# Amines

## NCERT FOCUS ANSWERS

## Topic 1

**1.** (i) Propan-2-amine (primary),
(ii) Propan-1-amine (primary),
(iii) *N*-Methylpropan-2-amine (secondary),
(iv) 2-Methylpropan-2-amine (primary),
(v) *N*-Methylbenzenamine or *N*-Methylaniline (secondary),
(vi) *N*-Ethyl-*N*-methylethanamine (tertiary),
(vii) 3-Bromobenzenamine or 3-Bromoaniline (primary).

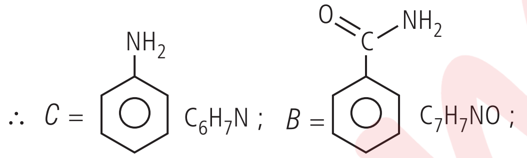
**2.** Given scheme of reactions is

$$\underset{\text{Aromatic compound.}}{A} \xrightarrow{\text{aq. } NH_3/\Delta} B \xrightarrow{Br_2/KOH} \underset{C_6H_7N}{C}$$

(i) Looking at the given scheme, we can clearly see that reaction $B \rightarrow C$ is Hofmann bromamide reaction.

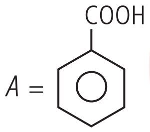
Thus, $C$ is an amine (1°) while $B$ must be an amide with molecular formula $C_7H_7NO$.

(ii) Further, the ratio of C and H in $B$ and $C$ are indicative of the fact that it is an aromatic compound.



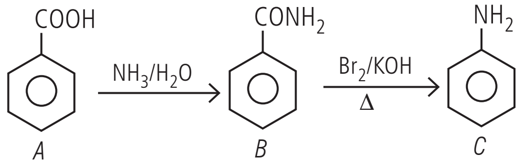
Aniline        Benzamide

Since, $B$ is formed by the action of ammonia on $A$, $A$ must be a carboxylic acid,

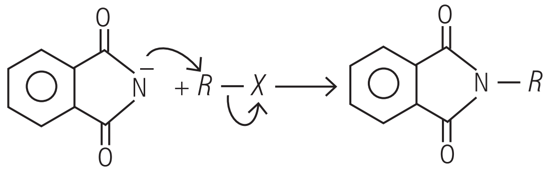


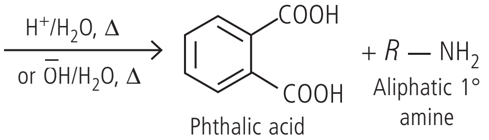
Benzoic acid

The reactions are



**3.** (i) Gabriel phthalimide reaction involves the nucleophilic attack of the phthalimide on the alkyl halide.

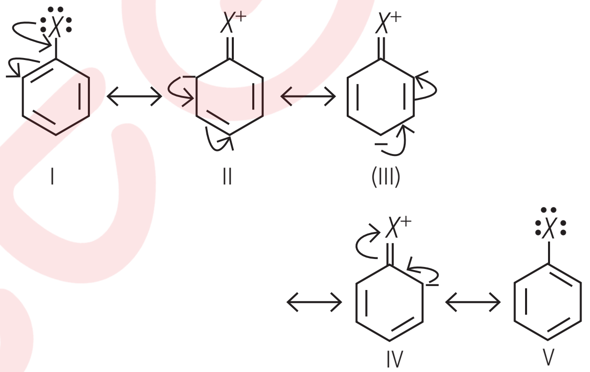




(ii) Such a nucleophilic substitution reaction is not possible if the substrate is an aryl halide.

(iii) The reason for it can be explained on the basis of

(a) Partial double bond character of $C — X$ bond in aryl halide. Consider the following structures :



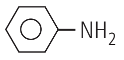
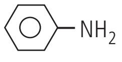
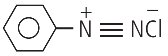
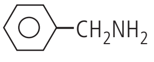
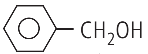
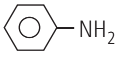
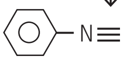
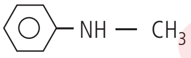
From the resonance structures we see that the $C — X$ bond has a double bond character in structures II, III and IV and this makes cleavage of $C — X$ bond difficult.

(b) Also the steric hindrance by the bulky aryl group prevents the incoming nucleophile.

## Topic 2

**1.**

| **Test / Reagent** | **Compound I** | **Compound II** |
|---|---|---|
| (i) Carbylamine test<br>$CHCl_3$ +<br>*alc.* KOH + Δ | $CH_3NH_2$ (1° amine)<br>Methylamine<br>↓<br>$CH_3NC + 3KCl + 3H_2O$<br>foul smell | $(CH_3)_2NH$ (2° amine)<br>Dimethylamine<br>↓<br>No reaction |
| (ii) Hinsberg's test<br>$C_6H_5SO_2Cl$ | $R_2NH + C_6H_5SO_2Cl$<br>↓<br>$C_6H_5SO_2NR_2$ + HCl<br>(Insoluble in alkali) | $R_3N + C_6H_5SO_2Cl$<br>↓<br>No reaction |

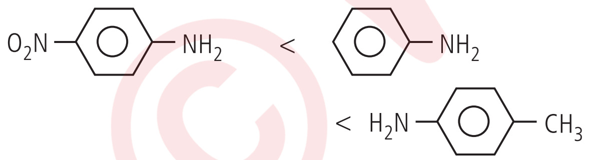
| | | |
|---|---|---|
| (iii) Nitrous acid test<br>NaNO$_2$ + HCl | $C_2H_5NH_2$<br>Ethylamine (1° amine)<br>$\downarrow$<br>$ROH + N_2\uparrow + HCl$<br>(effervescence) | <br>Aniline<br>$\downarrow$<br>$C_6H_5 - N_2^+Cl^-$<br>Benzenediazonium chloride |
| (iv) Azo dye test<br>(I) NaNO$_2$ + dil. HCl<br>(0-5°C)<br>(II) β-naphthol | <br>Aniline<br>(I) $\downarrow$<br><br>Benzene diazonium chloride<br>(II) $\downarrow$<br>Orange dye | <br>Benzylamine<br>(I) $\downarrow$<br><br>$+ N_2\uparrow + HCl$<br>(effervescence)<br>(II) $\downarrow$<br>No reaction |
| (v) Carbylamine test<br>$CHCl_3$+Alc. KOH+Δ | <br>Aniline (1° amine)<br>$\downarrow$<br><br>$+ 3KCl + 3H_2O$<br>(Unpleasant odour) | <br>*N*-methylaniline<br>(2° amine)<br>$\downarrow$<br>No reaction |

**2.** (i) The order of p$K_b$ will decrease as:

$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2\,NH$

(ii) $C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$

(iii) (a) *p*-Nitroaniline < Aniline < *p*-Toluidine



The availability of *l.p.* on N of *p*-nitroaniline is drastically reduced by presence of electron withdrawing $-NO_2$ group on it.

In contrast, presence of electron releasing $-CH_3$ group increases the electron density on N atom and improves basicity in *p*-toluidine.

(b) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$

Involvement of *l.p.* of N in resonance causes aniline to have low basicity. In *N*-methylaniline, the –Me group through its +*I* effect improves the electron density on N and therefore its basic strength increases. In Benzylamine, the $-NH_2$ is farther off from benzene ring and hence *l.p.* is localized on it and hence the basic strength is highest.

(iv) In gas phase, basicity follows the order :

$(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$

In gas phase, the stabilization by solvation is not present and hence basic strength follows the expected order based on +*I* effect of alkyl groups.

(v) $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

(vi) $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

Amines can form hydrogen bonds with water and are therefore soluble in it. However, the solubility decreases if the mass of the hydrocarbon part increases.

**3.** (i) $$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow{SOCl_2} \underset{\text{Ethanoyl chloride}}{CH_3COCl} \xrightarrow{NH_3\text{ (excess)}}$$

$$\underset{\text{Ethanamide}}{CH_3CONH_2} \xrightarrow[\text{(Hofmann bromamide reaction)}]{Br_2/KOH} \underset{\text{Methanamine}}{CH_3NH_2}$$

(ii) $$\underset{\text{Hexanenitrile}}{CH_3(CH_2)_4CN} \xrightarrow[\text{Hydrolysis}]{H_3O^+} \underset{\text{Hexanoic acid}}{CH_3(CH_2)_4COOH}$$

$$\Big\downarrow PCl_5$$

$$CH_3(CH_2)_4CONH_2 \xleftarrow{NH_3\text{ (excess)}} \underset{\text{Hexanoyl chloride}}{CH_3(CH_2)_4COCl}$$

$$\Big\downarrow Br_2/KOH$$

$$\underset{\text{1-Aminopentane}}{CH_3(CH_2)_4NH_2}$$

(iii) $$\underset{\text{Methanol}}{CH_3OH} \xrightarrow{PCl_5} CH_3Cl \xrightarrow{KCN\text{ (alc.)}} \underset{\text{Ethanenitrile}}{CH_3CN}$$

$$\Big\downarrow H_3O^+$$

$$\underset{\text{Ethanoic acid}}{CH_3COOH}$$

(iv) $$\underset{\text{Ethanamine}}{CH_3CH_2NH_2} \xrightarrow{HCl\,+\,NaNO_2} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

$$\Big\downarrow K_2Cr_2O_7/H_2SO_4$$

$$CH_3COONH_4 \xleftarrow{NH_3} \underset{\text{Ethanoic acid}}{CH_3COOH}$$

$$\Delta \Big\downarrow -H_2O$$

$$\underset{\text{Ethanamide}}{CH_3CONH_2} \xrightarrow{Br_2/KOH} \underset{\text{Methanamine}}{CH_3NH_2}$$

(v) $$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[\text{Reduction}]{LiAlH_4} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{P/I_2} \underset{\text{Ethyl iodide}}{CH_3CH_2I}$$

$$KCN \Big\downarrow -KI$$

$$\underset{\text{Propanoic acid}}{CH_3CH_2COOH} \xleftarrow{H_2O/H^+} \underset{\text{Ethyl cyanide}}{CH_3CH_2CN}$$

(vi) $$\underset{\text{Methanamine}}{CH_3NH_2} \xrightarrow[-N_2,\,-H_2O]{HONO} CH_3OH \xrightarrow{P/I_2} \underset{\text{Methyl iodide}}{CH_3I}$$

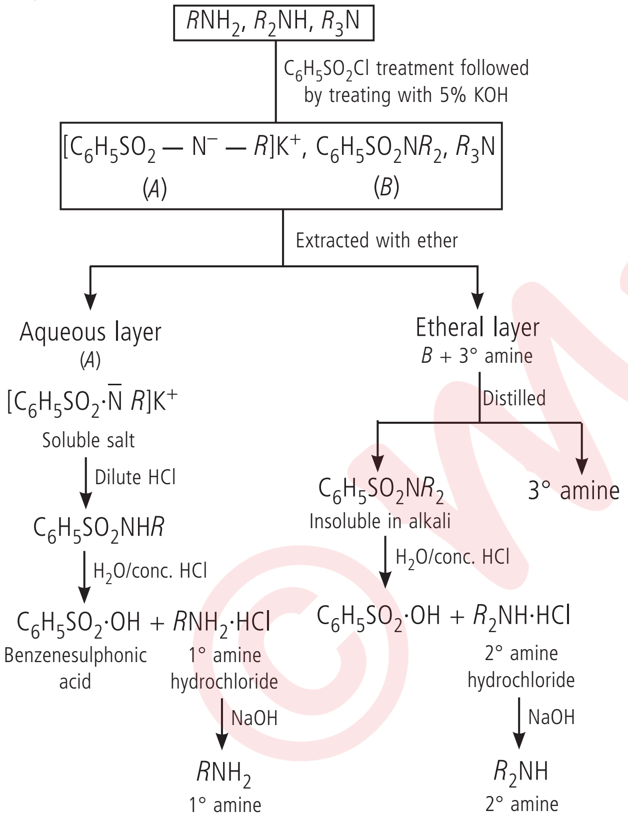
$$KCN \Big\downarrow -KI$$

$$\underset{\text{Ethanamine}}{CH_3CH_2NH_2} \xleftarrow[\text{Reduction}]{Na/C_2H_5OH} CH_3CN$$

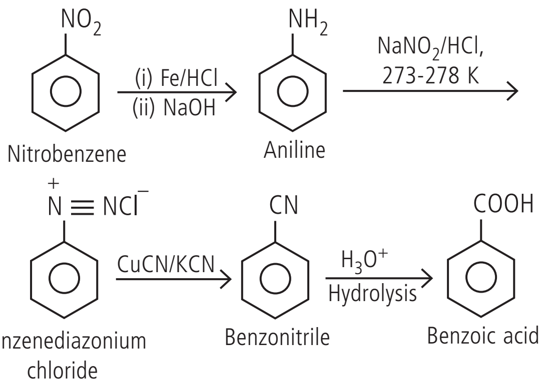
(vii)
$$\begin{tikzcd}
\underset{\text{Nitromethane}}{CH_3NO_2} \arrow[r, "Sn/HCl"] & \underset{\text{Methylamine}}{CH_3NH_2} \arrow[r, "CHCl_3 + KOH"] & CH_3NC \arrow[d, "Na/C_2H_5OH"', "\text{(Reduction)}"] \\
 & & \underset{\text{Dimethylamine}}{CH_3NHCH_3}
\end{tikzcd}$$

(viii)
$$\begin{tikzcd}
\underset{\text{Propanoic acid}}{CH_3CH_2COOH} \arrow[r, "NH_3"] & CH_3CH_2COONH_4 \arrow[d, "\Delta"', "-H_2O"] \\
CH_3CH_2NH_2 \arrow[d, "\text{dil. HCl} + NaNO_2"'] & CH_3CH_2CONH_2 \arrow[l, "Br_2/KOH"'] \\
CH_3CH_2OH \arrow[r, "K_2Cr_2O_7", "H_2SO_4"'] & \underset{\text{Ethanoic acid}}{CH_3COOH}
\end{tikzcd}$$

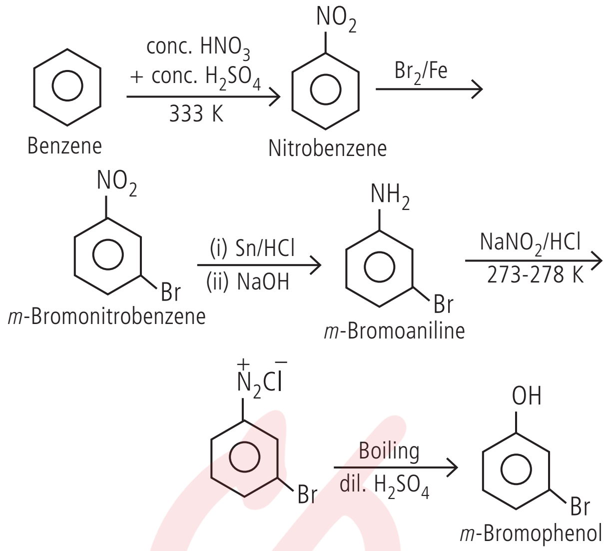
**4.** 1°, 2° and 3° amines can be distinguished by Hinsberg's reagent



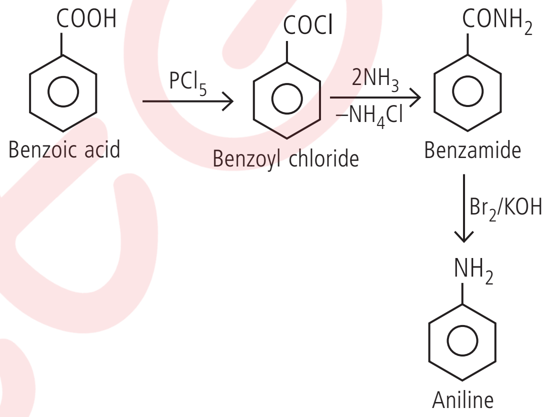
**5.** (i)



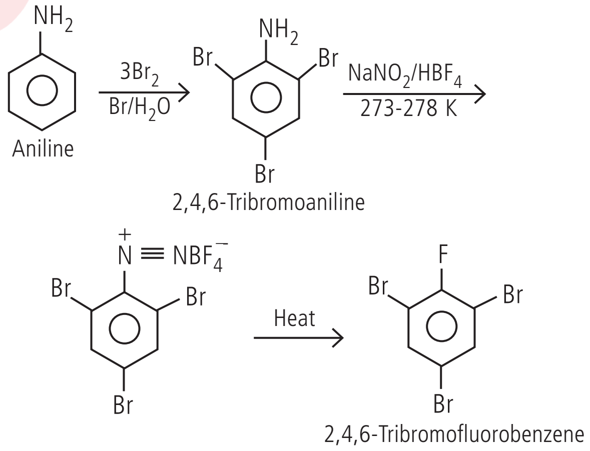
(ii)



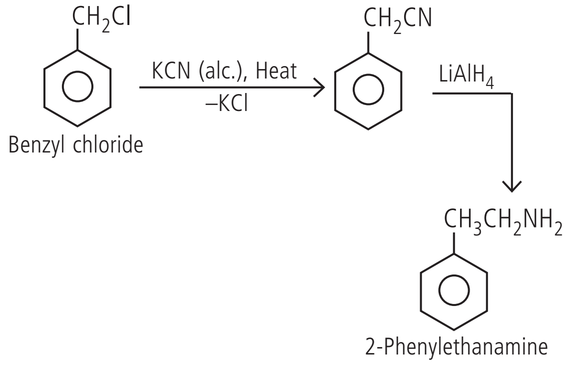
(iii)



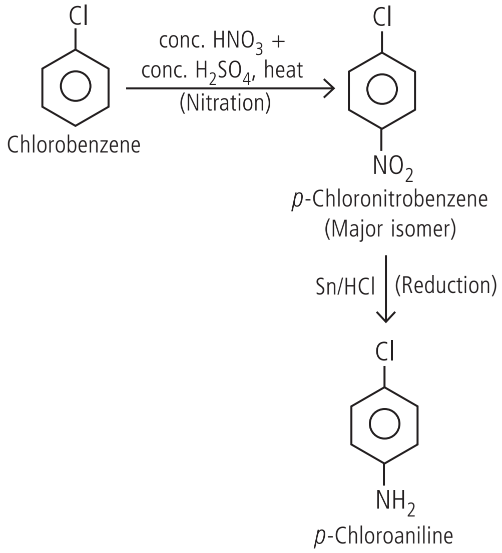
(iv)



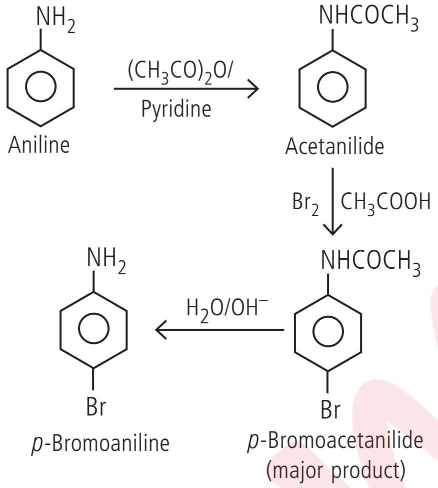
(v)



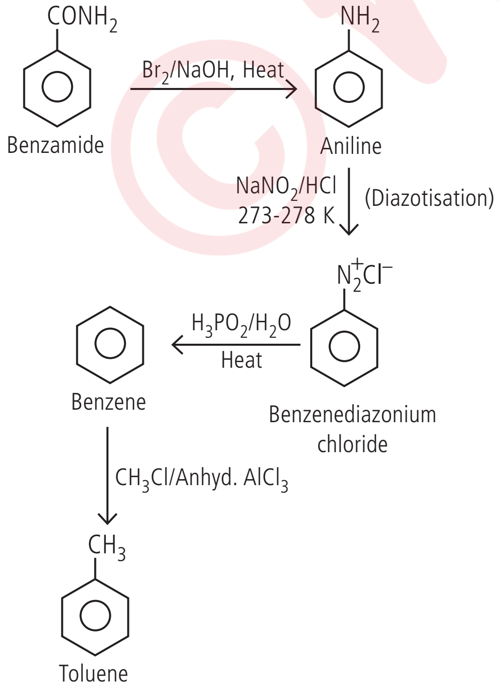
(vi)



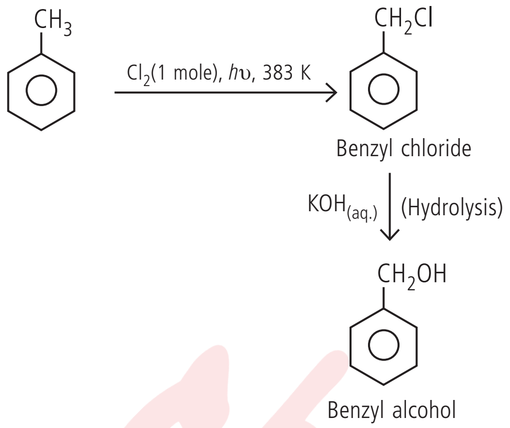
(vii)



(viii)



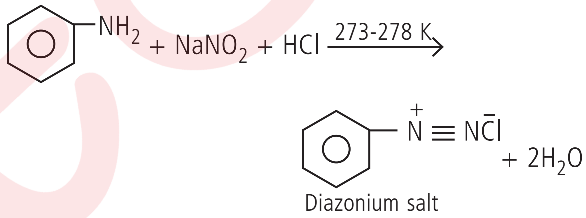
(ix) Write reactions from aniline to toluene as given in (viii) and then,



**6.** Amines do not directly react with nitrous acid, rather they react with a mixture of dil. HCl and $NaNO_2$ and $HNO_2$ is produced in situ.

The reactions are:

(i)



(ii) $CH_3CH_2NH_2 + NaNO_2 + HCl \xrightarrow{273\text{-}278\ K} [CH_3CH_2-\overset{+}{N}\equiv N]Cl^- \xrightarrow{H_2O} CH_3CH_2OH + N_2\uparrow + HCl$

**7.** (i) Loss of a proton from an amine gives $RNH^-$ ion while loss of a proton from alcohol gives $RO^-$ ion as shown below:

$$R-NH_2 \longrightarrow R-NH^- + H^+$$
$$R-O-H \longrightarrow R-O^- + H^+$$

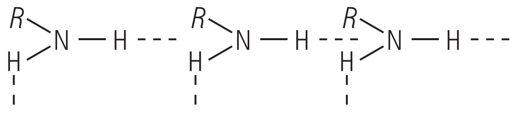
As O is more electronegative than N, $RO^-$ can accommodate the negative charge more easily than the $RNH^-$ can.

As, $RO^-$ is more stable than $RNH^-$ and hence the former is formed more. As a result, amines are less acidic than alcohols.

(ii) At boiling point, the molecules in a compound break free from their intermolecular forces and escape into the vapour phase. Weaker the inter-molecular forces, lower will be the boiling point.

In 1° amines, there is strong H-bonding that binds the amine molecules together. Whereas in 3° amine absence of H on N atom prevents hydrogen bonding completely.

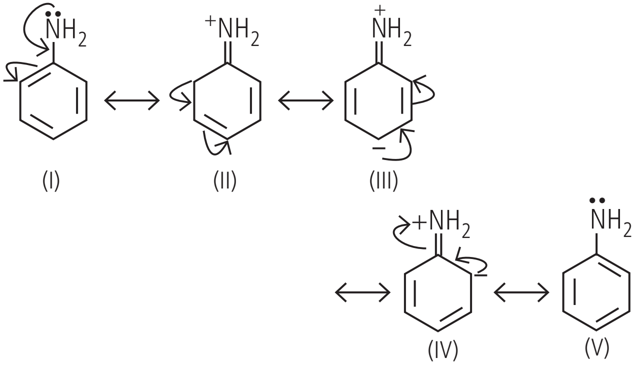
This is why 1° amines have higher boiling point.



H-bonding in 1° amines

(iii) The basic nature of amines is a result of the presence of *l.p.* of electron on the N atom. Also the electron density is increased on N due to the +*I* effect of alkyl group.

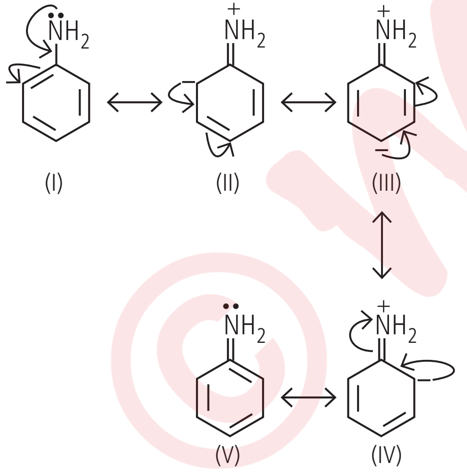
In aryl amines the *l.p.* on N is involved in resonance with the benzene ring and hence less available for protonation.



In aliphatic amines there is no such delocalisation and hence it is more basic.

## Topic 3

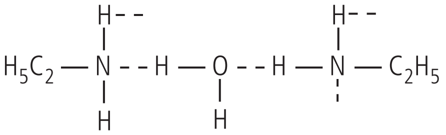
**1.** (i) If the p$K_b$ value of any base or compound is higher than that of another, it implies that the former is a weaker base than the latter. In aniline, the N-atom is attached to the benzene ring and therefore the lone pair on N is delocalised over the entire benzene ring. As a result, it cannot accept a proton or any other electrophile.



This is why it has a lower $K_b$ value (lower basic strength) and high corresponding p$K_b$ value.

In methylamine, $CH_3NH_2$, the electron density on nitrogen is greater than that in case of aniline. This is because $-CH_3$ group in methylamine, by virtue of its +*I* effect, increases electron density on *N*, which is more available for protonation.

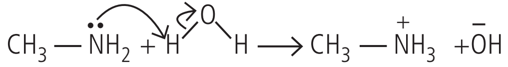
(ii) Any compound capable of forming hydrogen bonds with water, dissolves in it. Ethylamine is able to do the same and hence it is soluble in water.



$$H_5C_2-\underset{H}{\overset{H--}{N}}--H-\underset{H}{O}--H-\overset{H--}{N}-C_2H_5$$

However, in aniline, the bulky hydrocarbon part $-C_6H_5$ prevents the formation of effective hydrogen bonding and therefore it is not soluble.

(iii) The formation of hydrated ferric oxide may be understood by taking into consideration the basic strength of $CH_3NH_2$. In presence of $CH_3NH_2$, water hydrolyses as

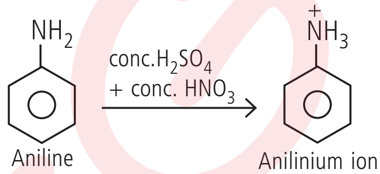


$$CH_3-\ddot{N}H_2+H-O-H \longrightarrow CH_3-\overset{+}{N}H_3+\overset{-}{O}H$$

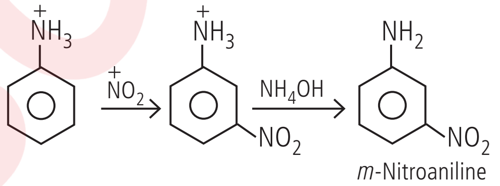
These $\overline{O}H$ ions react with $FeCl_3$ as:

$$2FeCl_3 + 6\overline{O}H \longrightarrow 2Fe(OH)_3 \text{ or } \underset{\text{Hydrated ferric oxide}}{Fe_2O_3 \cdot 3H_2O}$$

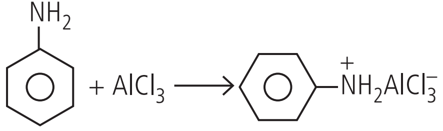
(iv) During nitration, the nitration mixture used (conc. $HNO_3$ and conc. $H_2SO_4$) protonates the $NH_2$ group to produce anilinium ion as



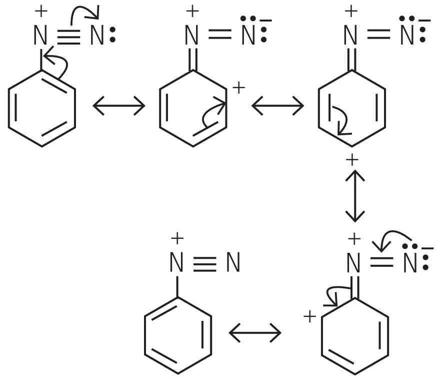
This anilinium ion acts as a deactivating group and directs the incoming nucleophile $-\overset{+}{N}O_2$ to *meta* position and the *meta*-isomer of nitroaniline is obtained.



(v) In Friedel — Crafts reaction, $AlCl_3$ is added as a catalyst which is a Lewis acid. It forms a salt with aniline due to which the nitrogen of aniline acquires positive charge. This positively charged nitrogen acts as a strong deactivating group, hence aniline does not undergo Friedel — Crafts reaction.



(vi) Diazonium salts carry a N atom with a positive charge. This positive charge is well dispersed in aromatic diazonium salts through resonance as shown below:



Such a charge delocalisation is not possible in aliphatic amines and hence they are less stable.

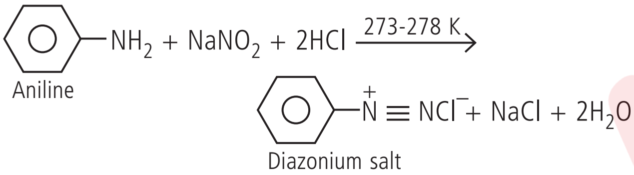
(vii) Gabriel phthalimide reaction gives pure primary amines without any contamination of secondary and tertiary amines. Therefore, it is preferred for synthesising primary amines.

**2.** **(i) Carbylamine reaction :** Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamine reaction or isocyanide test and is used as a test for primary amines.

$$R - NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{Heat}} \underset{\substack{\text{Carbylamine} \\ \text{(foul smell)}}}{R - NC} + 3KCl + 3H_2O$$

**(ii) Diazotisation:** The conversion of primary aromatic amines into diazonium salts is known as diazotisation.

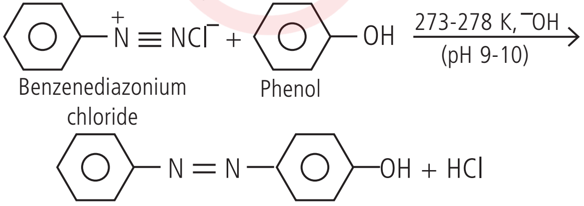
The conversion is brought about by reacting the amine with $HNO_2$ which is prepared *in situ*.



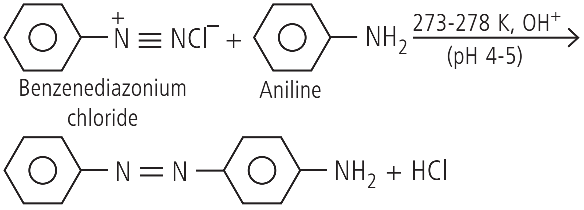
**(iii) Hofmann's bromamide reaction :** Primary amides when heated with $Br_2$ and (aqueous or ethanoic solution of) NaOH lose a carbon atom and are converted to the corresponding amines. It is an example of step-down reaction.

$$\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4NaOH \xrightarrow{\Delta} CH_3NH_2 + 2NaBr + Na_2CO_3 + 2H_2O$$

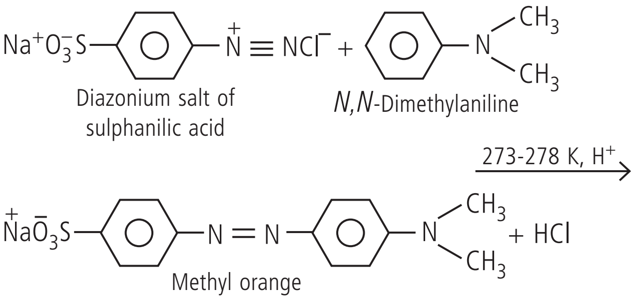
**(iv) Coupling reaction :** The reaction of diazonium salts with phenols and aromatic amines to form azo compounds having an extended conjugate system with both aromatic rings joined through the —N=N— bond, is called coupling reaction. In this reaction, the nitrogen atoms of the diazo group are retained in the product. The coupling with phenols takes place in mildly alkaline medium while that with amines occurs under faintly acidic conditions. For example,



*p*-Hydroxyazobenzene(orange dye)

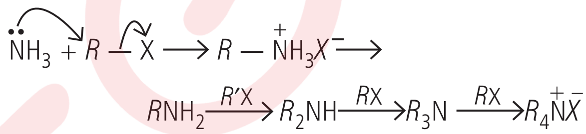


*p*-Aminoazobenzene(yellow dye)



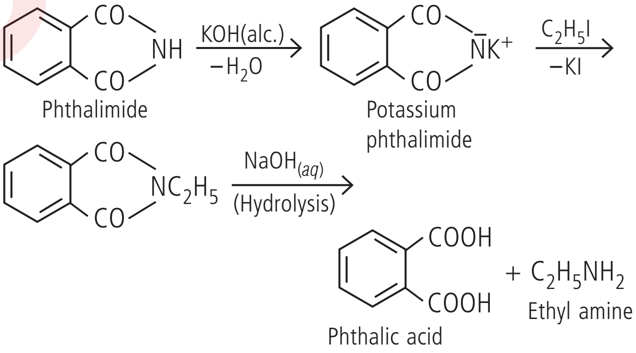
Coupling generally occurs at the *p*-position with respect to the hydroxyl or the amino group, if free, otherwise it takes place at the *o*-position.

**(v) Ammonolysis:** The process of cleavage of the C—*X* bond in alkyl halides by ammonia molecule is called ammonolysis. 1° amine thus obtained behaves as a nucleophile and further reacts with alkyl halide to form 2°, 3° and finally quaternary ammonium salt.



$$\ddot{N}H_3 + R - X \longrightarrow R - \overset{+}{N}H_3X^- \longrightarrow RNH_2 \xrightarrow{R'X} R_2NH \xrightarrow{RX} R_3N \xrightarrow{RX} R_4\overset{+}{N}\overset{-}{X}$$

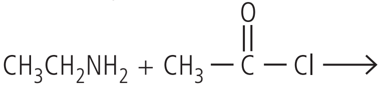
**(vi) Gabriel phthalimide synthesis :** In this reaction phthalimide is converted into its potassium salt by treating it with alcoholic potassium hydroxide. Then potassium phthalimide is heated with an alkyl halide to yield an *N*-alkylphthalimide which is hydrolysed to phthalic acid and primary amine by alkaline hydrolysis.



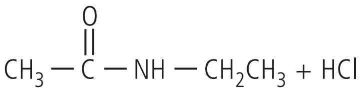
This synthesis is very useful for the preparation of pure aralkyl and aliphatic primary amines. However, aromatic primary amines cannot be prepared by this method.

**(vii) Acetylation :** The process of introducing an acetyl group ($CH_3-\overset{O}{\overset{\|}{C}}-$) into a molecule is called acetylation. The reaction occurs by nucleophilic substitution. There occurs a replacement of hydrogen atom of $-NH_2$ or >NH by the acetyl group.

Common acetylating agents used are acetyl chloride and acetic anhydride.

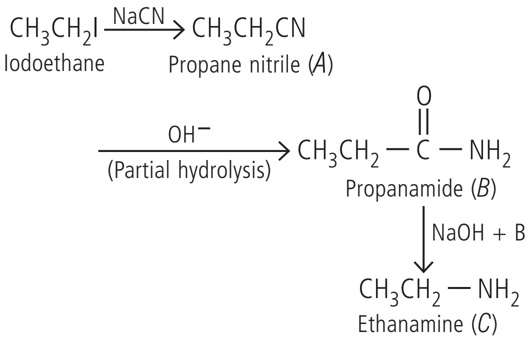


$$CH_3CH_2NH_2 + CH_3 - \overset{O}{\overset{\|}{C}} - Cl \longrightarrow$$



$$CH_3-\overset{\overset{O}{\|}}{C}-NH-CH_2CH_3 + HCl$$

N-Ethylacetamide



**3**. (i) $CH_3CH_2I \xrightarrow{NaCN} CH_3CH_2CN$

Iodoethane → Propane nitrile (A)

$$\xrightarrow[\text{(Partial hydrolysis)}]{OH^-} CH_3CH_2-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{NaOH + Br_2} CH_3CH_2-NH_2$$

Propanamide (B); Ethanamine (C)

(ii) $C_6H_5N_2Cl \xrightarrow{CuCN} C_6H_5CN \xrightarrow[\text{Hydrolysis}]{H_2O/H^+} C_6H_5COOH$

Benzenediazonium chloride; Cyanobenzene (A); Benzoic acid (B)

$$[C_6H_5COONH_4] \xleftarrow{NH_3} C_6H_5COOH$$

$$[C_6H_5COONH_4] \xrightarrow{Heat} C_6H_5CONH_2$$

Benzamide (C)

(iii) $CH_3CH_2Br \xrightarrow{KCN} CH_3CH_2CN \xrightarrow[\text{(Reduction)}]{LiAlH_4} CH_3CH_2CH_2NH_2 \xrightarrow{HNO_2,\ 0°C} CH_3CH_2CH_2OH$

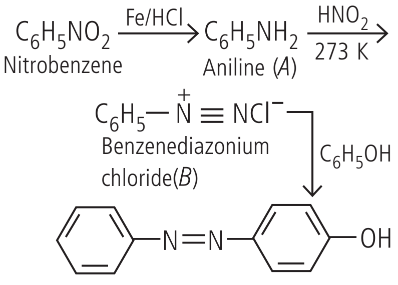
Ethyl bromide; Ethyl cyanide (A); Propyl amine (B); Propanol (C)

(iv) $C_6H_5NO_2 \xrightarrow{Fe/HCl} C_6H_5NH_2 \xrightarrow[273\ K]{NaNO_2/HCl} C_6H_5\overset{+}{N}\equiv NCl^- \xrightarrow[\text{Heat}]{H_2O/H^+} C_6H_5OH$

Nitrobenzene; Aniline (A); Benzenediazonium chloride (B); Phenol (C)

(v) $CH_3COOH \xrightarrow[\text{Heat}]{NH_3} CH_3CONH_2 \xrightarrow{NaOBr} CH_3NH_2 \xrightarrow{NaNO_2/HCl} CH_3OH$

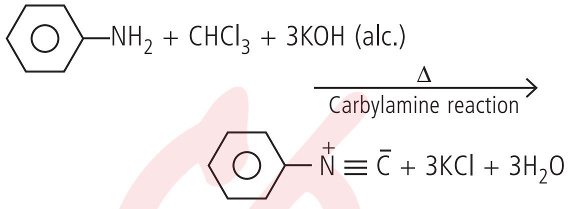
Ethanoic acid; Ethanamide (A); Methanamine (B); Methanol (C)



(vi) $C_6H_5NO_2 \xrightarrow{Fe/HCl} C_6H_5NH_2 \xrightarrow[273\ K]{HNO_2} C_6H_5-\overset{+}{N}\equiv NCl^- \xrightarrow{C_6H_5OH}$

Nitrobenzene; Aniline (A); Benzenediazonium chloride(B)

p-Hydroxyazobenzene (C)



**4.** (i) $C_6H_5-NH_2 + CHCl_3 + 3KOH\ (alc.) \xrightarrow[\text{Carbylamine reaction}]{\Delta} C_6H_5-\overset{+}{N}\equiv\bar{C} + 3KCl + 3H_2O$

(ii) $C_6H_5\overset{+}{N_2}\overset{-}{Cl} + H_3PO_2 + H_2O \xrightarrow[\text{(Reduction)}]{Cu^+} C_6H_6N_2 + H_3PO_3 + HCl$

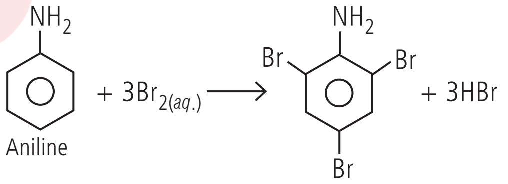
Benzenediazonium chloride; Benzene

(iii) $C_6H_5NH_2 + H_2SO_4\ (conc.) \longrightarrow C_6H_5\overset{+}{N}H_3HSO_4^-$

Aniline; Anilinium hydrogen sulphate

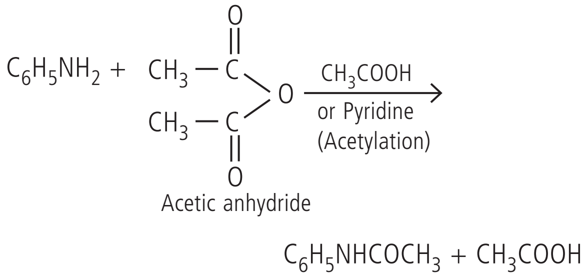
(iv) $C_6H_5\overset{+}{N_2}\overset{-}{Cl} + C_2H_5OH \xrightarrow{Reduction} C_6H_6 + CH_3CHO + N_2 + HCl$

Benzenediazonium chloride; Benzene; Ethanal



(v) Aniline $+ 3Br_{2(aq.)} \longrightarrow$ $+ 3HBr$

2, 4, 6-Tribromoaniline



(vi) $C_6H_5NH_2 + (CH_3CO)_2O \xrightarrow[\text{or Pyridine (Acetylation)}]{CH_3COOH} C_6H_5NHCOCH_3 + CH_3COOH$

Acetic anhydride; Acetanilide

(vii) $C_6H_5\overset{+}{N_2}\overset{-}{Cl} \xrightarrow{HBF_4} C_6H_5\overset{+}{N_2}BF_4^- \xrightarrow[\text{Heat}]{NaNO_2/Cu} C_6H_5NO_2 + N_2 + NaBF_4$

Benzenediazonium chloride; Aniline; Nitrobenzene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