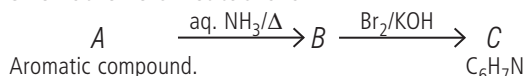


Amines

Topic 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).

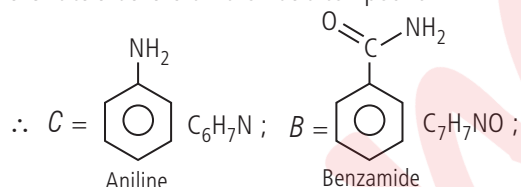
2. Given scheme of reactions is



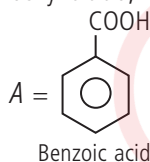
(i) Looking at the given scheme, we can clearly see that reaction $B \rightarrow C$ is Hofmann bromamide reaction.

Thus, C is an amine (1°) while B must be an amide with molecular formula $\text{C}_7\text{H}_7\text{NO}$.

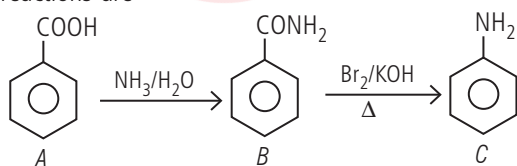
(ii) Further, the ratio of C and H in B and C are indicative of the fact that it is an aromatic compound.



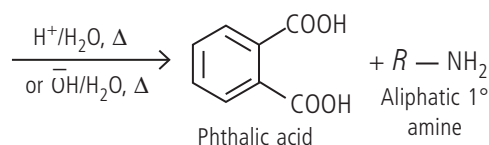
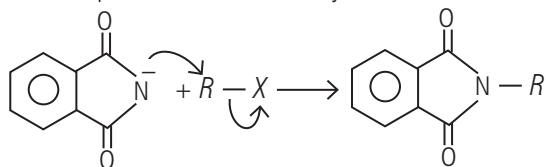
Since, B is formed by the action of ammonia on A , A must be a carboxylic acid,



The reactions are



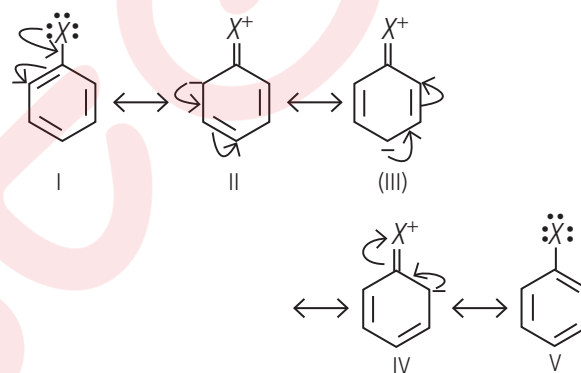
3. (i) Gabriel phthalimide reaction involves the nucleophilic attack of the phthalimide on the alkyl halide.



(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 $\text{C}-\text{X}$ bond in aryl halide. Consider the following structures :



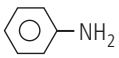
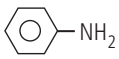
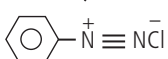
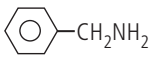
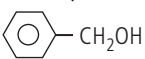
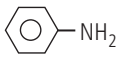
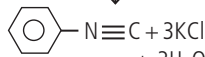
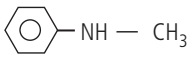
From the resonance structures we see that the $\text{C}-\text{X}$ bond has a double bond character in structures II, III and IV and this makes cleavage of $\text{C}-\text{X}$ bond difficult.

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

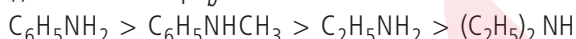
Topic 2

1.

Test / Reagent	Compound I	Compound II
(i) Carbylamine test $\text{CHCl}_3 + \text{alc. KOH} + \Delta$	CH_3NH_2 (1° amine) Methylamine \downarrow $\text{CH}_3\text{NC} + 3\text{KCl} + 3\text{H}_2\text{O}$ foul smell	$(\text{CH}_3)_2\text{NH}$ (2° amine) Dimethylamine \downarrow No reaction
(ii) Hinsberg's test $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$	$\text{R}_2\text{NH} + \text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ \downarrow $\text{C}_6\text{H}_5\text{SO}_2\text{NR}_2 + \text{HCl}$ (Insoluble in alkali)	$\text{R}_3\text{N} + \text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ \downarrow No reaction

(iii) Nitrous acid test $\text{NaNO}_2 + \text{HCl}$	$\text{C}_2\text{H}_5\text{NH}_2$ Ethylamine (1° amine) ↓ $\text{ROH} + \text{N}_2\uparrow + \text{HCl}$ (effervescence)	 Aniline ↓ $\text{C}_6\text{H}_5 - \text{N}_2^+\text{Cl}^-$ Benzenediazonium chloride
(iv) Azo dye test $\text{NaNO}_2 + \text{dil. HCl}$ (0-5°C)	 Aniline ↓  Benzene diazonium chloride	 Benzylamine ↓  $+ \text{N}_2\uparrow + \text{HCl}$ (effervescence)
(v) Carbylamine test $\text{CHCl}_3 + \text{Alc. KOH} + \Delta$	 Aniline (1° amine) ↓  (Unpleasant odour)	 <i>N</i> -methylaniline (2° amine) ↓ No reaction

2. (i) The order of pK_b will decrease as:



(ii) $\text{C}_6\text{H}_5\text{NH}_2 < \text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2 < \text{CH}_3\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH}$

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



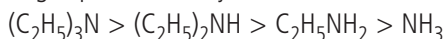
The availability of *l.p.* on N of *p*-nitroaniline is drastically reduced by presence of electron withdrawing $-\text{NO}_2$ group on it.

In contrast, presence of electron releasing $-\text{CH}_3$ group increases the electron density on N atom and improves basicity in *p*-toluidine.

(b) $\text{C}_6\text{H}_5\text{NH}_2 < \text{C}_6\text{H}_5\text{NHCH}_3 < \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$

Involvement of *l.p.* of N in resonance causes aniline to have low basicity. In *N*-methylaniline, the $-\text{Me}$ group through its $+I$ effect improves the electron density on N and therefore its basic strength increases. In Benzylamine, the $-\text{NH}_2$ 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 :



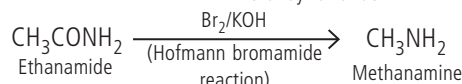
In gas phase, the stabilization by solvation is not present and hence basic strength follows the expected order based on $+I$ effect of alkyl groups.

(v) $(\text{CH}_3)_2\text{NH} < \text{C}_2\text{H}_5\text{NH}_2 < \text{C}_2\text{H}_5\text{OH}$

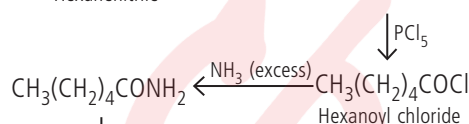
(vi) $\text{C}_6\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH} < \text{C}_2\text{H}_5\text{NH}_2$

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) $\text{CH}_3\text{COOH} \xrightarrow{\text{SOCl}_2} \text{CH}_3\text{COCl} \xrightarrow{\text{NH}_3 (\text{excess})}$



(ii) $\text{CH}_3(\text{CH}_2)_4\text{CN} \xrightarrow{\text{H}_3\text{O}^+} \text{CH}_3(\text{CH}_2)_4\text{COOH}$

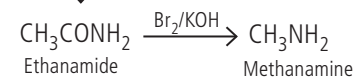
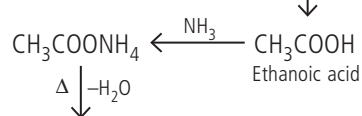


(iii) $\text{CH}_3\text{OH} \xrightarrow{\text{PCl}_5} \text{CH}_3\text{Cl} \xrightarrow{\text{KCN} (\text{alc.})} \text{CH}_3\text{CN} \xrightarrow{\text{H}_3\text{O}^+} \text{CH}_3\text{COOH}$

Methanol Ethanenitrile Ethanoic acid

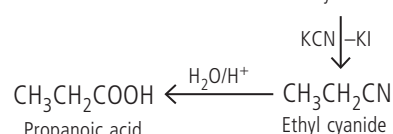
(iv) $\text{CH}_3\text{CH}_2\text{NH}_2 \xrightarrow{\text{HCl} + \text{NaNO}_2} \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4} \text{CH}_3\text{COOH}$

Ethanamine Ethanol Ethanoic acid



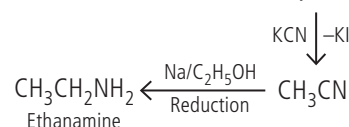
(v) $\text{CH}_3\text{COOH} \xrightarrow{\text{LiAlH}_4} \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{P/I}_2} \text{CH}_3\text{CH}_2\text{I}$

Ethanoic acid Ethanol Ethyl iodide



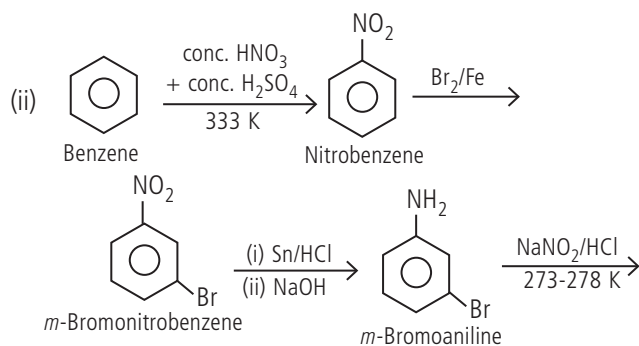
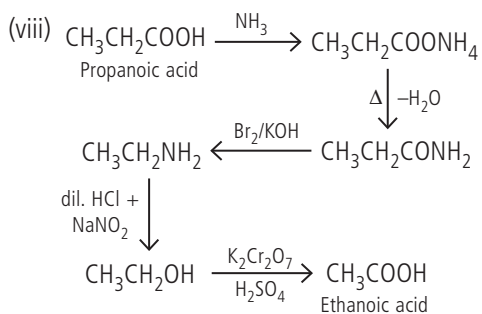
(vi) $\text{CH}_3\text{NH}_2 \xrightarrow{\text{HONO}, -\text{N}_2, -\text{H}_2\text{O}} \text{CH}_3\text{OH} \xrightarrow{\text{P/I}_2} \text{CH}_3\text{I}$

Methanamine Methyl iodide

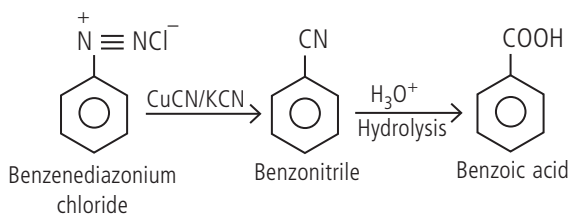
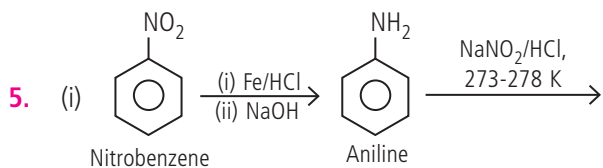
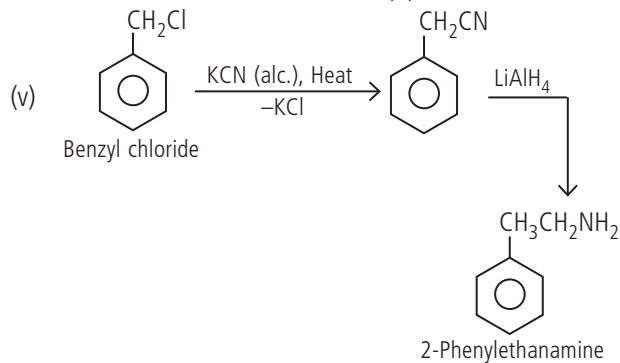
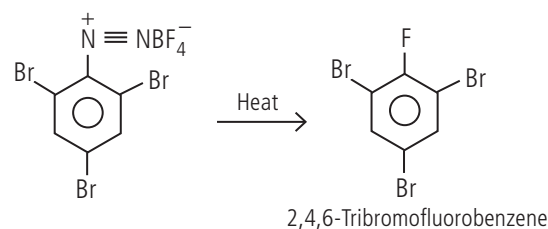
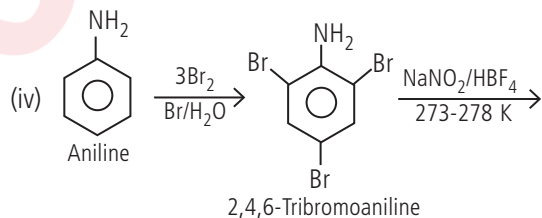
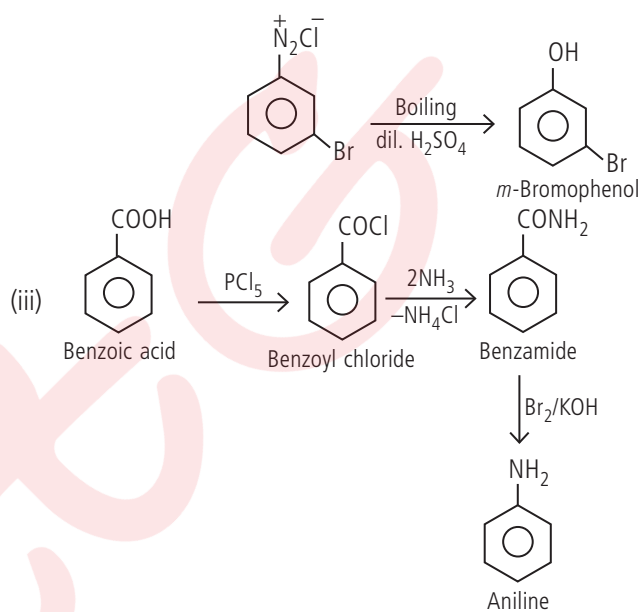
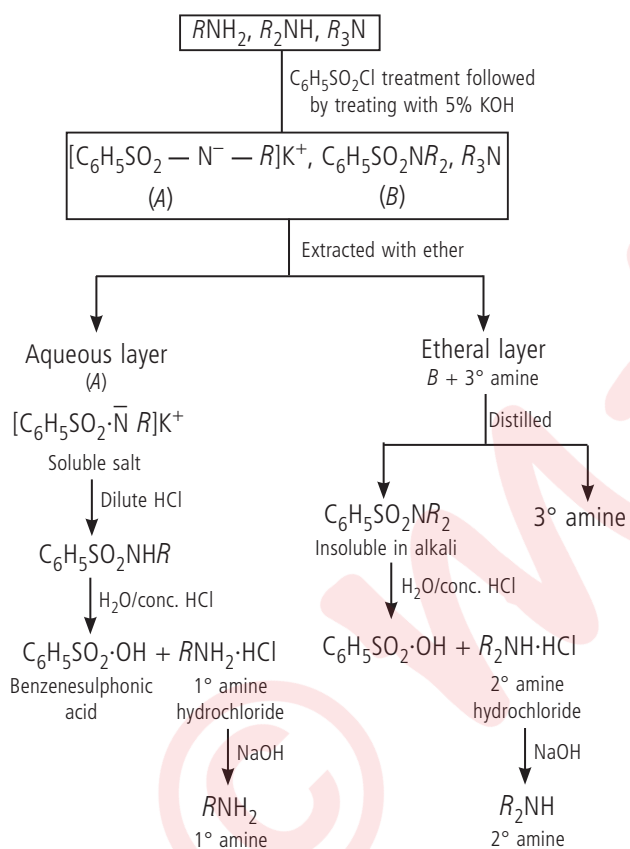


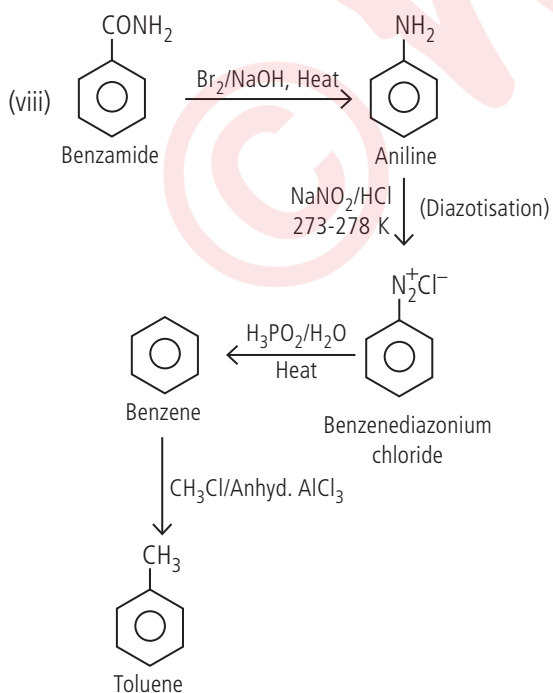
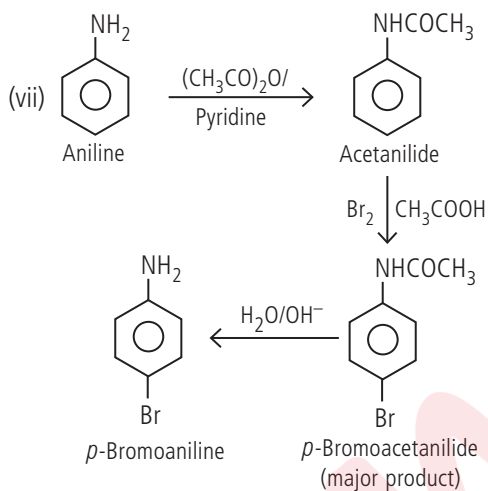
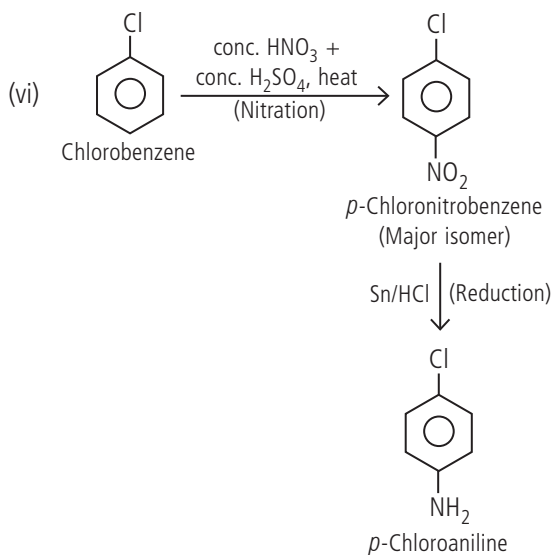
(vii) $\text{CH}_3\text{NO}_2 \xrightarrow{\text{Sn}/\text{HCl}} \text{CH}_3\text{NH}_2 \xrightarrow{\text{CHCl}_3 + \text{KOH}} \text{CH}_3\text{NC} \xrightarrow{\text{Na}/\text{C}_2\text{H}_5\text{OH} (\text{Reduction})} \text{CH}_3\text{NHCH}_3$

Nitromethane Methylamine Dimethylamine

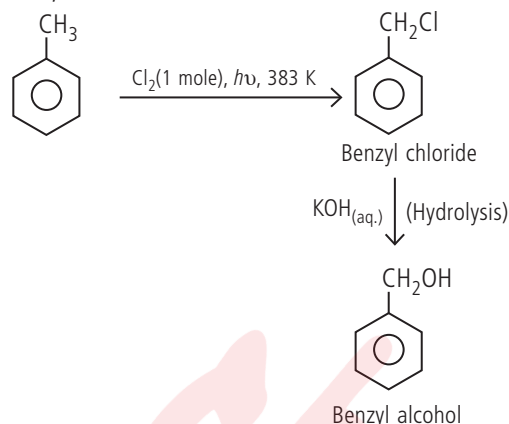


4. 1°, 2° and 3° amines can be distinguished by Hinsberg's reagent



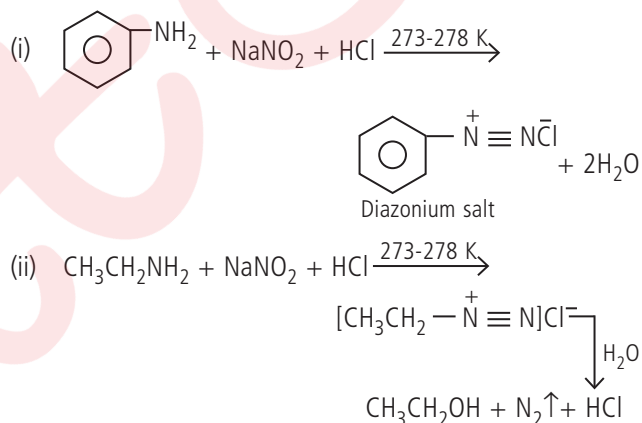


(ix) Write reactions from aniline to toluene as given in (viii) and then,

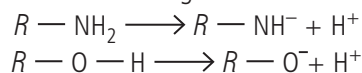


6. Amines do not directly react with nitrous acid, rather they react with a mixture of dil. HCl and NaNO₂ and HNO₂ is produced in situ.

The reactions are:



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:



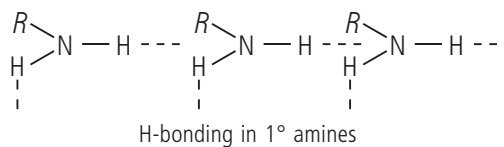
As O is more electronegative than N, RO⁻ can accommodate the negative charge more easily than the RNH⁻ can.

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.

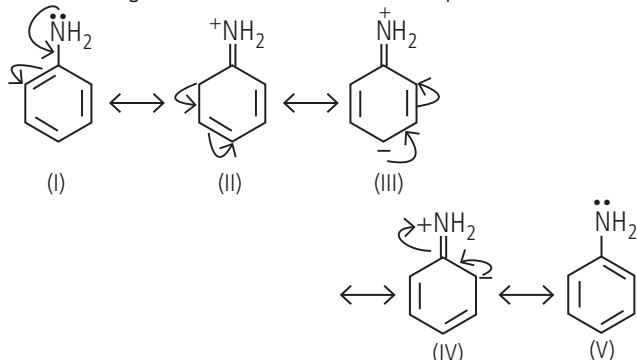
In 1° amines, there is strong H-bonding that binds the amine molecules together. Whereas in 3° amine absence of H on N atom prevents hydrogen bonding completely.

This is why 1° amines have higher boiling point.



(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.

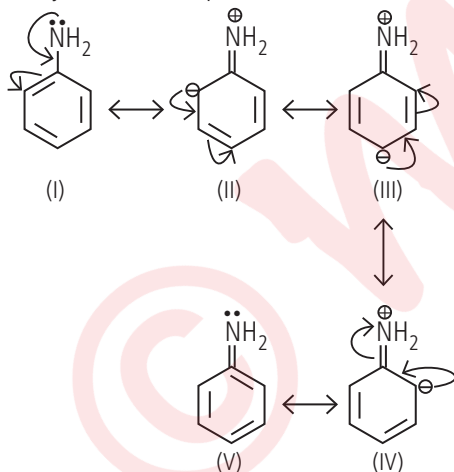
In aryl amines the *l.p.* on N is involved in resonance with the benzene ring and hence less available for protonation.



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

Topic 3

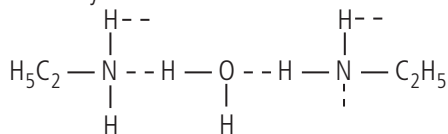
1. (i) If the pK_b value of any base or compound is higher than that of another, it implies that the former is a weaker base than the latter. In aniline, the N-atom is attached to the benzene ring and therefore the lone pair on N is delocalised over the entire benzene ring. As a result, it cannot accept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



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

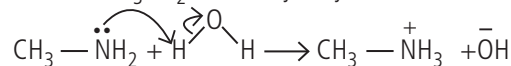
In methylamine, CH_3NH_2 , the electron density on nitrogen is greater than that in case of aniline. This is because $-\text{CH}_3$ group in methylamine, by virtue of its +I effect, increases electron density on N, which is more available for protonation.

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

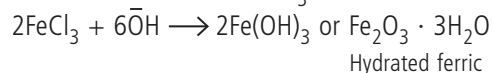


However, in aniline, the bulky hydrocarbon part $-\text{C}_6\text{H}_5$ prevents the formation of effective hydrogen bonding and therefore it is not soluble.

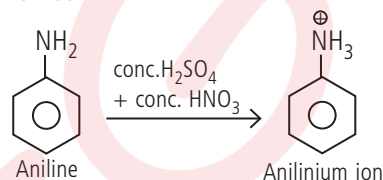
(iii) The formation of hydrated ferric oxide may be understood by taking into consideration the basic strength of CH_3NH_2 . In presence of CH_3NH_2 , water hydrolyses as



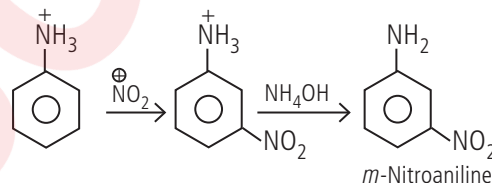
These $\overset{\ominus}{\text{O}}\text{H}$ ions react with FeCl_3 as:



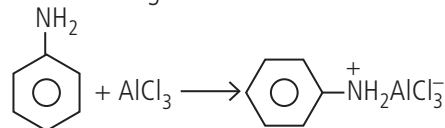
(iv) During nitration, the nitration mixture used (conc. HNO_3 and conc. H_2SO_4) protonates the NH_2 group to produce anilinium ion as



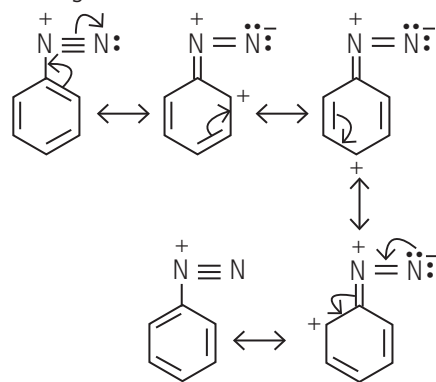
This anilinium ion acts as a deactivating group and directs the incoming nucleophile $-\overset{\oplus}{\text{N}}\text{O}_2$ to *meta* position and the *meta*-isomer of nitroaniline is obtained.



(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.



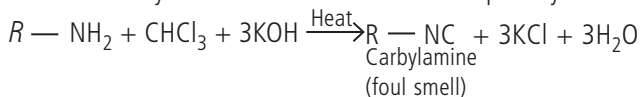
(vi) Diazonium salts carry a N atom with a positive charge. This positive charge is well dispersed in aromatic diazonium salts through resonance as shown below:



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

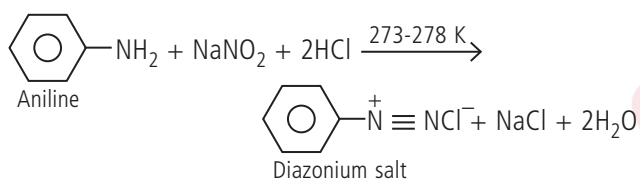
(vii) Gabriel phthalimide reaction gives pure primary amines without any contamination of secondary and tertiary amines. Therefore, it is preferred for synthesising primary amines.

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.

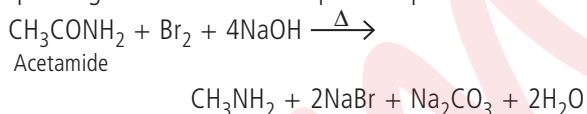


(ii) Diazotisation: The conversion of primary aromatic amines into diazonium salts is known as diazotisation.

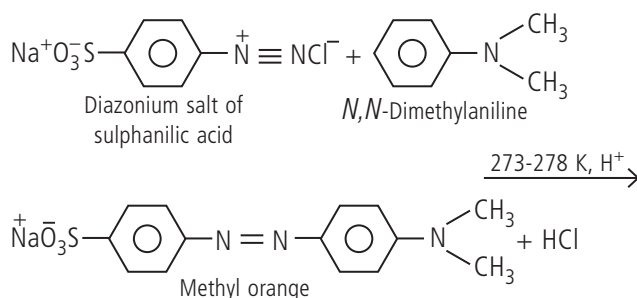
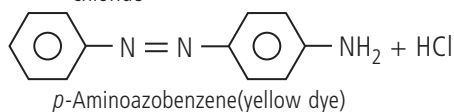
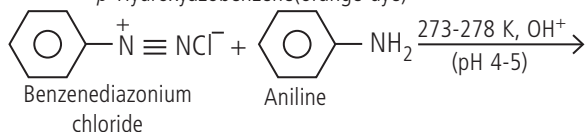
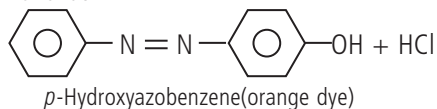
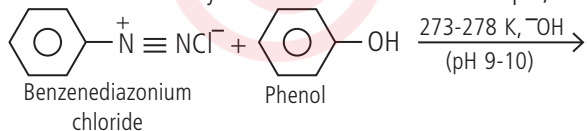
The conversion is brought about by reacting the amine with HNO_2 which is prepared *in situ*.



(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.

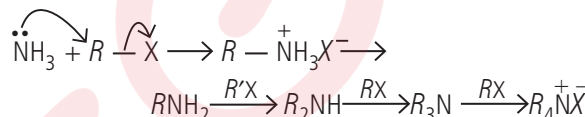


(iv) Coupling reaction : The reaction of diazonium salts with phenols and aromatic amines to form azo compounds having an extended conjugate system with both aromatic rings joined through the $-N=N-$ bond, is called coupling reaction. In this reaction, the nitrogen atoms of the diazo group are retained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

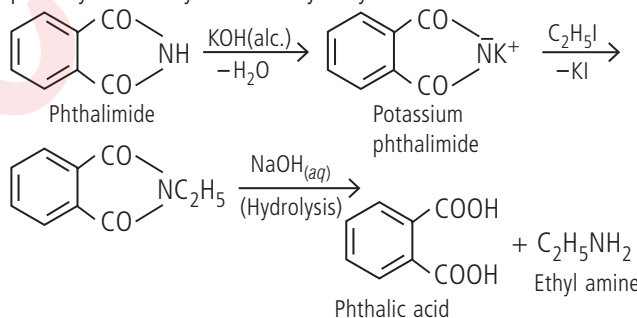


Coupling generally occurs at the *p*-position with respect to the hydroxyl or the amino group, if free, otherwise it takes place at the *o*-position.

(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.



(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 aromatic and aliphatic primary amines. However, aromatic primary amines cannot be prepared by this method.

(vii) Acetylation : The process of introducing an acetyl group

($CH_3-C(=O)-$) 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.

