2 \\ \xrightarrow[+2R]{-2H} R_2NH \quad 2^\circ \text{ amine } >NH \\ \xrightarrow[+3R]{-3H} R_3N \quad 3^\circ \text{ amine } >N- \end{cases}$$

where, R = alkyl group or aryl group.

→ 2° and 3° amines may be simple or mixed.

E.g:- simple Amines:

$CH_3-NH-CH_3$, $CH_3-\overset{CH_3}{N}-CH_3$

Mixed amines :-

$CH_3-\overset{H}{N}-C_2H_5$, $CH_3-\overset{C_2H_5}{N}-C_3H_7$

Besides these 3 classes of amine there is another class of compound in which N-atom is quarternary compounds are called quarternary ammonium salts.

$\overset{\oplus\ominus}{R_4NX}$ → Quarternary ammonium salts.

Eg:- $[(C_2H_5)_4N]^+Cl^-$ → Tetraethyl ammonium chloride

$[(CH_3)_4N]^+Br^-$ → Tetramethyl ammonium bromide

3. From the reduction of alkyl cyanides or isocyanides with Li Al H_4 or Na/C_2H_5OH.

→ Reduction of alkyl cyanides give 1° amines.

$$R-C\equiv N + 4[H] \xrightarrow{LiAlH_4} R-CH_2-NH_2.$$

eg:-

$$CH_3-C\equiv N + 4[H] \xrightarrow{LiAlH_4} CH_3CH_2-NH_2.$$

$$C_6H_5-C\equiv N + 4[H] \xrightarrow{''} C_6H_5CH_2NH_2.$$

→ Reductions of isocyanides gives 2° amine.

$$R-N\overset{\rightarrow}{\equiv}C + 4[H] \xrightarrow{LiAlH_4} R-\underset{\underset{H}{|}}{N}-CH_3$$

e.g $CH_3-N\overset{\rightarrow}{\equiv}C + 4[H] \xrightarrow{LiAlH_4} CH_3-NH-CH_3.$

$C_6H_5-N\overset{\rightarrow}{\equiv}C + 4[H] \xrightarrow{LiAlH_4} C_6H_5-NH-CH_3.$

4. From amides :-

a) From reductions of amides with LiAlH4 or sodium & ethanol

$$R-\overset{O}{\overset{\|}{C}}-NH_2 + 4[H] \xrightarrow{LiAlH_4} R-CH_2-NH_2 + H_2O.$$

E.g:-

$$CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + 4[H] \xrightarrow{LiAlH_4} CH_3-CH_2-NH_2 + H_2O.$$

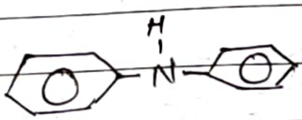
$$C_6H_5-\overset{O}{\overset{\|}{C}}-NH_2 + 4[H] \xrightarrow{LiAlH_4} C_6H_5CH_2-NH_2 + H_2O.$$

b) From Hofmann's bromamide (degradation) →

→ 1°- amines are formed by treatment with Br_2 and NaOH

$$R-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4NaOH \xrightarrow{\Delta} \underset{1^\circ\ amine}{R-NH_2} + Na_2CO_3 + 2NaBr + 2H_2O.$$

eg:- $CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4NaOH \xrightarrow{\Delta} CH_3-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O.$

	C/N	I/N
	phenyl amine (Aniline)	Benzamine (Aminobenzene)
	N-methyl aniline	N-methyl benzenamine
	~~N-phenyl aniline~~	~~N-phenyl benzenamine~~

General Methods of preparations.

1. From haloalkanes (alkyl halides) (Hofmann's ammnoloysis) → When a mixture of alkyl halide and alcoholic ammonia is heated in a sealed tube a mixture of 3 types of amines and quarternary ammonium salt is formed.

$$R-X \xrightarrow[-HX]{alc.NH_3} \underset{1^0}{R-NH_2} \xrightarrow[-HX]{RX} \underset{2^0}{R_2NH} \xrightarrow{RX} \underset{3^0}{R_3N} \xrightarrow{RX} \underset{Q.A.S}{R_4\overset{\oplus}{N}\overset{\ominus}{X}}$$

E.g.:-

$$C_2H_5Br \xrightarrow[-HBr]{NH_3} C_2H_5-NH_2 \xrightarrow[-HBr]{C_2H_5Br} (C_2H_5)_3NH \xrightarrow[-HBr]{C_2H_5Br} \underset{Br}{(C_2H_5)_4N}$$

→ This method is not suitable for the preparation of aryl amines.

2. From the reduction of nitrocompounds with metal acid mixture →
when nitroalkane is treated with metal Sn in the presence of conc. HCl gives amine.

$$R-NO_2 + 6[H] \xrightarrow{Sn/HCl} R-NH_2 + 2H_2O.$$

e.g.:-

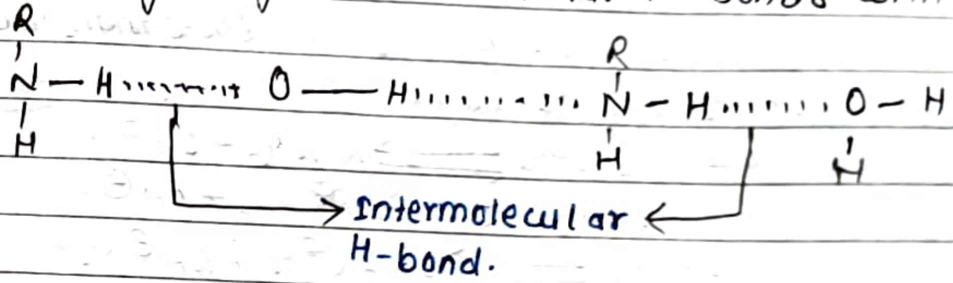
$$CH_3-CH_2-NO_2 + 6[H] \xrightarrow{Sn/HCl} CH_3-CH_2-NH_2 + 2H_2O.$$

$$C_6H_5NO_2 + 6[H] \xrightarrow{Sn/HCl} \underset{Aniline}{C_6H_5NH_2} + 2H_2O$$

→ Aniline is liquid with unpleasant smell.

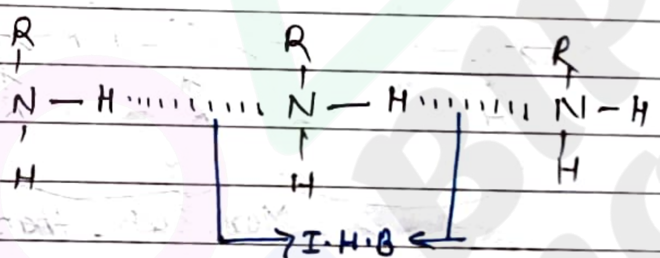
2. **Solubility** → Lower 1° and 2° amines are soluble in water because they can form intermolecular H-bonds with water.

N - C_2H_5



→ This water solubility decreases with increase in molecular mass

3. **Boiling points** → Amines have higher boiling points then that of non polar compounds of comparable molecular mass. It is because of intermolecular H-bonds between amine molecule.



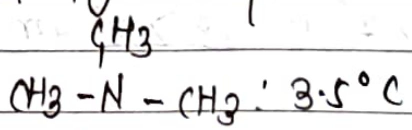
But amines have lower boiling point then that of corresponding alcohol and carboxylic acids. It is due to lower polarity of N-H bond than that of O-H bond.

Among the isomeric amines 1° amines have highest and tertiary amines have lowes bpt. It is because 1° amines have maximum H-bonding and 3° amines have no Hydrogen bonding.

e.g:-

$CH_3-CH_2-CH_2-NH_2$:- 50°C , $CH_3-CH_2-NH-CH_3$:- 34°C

n-propyl amine, ethyl methyl amine

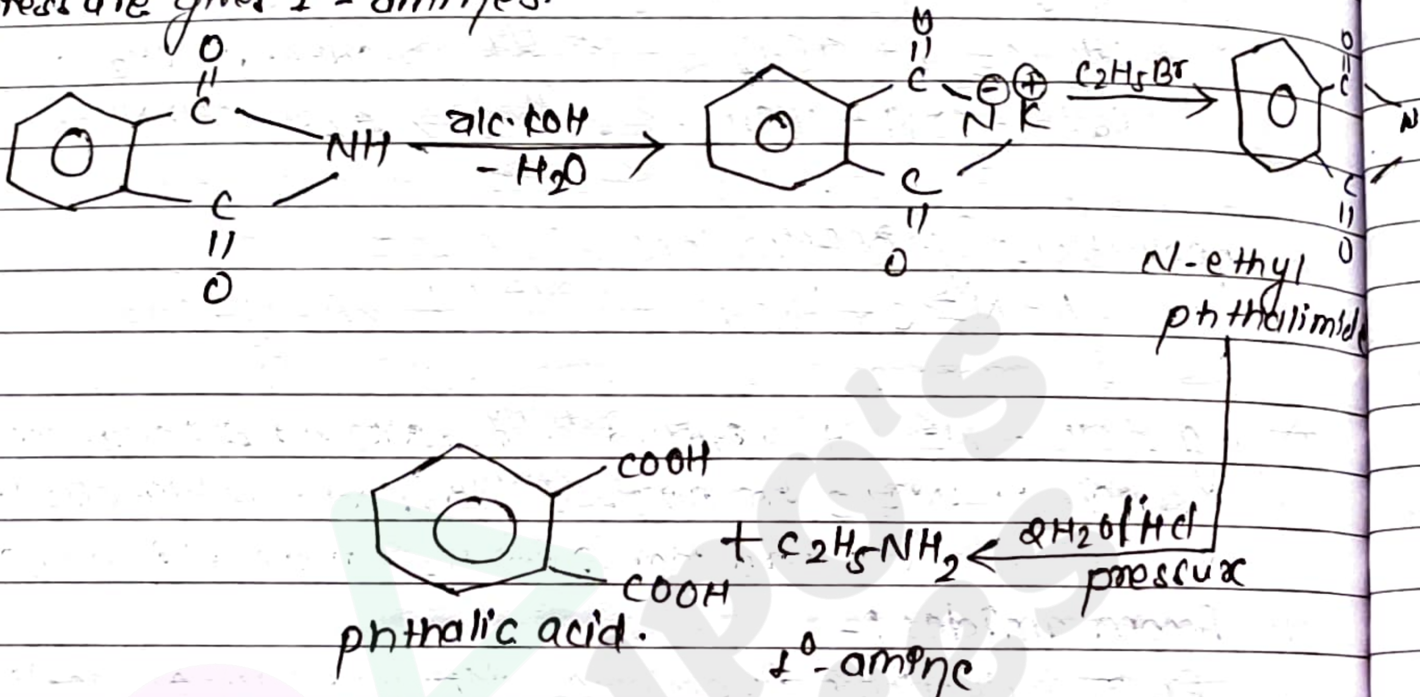


$$CH_3-\overset{CH_3}{\underset{}{N}}-CH_3 : 3.5°C$$

[Tetramethyl amine].

N-I for theory
But for objective.

5. From Gabriel phthalimide synthesis ⟶ when the phthalimide is treated with alc-KOH gives potassium phthalimide, which then reacts with alkyl halide gives N-alkyl phthalimide, N-alkyl phthalimide on hydrolysis with dil-HCl under pressure gives 1°-amines.



6. From alcohols ⟶ when mixtures of vapours of alcohols and ammonia passed over heated alumina at 300°c gives lower aliphatic amines.

$$\underset{}{R-OH + NH_3} \xrightarrow[-H_2O]{Al_2O_3\,/\,300°c} \underset{1°\text{-amine}}{R-NH_2} \xrightarrow[-H_2O]{R-OH} \underset{2°\text{amine}}{R_2NH} \xrightarrow{ROH} \underset{3°\text{-amine}}{R_3N}$$

→ the mixture of 1°, 2° & 3° amines is separated by fractional distillation.

Physical properties :-

1. physical state ⟶ lower aliphatic amines are gases with smell of NH_3. Higher aliphatic amines are liquid with fishy smell.

Explanation:-

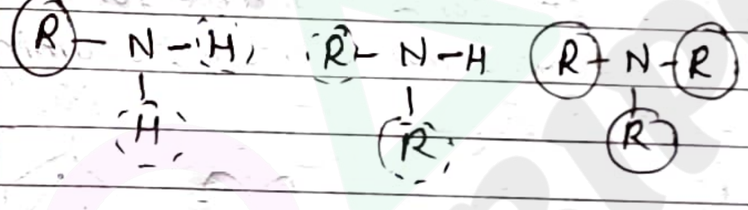
The basic strength of amines in aqueous solution depends upon three factors.

a) **Inductive effect** → According to this effect the order of basic strength of amines follows the order:-

$\boxed{3^\circ > 2^\circ > 1^\circ \text{ amines}}$

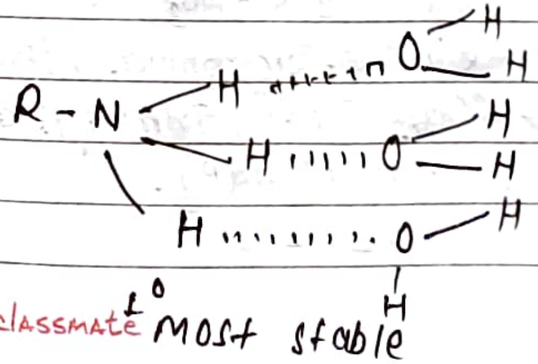
b) **Stearic effect** → It refers to the crowding of alkyl group around the N-atom which hinders the attack of proton on amines and decrease its basic strengths. As the crowding of alkyl group increases from 1° to 3° amines. The basic strength of amines decreases in the order

$\boxed{1^\circ > 2^\circ > 3^\circ \text{ amines}}$

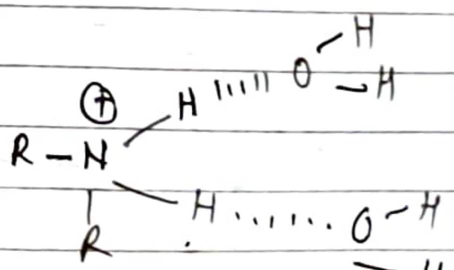


c) **Hydration effect**:- ~~It refers to the st~~. It refers to the stabilization of protonated amine by forming H-bonds with water molecules. Greater the number of H-bonds formed by the protonated amines greater is the stabilization and greater is the basic strength of corresponding acids. Hence according to this effect the basic strength of amines follows the order.

$\boxed{1^\circ > 2^\circ > 3^\circ \text{ amines}}$



1° most stable



2°.

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Chemical properties of Amine.

1. **Basic nature :-** Amines are basic in nature due to presence of lone pair of electron on N- atom.

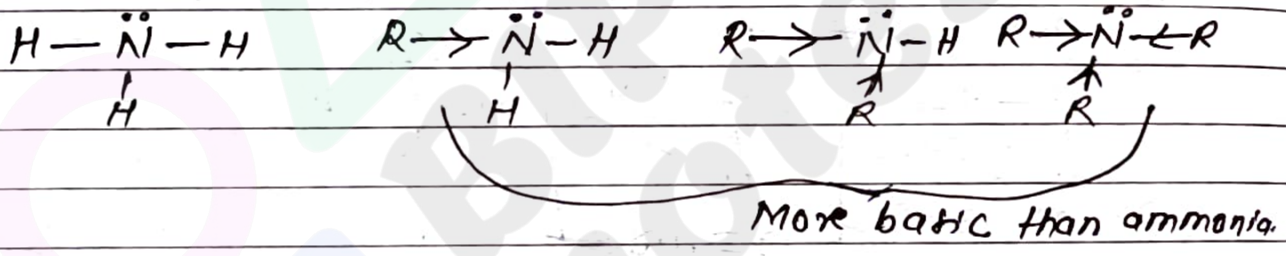
They are more stronger bases than water. Hence they are protonated by water.

$$R-NH_2 + H_2O \rightleftharpoons \overset{\oplus}{R}NH_3 + OH^{\ominus}.$$

$$R_2-NH + H_2O \rightleftharpoons \overset{\oplus}{R_2}NH_2 + OH^{\ominus}.$$

$$R_3N + H_2O \rightleftharpoons R_3N^{\oplus}H + OH^{\ominus}.$$

Amines are more basic than ammonia, it is because the electron releasing alkyl groups increases electron density at the nitrogen atoms. Hence the lone pair of nitrogen is easily available for protonation.



\# Comparision of basic strength of 1°, 2°, 3° amines:-

As the number of electron relasing alkyl groups 1° to 3° amines, the basic strength of amines follows the order:-

$$\boxed{3^\circ > 2^\circ > 1^\circ \text{ amines.}}$$

→ This order is formed to be so only in gaseous state. But in aqueous solution the basic strength is found to be

$$\boxed{2^\circ \text{ amine} > 1^\circ \text{ amine} > 3^\circ \text{ amine}}$$

2) Reaction with alkyl halides → Amines of lower classes reacts with alkyl halides to form amines of higher classes & quarternary ammonium salt.

$$CH_3-NH_2 \xrightarrow[-HCl]{CH_3Cl} (CH_3)_2NH \xrightarrow[-HCl]{CH_3Cl} (CH_3)_3N$$

$$(CH_3)_3N \xrightarrow[-Cl]{CH_3} [(CH_3)_4\overset{+}{N}]Cl^{\ominus}$$

(Quarternary ammonium salt.)

3) Reaction with acid chloride or acid anhydride (acylation)

1° and 2° amines reacts with acid chloride or acid anhydride to give substituted amide.

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + H-\underset{H}{\underset{|}{N}}-C_2H_5 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-NHC_2H_5 + HCl$$

N-~~meth~~ ethyl acetamide.

$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-C_2H_5 + H_2N-C_2H_5 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-NHC_2H_5 + CH_3COOH.$$

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + H-N\begin{matrix} CH_3 \\ CH_3 \end{matrix} \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-N(CH_3)_2 + HCl.$$

N-N-dimethyl acetamide

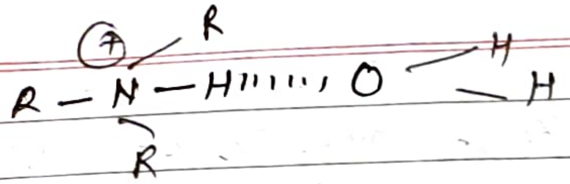
4. Reaction with nitrous acid → when Aliphatic 1° amine reacts with HNO_2 gives alcohol and N_2.

$$CH_3-CH_2-NH_2 + HNO_3 \xrightarrow[0-5°C]{NaNO_2/HCl} CH_3-CH_2-OH + N_2 + H_2O.$$

5. Reaction with chloroform → [carbylamine reaction]

when primary amines heated with chloroform and alc. KOH gives offensive ~~heated with a~~ smelling compound called carbylamine or Isocyanide.

$$CH_3-NH_2 + CHCl_3 + 3KOH \longrightarrow CH_3-N \overset{\rightarrow}{\equiv} C + 3KCl + H_2O.$$



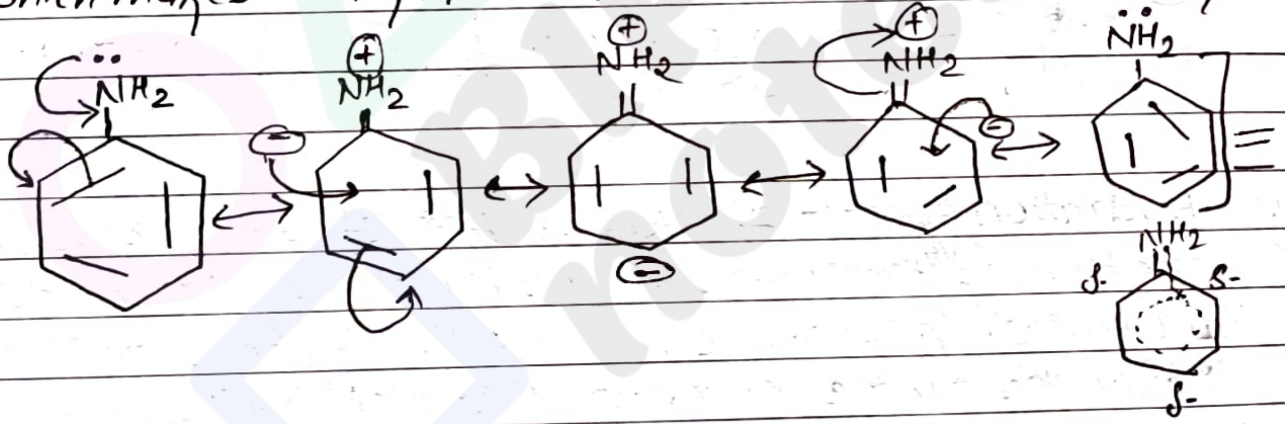
3° Least stable

→ As a results of combined effect of these three factors 2° amine is most basic and 3° amine is least basic Hence in aqueous solution, the basic strength follows the order:

$$\boxed{2^\circ \text{ amine} > 1^\circ \text{ amine} > 3^\circ \text{ amine}}$$

Q Aniline is less basic than ammonia or amines? why.

→ In aniline the lone pair of electrons present on N-atoms undergoes resonance with π-electrons of the benzene ring. Hence lone pair is not easily available for protonation which makes aniline less basic than ammonia or amines.



1\. Reaction with mineral acids → All amines react with mineral acids to form water soluble salts.

$CH_3NH_2 + HCl \longrightarrow CH_3\overset{+}{N}H_3\overset{-}{Cl}$ [Methyl ammonium chloride]

$(CH_3)_2NH + HNO_3 \longrightarrow (CH_3)_2\overset{+}{N}H_3\,\overset{-}{NO_3}$ Dimethyl ammonium nitrate.

$(CH_3)_2N + HCl \longrightarrow (CH_3)_3\overset{+}{N}H\overset{-}{Cl}$ [Trimethyl ammonium chloride].

NVI

6. Reaction with aldehydes and ketones → When aldehydes & ketones reacts with primary amines gives Schiffs base.

$$>C=O + H_2NR \rightarrow >C=N-R$$

eg:- $CH_3CHO + H_2NC_2H_5 \rightarrow CH_3-CH=N-C_2H_5 + H_2O$.

ethylidine ethylamine.

$$CH_3-\overset{CH_3}{C}=O + H_2N-C_2H_5 \rightarrow CH_3-\overset{CH_3}{C}=N-C_2H_5 + H_2O.$$

Isopropylidene ethylamine.

N.V.I

7. Reaction with benzeyl chloride (Benzoylation) → when 1° and 2° amines reacts with benzoyl chloride gives substituted benzamide.

$$C_6H_5-\overset{O}{\overset{\|}{C}}-Cl + H-HNC_2H_5 \rightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-NHC_2H_5 + HCl$$

N-ethyl benzamide.

$$C_6H_5-\overset{O}{\overset{\|}{C}}-Cl + HN(C_2H_5)_2 \rightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-N(C_2H_5)_2 + HCl$$

N,N-diethyl benzamide.

Aromatic amine

* Laboratory preparation of Aniline ($C_6H_5NH_2$)

Theory:-

It is prepared in lab by the reduction of nitrobenzene with tin and conc. HCl

$$C_6H_5NO_2 + 6[H] \xrightarrow{Sn/HCl(conc)} C_6H_5NH_2 + 2H_2O.$$

Procedure:- 20gm of nitrobenzene and 40gm of granulated tin are taken into a round bottom flask. 100 ml of conc. HCl is added to it, little at a time (10 ml) shaking and cooling after each addition so that temperature may not rise above 90°c. When whole of acids is added the flask is refluxed on water bath for about 1 hr till the oily drops of nitrobenze disappear. On cooling the mixture, a solid mass is obtained.

I). $Sn + 4[HCl] \longrightarrow 2SnCl_4 + 8[H]$.

II). $C_6H_5NO_2 + 6[H] \longrightarrow C_6H_5NH_2 \cdot SnCl_4$.

III) $2C_6H_5NH_2 + 2HCl + SnCl_4 \longrightarrow (C_6H_5NH_2 \cdot HCl)_2 \cdot SnCl_4$
(solid mass)

Calculated amount of NaOH is added to liberate aniline in liquid state which floods on the surface as dark drown oil

$$(C_6H_5NH_2HCl)_2 \cdot SnCl_4 + 3NaOH \longrightarrow \underset{(liquid)}{2C_6H_5NH_2} + Na_2SnO_3 + 6NaCl + 5H_2O$$

The aniline is recovered from the mixture by stem distillation. Aniline being slightly soluble in water, common salt is added to the distillate till saturation to liberate whole of the aniline from water.

The aniline is then entracted with ether in small loss and ether is removed by evapouration. The moisture is absorbed by solid NaOH or KOH and finally redistilled to obtain pure aniline.

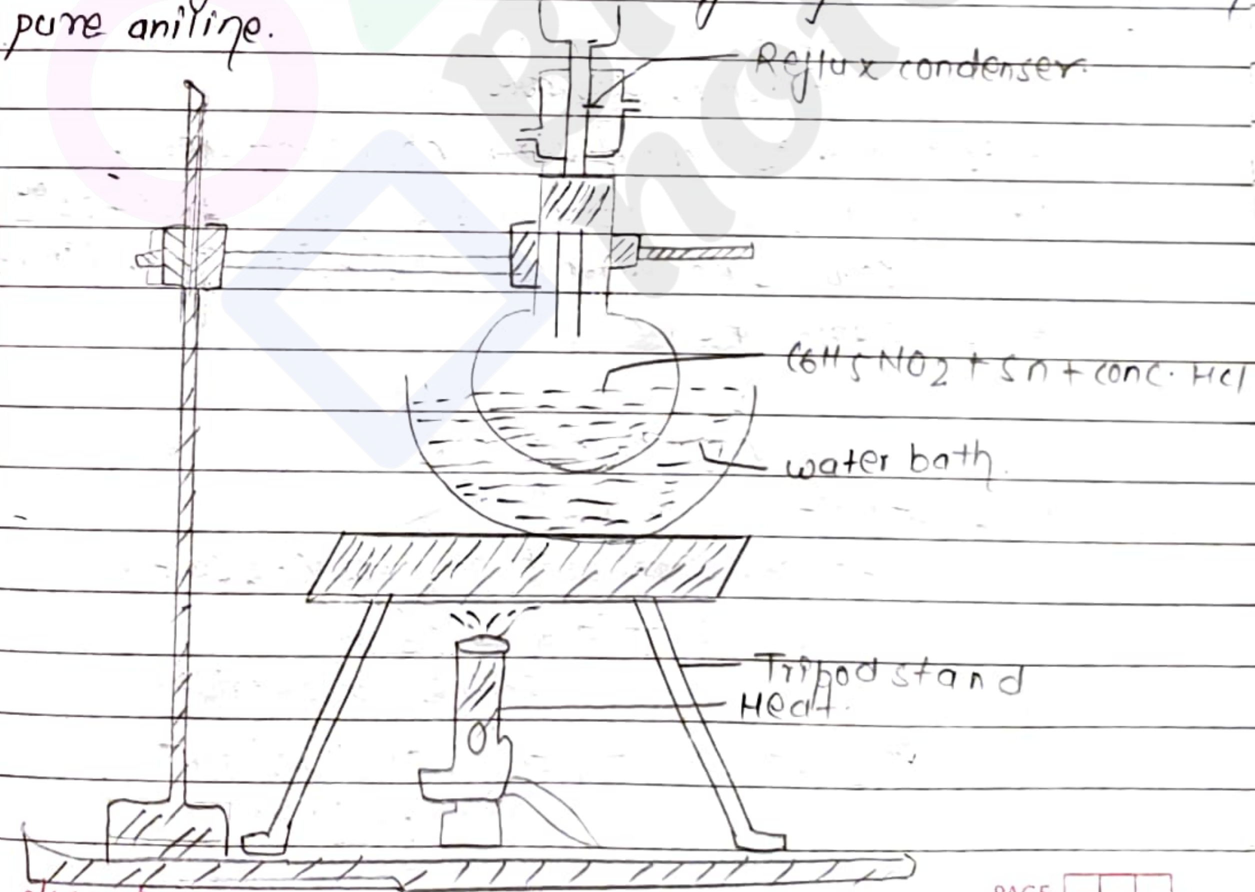


Fig:- Refluxing of mixture (lab prepn of Aniline).

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Physical properties

1. It is colourless liquid with unpleasant smell.
2. It's boiling point is 184°C & sp. grv 1.02 + 20°C.
3. Slightly soluble in water but readily in organic solvents.
4. It is volatile in stem

Chemical properties

a) Basic nature:-

Aniline reacts with acid to give salt.

$C_6H_5NH_2 + HCl \longrightarrow C_6H_5\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$

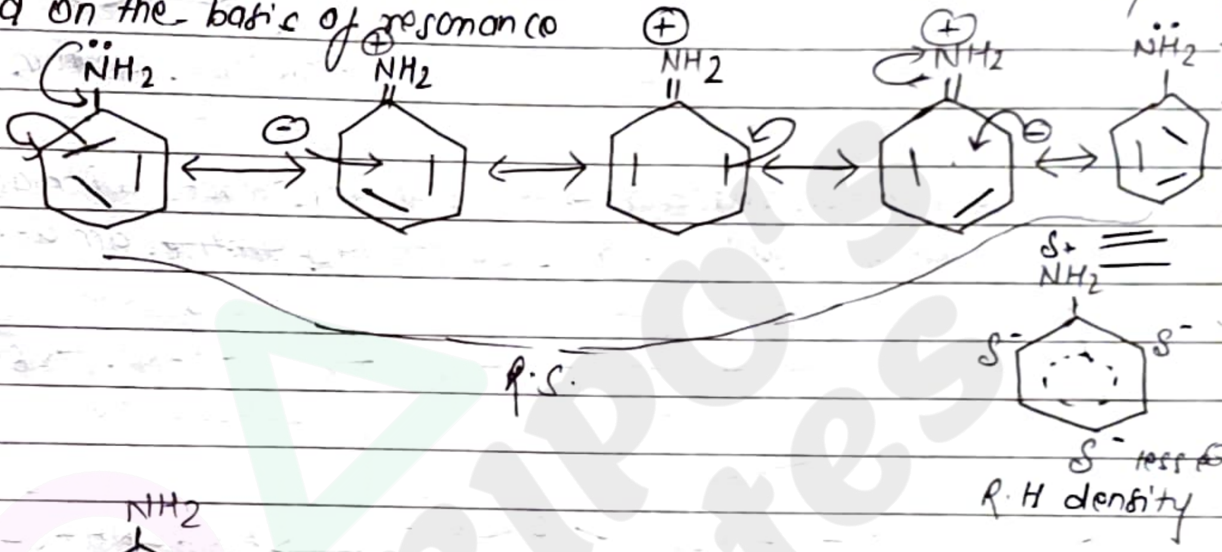
Aniline hydrochloride.

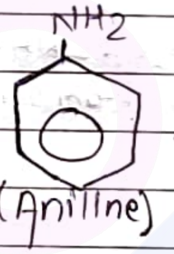
$2C_6H_5NH_2 + H_2SO_4 \longrightarrow (C_6H_5NH_3)_2\ SO_4^-$

Aniline sulfate

* Comparison of basic strength of alkyl and aryl amines → Aniline (Arylamine) is less basic than ammonia. In aniline $-NH_2$ group is directly attached to aromatic ring. Aromatic ring is electron with drawing as compared to hydrogen. So presence of an aromatic ring reduces e⊖ density at nitrogen and results the aryl aminea weaker base.

→ The aniline is less basic than ammonia ~~of~~ aniline can be explained on the basis of resonance





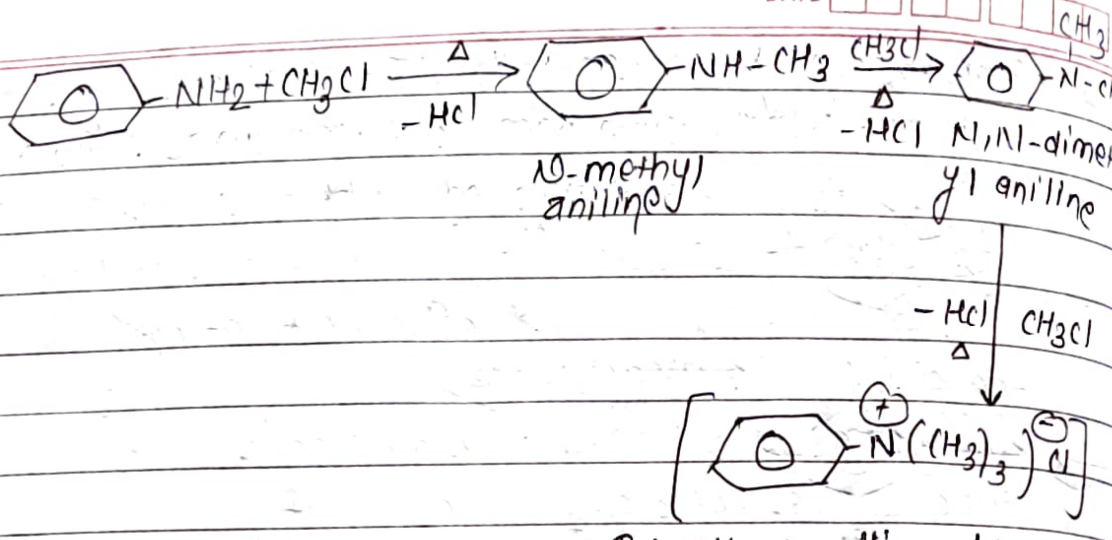
(Aniline) < NH_3 < $R-NH_2$

Ammonia Amine

⟶ basicity order.

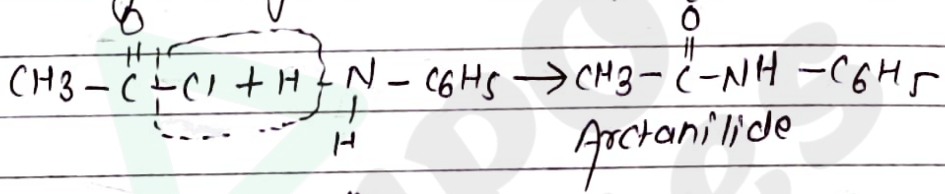
→ Due to resonance, the lone pair of e⁻⁻ is less readily available for protonation, where as in alkyl amines, alkyl group are e⊖ releasing group increases e⊖ density at nitrogen, thus lone pair of electrons is readily available for protonation. Therefore aniline is weaker bases than alkyl amines

b) Alkylation → when aniline reacts with alkyl halides gives mixture of amines along with quarternary ammonium salt.



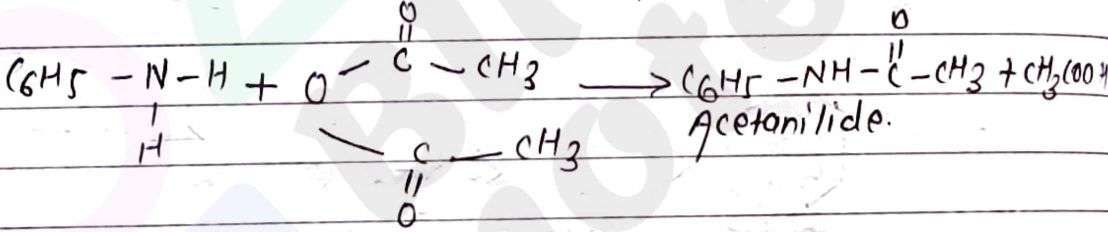
Trimethyl anilium chloride.

c) Acylation reaction:- when aniline reacts with acid hallde or acid anhydride gives substituted ~~amine~~. amide.



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + H-\underset{H}{\underset{|}{N}}-C_6H_5 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH-C_6H_5$$

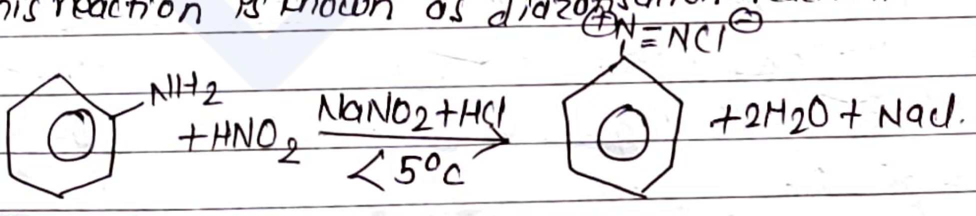
Acetanilide



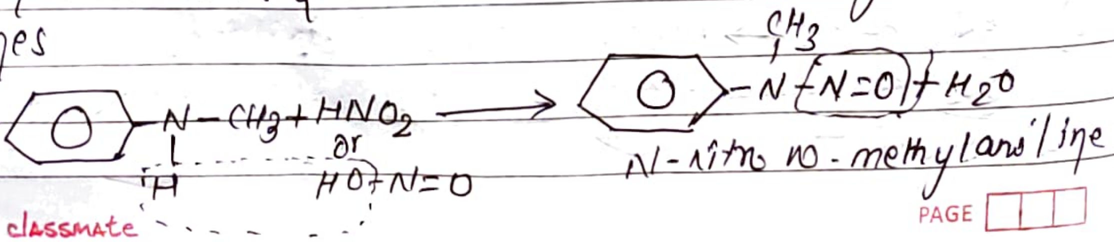
$$C_6H_5-\underset{H}{\underset{|}{N}}-H + O\begin{matrix}\diagup \overset{O}{\overset{\|}{C}}-CH_3 \\ \diagdown \underset{O}{\underset{\|}{C}}-CH_3\end{matrix} \longrightarrow C_6H_5-NH-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3COOH$$

Acetanilide.

d) Diazotization reaction → when aniline reacts with nitrous acid ($NaNO_2 + HCl$) below 5°C gives benzene diazonium chloride (salt) this reaction is known as diazotisation reaction.

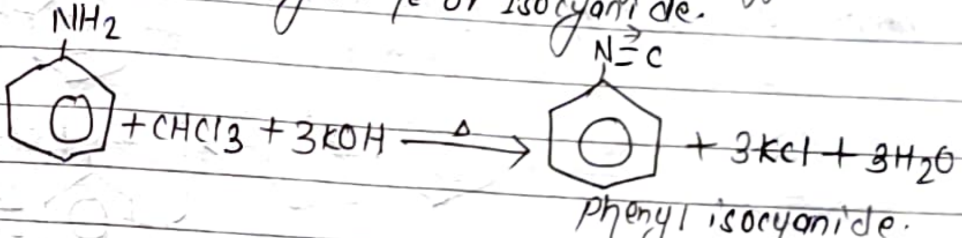


→ when Aromatic 2° amine reacts with HNO_2 gives Nitroamines



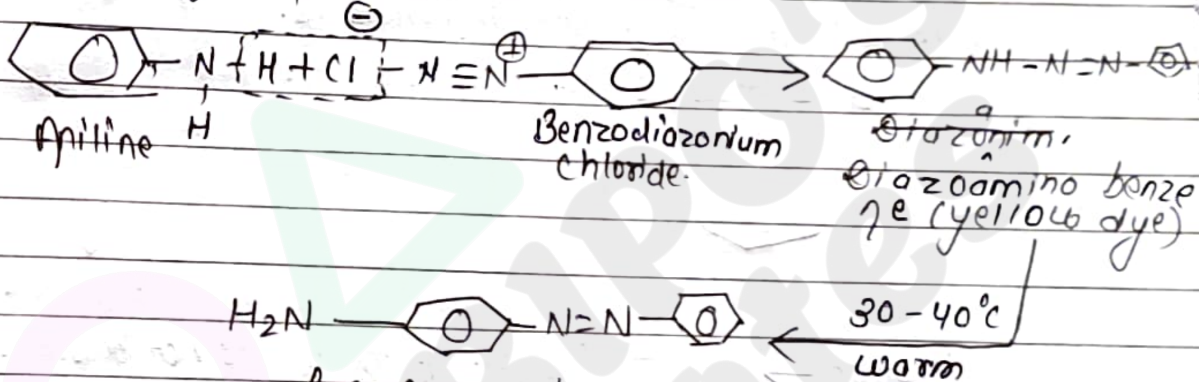
N-Nitro so-methylaniline

ⓔ carbylamine reaction → when aniline reacts with chloroform and alcoholic KOH in the presence of heat gives offensive smelling compound called carbylamine or Isocyanide.



Phenyl isocyanide.
(offensive smell).

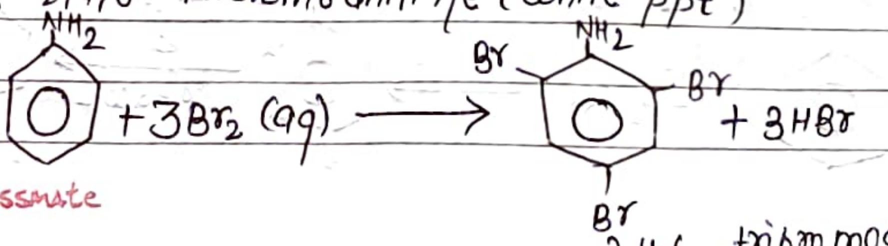
ⓕ coupling reaction → (rxn with diazonium salt):- when aniline reacts with benzene diazonium chloride gives P-aminoazo benzene as final product.



Electrophilic substitution Rxn →

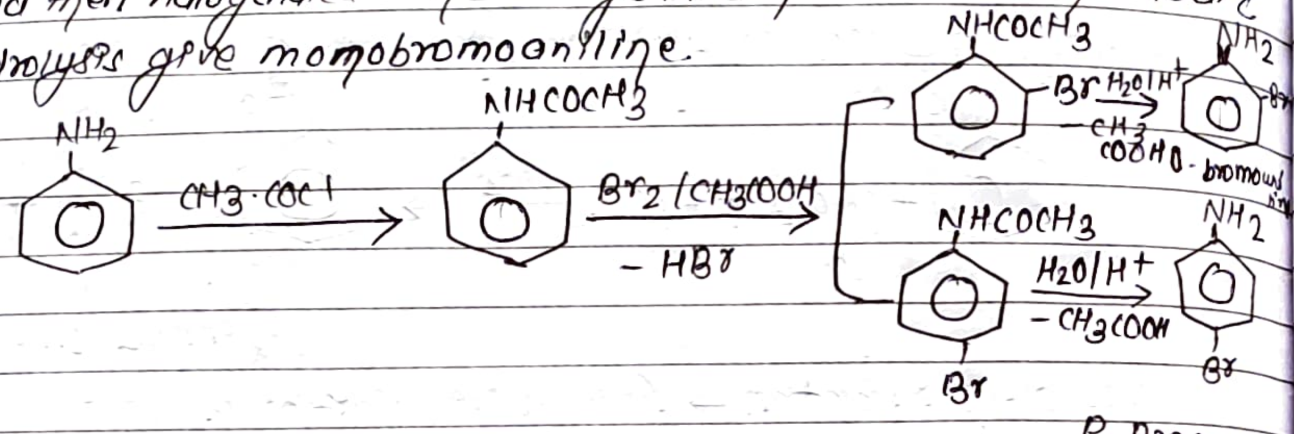
The amino group is electron releasing group and hence it activates the benzene ring towards electrophilic substitution reaction. It increases electron density specially at an ortho and para position therefore it is O & P directing toward electrophilic substitution reaction.

4) Halogenation → when aniline reacts with aqueous bromine gives 2,4,6 - tribromo aniline (white ppt)



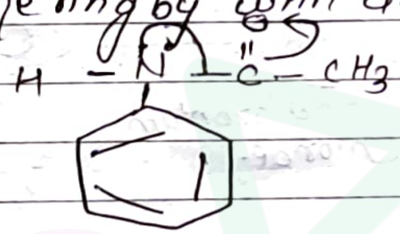
2,4,6 – tribromoaniline

To obtain monobromoaniline it is first acetylated and then halogenated. The halogenated product on the acidic hydrolysis give monobromoaniline.

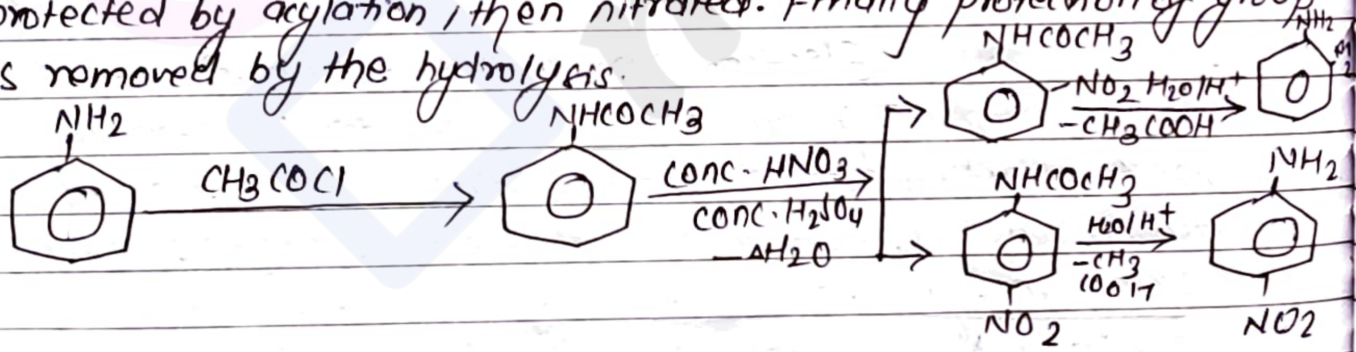


P-Bromoaniline

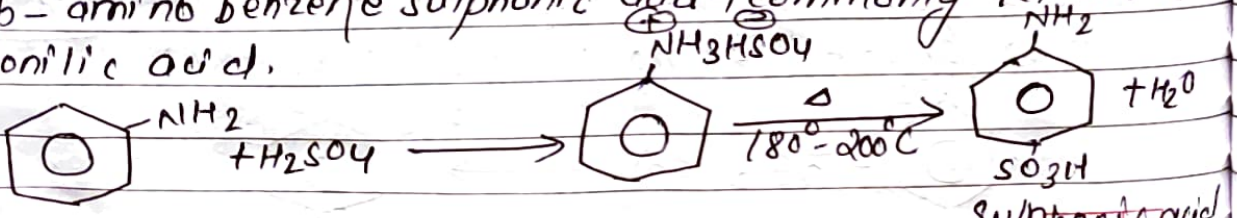
→ It is because the acetyl group (CH_3CO-) decreases the reactivity of benzene ring by withdrawing electrons.



(b) Nitration → Direct nitration of aniline is not possible because it is oxidised to various products. Hence the aminogroup is first protected by acylation, then nitrated. Finally protection of group is removed by the hydrolysis.



(c) ~~sulp~~ sulphonation → when aniline is heated with conc. H_2SO_4 gives p-amino benzene sulphonic acid, commonly known as sulphanilic acid.



Sulphanilic acid

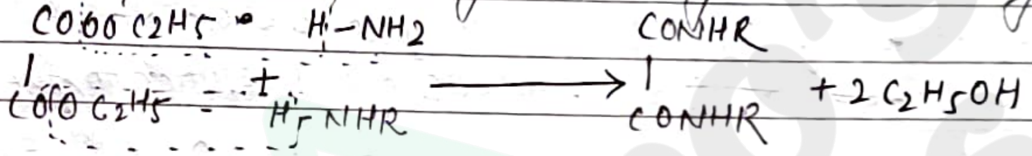
Uses of aniline

- → Used as solvents.
- → Used in manufacture of dyes, drugs and polymers.
- → Used for the preparation of organic reagents like
- → Used in prepn of alcohol, diazonium salts.

Separation of 1°, 2° and 3° amines →

V. Imp (A) By Hoffmann's method → In this method the given mixture of 1°, 2° and 3° amine is treated with diethyl oxalate.

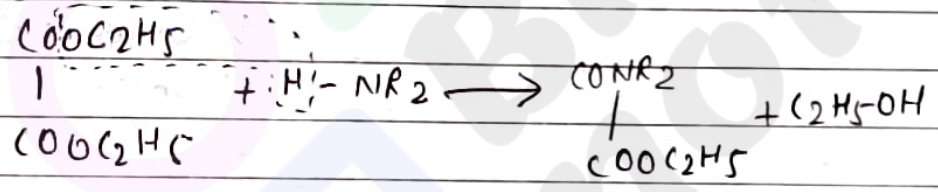
I) 1° amines reacts with diethyloxalate to form solid dialkyl oxamide.



$$\begin{matrix} COOC_2H_5 \\ | \\ COOC_2H_5 \end{matrix} + \begin{matrix} H-NH_2 \\ \\ H-NHR \end{matrix} \longrightarrow \begin{matrix} CONHR \\ | \\ CONHR \end{matrix} + 2C_2H_5OH$$

(solid) dialkyl oxamide.

II) 2° amines reacts with diethylonate to give liquid dialkyl oxamic ester.

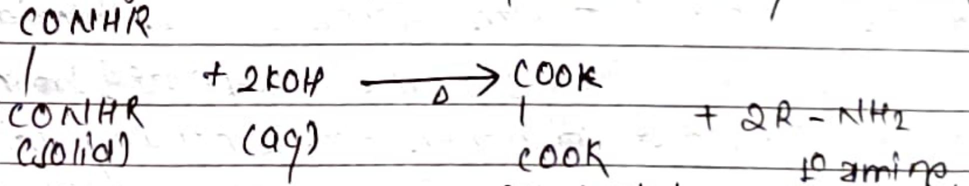


$$\begin{matrix} COOC_2H_5 \\ | \\ COOC_2H_5 \end{matrix} + H-NR_2 \longrightarrow \begin{matrix} CONR_2 \\ | \\ COOC_2H_5 \end{matrix} + C_2H_5OH$$

liquid (dialkyl oxamic ester)

III) 3° amines donot react with diethyl oxalate.

Now the mixture containing dialkyl oxamides, dialkyl oxamic ester, 3° amines and alcohols is filtered to separate solid dialkyl oxamide which is heated with aq. KOH to get 1° amine.



$$\begin{matrix} CONHR \\ | \\ CONHR \end{matrix} + 2KOH \xrightarrow{\Delta} \begin{matrix} COOK \\ | \\ COOK \end{matrix} + 2R-NH_2$$

(solid) (aq) Pot. Oxalate 1° amine.

The remaining mixture (filtrate) is then subjected to fractional distillation, where by 3° amine distil over first followed by alcohol. The remaining solution is then treated with aq. KOH and distilled fractionally to get 2° amine and alcohols in different fraction

$$\begin{array}{l} CONR_2 \\ | \\ CONR_2 \end{array} + 2KOH \longrightarrow \begin{array}{l} COOK \\ | \\ COOK \end{array} + \underset{(2^\circ \text{ amine})}{R_2NH} + C_2H_5OH.$$

Ⓑ Hinsberg method → In this method, the mixture of 1°, 2° & 3° amine is treated with benzene sulphenyl chloride (Hinsberg reagent) in the presence of aq. KOH.

a) 1° amine gives water soluble pottasium salt of N-alkyl benzene sulpho~~nide~~ amide ~~whi~~ which dissolve in KOH solution to give clear soln.

$$C_6H_5-SO_2-Cl \xrightarrow[HCl]{RNH_2} C_6H_5SO_2NHR \xrightarrow[-H_2O]{aq.KOH} [C_6H_5-SO_2\overset{\ominus}{N}-R]K^{\oplus}$$

$\downarrow$

Water soluble p. salt of benzene sulphoamide (soluble).

b) 2° amine give N,N-dialkyl benzene sulphonamides which is insoluble in aq. KOH soln.

$$C_6H_5-SO_2-Cl + H-NR_2 \longrightarrow \underset{\text{Solid.}}{C_6H_5-SO_2-\overset{R}{\overset{|}{N}}-R} \xrightarrow{KOH} \text{No reaction}$$

c) 3° amines doesnot react with benzene sulphonyl chloride.

Now 3° amines is seperated from the resulting mixture by distillation then the remaining mixture is filtered to separate N,N-dialkyl benzene sulphonamide which on hydrolysis give 2° amines.

$$C_6H_5-SO_2-\overset{R}{\overset{|}{N}}-R + H_2O \xrightarrow{H^+} \underset{\text{Benzene sulphonic acid.}}{C_6H_5SO_2\cdot OH} + \underset{\text{(2° amine.}}{R_2NH}$$

The remaining filterate is treated with dil HCl to get solid N-alkyl benzene sulphonamide, which on hydrolysis gives 1° amines.

$$[C_6H_5SO_2\overset{\ominus}{N}R]\overset{\oplus}{K} \xrightarrow[-KCl]{HCl} C_6H_5\cdot SO_2-\overset{H}{N}-R \xrightarrow{H_2O/H^+} C_6H_5SO_2\cdot OH + RNH_2$$

solid

1° amine.

Test for amines :-

1. Hinsberg test :→ In this test the given amine is shaked with benzene sulphonyl chloride (Hinsberg reagent) in the presence of aq. KOH.

→ 1°- amine gives clear solution.

→ 2°- amines gives insoluble solid N,N- dialkylbenzene sulphonamide.

→ 3°- amines remains as an oily layer because it does not react with benzene sulphonyl chloride.

2. Carbylamine Test ⇝ This test is used to identify 1° amines only [aliphatic or aromatic]

$$R-NH_2 + CHCl_3 + 3KOH \longrightarrow R-N\overset{\rightarrow}{=}C + 3KCl + 3H_2O.$$

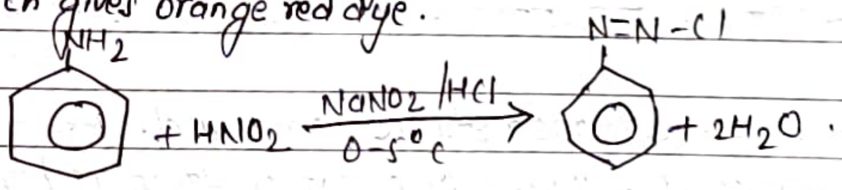
(offensive smell)

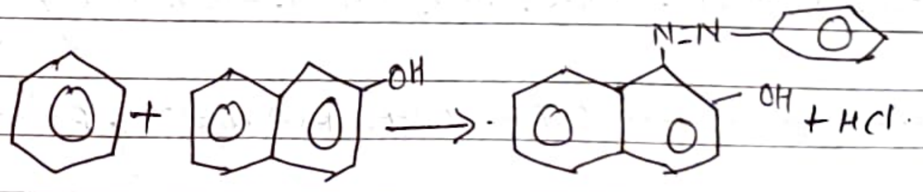
where; R = alkyl group or aryl group.

3. Azo dye test → (Nitrous acid test)

This test is given only by 1° aromatic amines

In this test the given amine is treated with nitrous acid in cold condition and the resulting solution is treated with β-napthol which gives orange red dye.





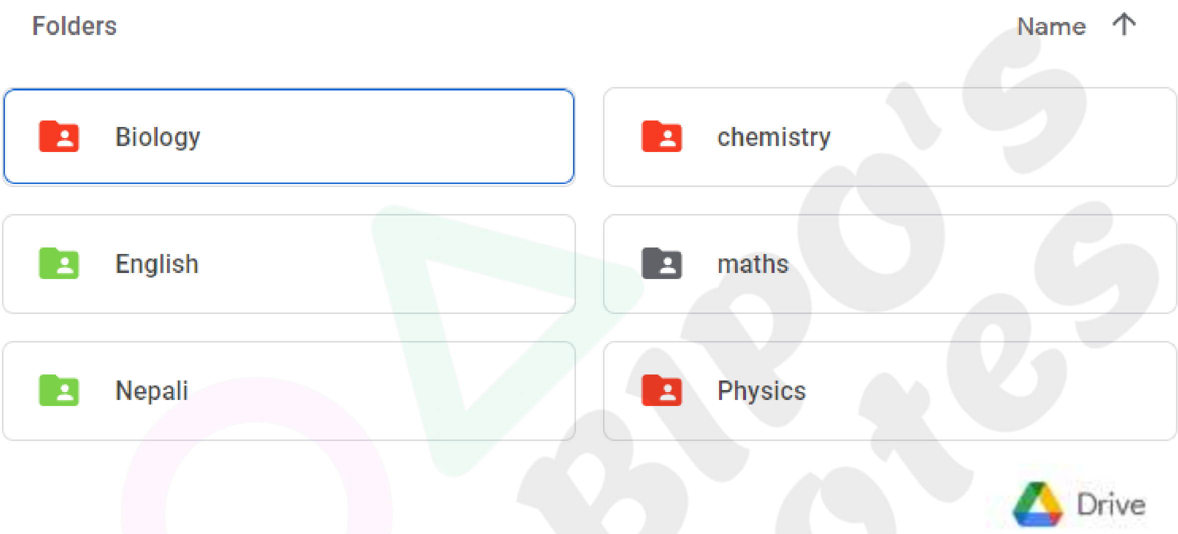
β-nepthol.

Orange red azodye

Bipin Khatri

(Bipo)

Class 12 complete notes and paper collection.



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