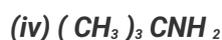
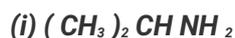


Class 12 Chemistry NCERT Solutions Chapter 13 Amines – Important Questions

Q . 13.1 :

Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines.



Solution :

(i) 1 - Methylethanamine (1^o amine)

(ii) Propan - 1 - amine (1^o amine)

(iii) N - Methyl - 2 - methyl ethanamine (2^o amine)

(iv) 2 - Methylpropan - 2 - amine (1^o amine)

(v) N - Methyl benzamine or N - methylaniline (2^o amine)

(vi) N - Ethyl - N - methyl ethanamine (3^o amine)

(vii) 3 - Bromobenzenamine or 3 - bromoaniline (1^o amine)

Q . 13.2 :

Give one chemical test to distinguish between the following pairs of compounds.

(i) Methylamine and dimethylamine (ii) Secondary and tertiary amines

(iii) Ethylamine and aniline (iv) Aniline and benzylamine

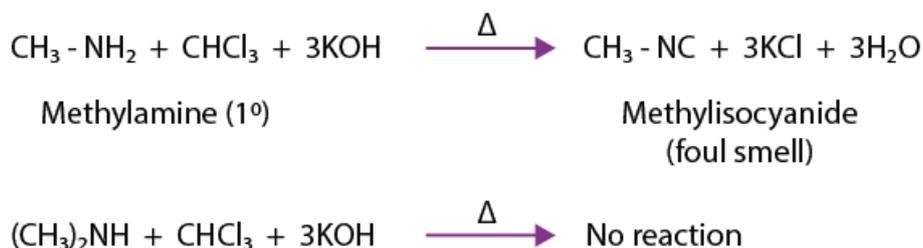
(v) Aniline and N-methylaniline

Solution :

(i) **Dimethylamine and Methylamine** can be made notable by the carbylamine test.

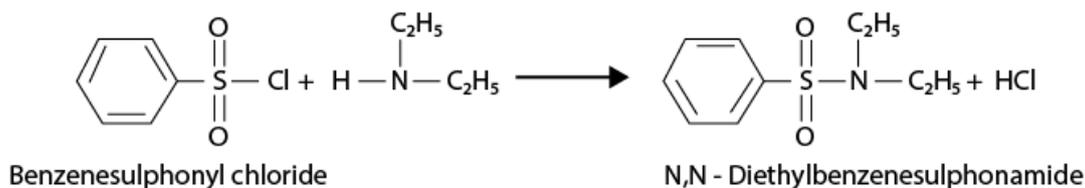
Carbylamine test: Foul-smelling isocyanides or carbylamines are formed when Aliphatic and aromatic primary amines are heated with chloroform and ethanol potassium hydroxide.

Methylamine (being an aliphatic primary amine) gives a positive carbylamine test, but dimethylamine does not.



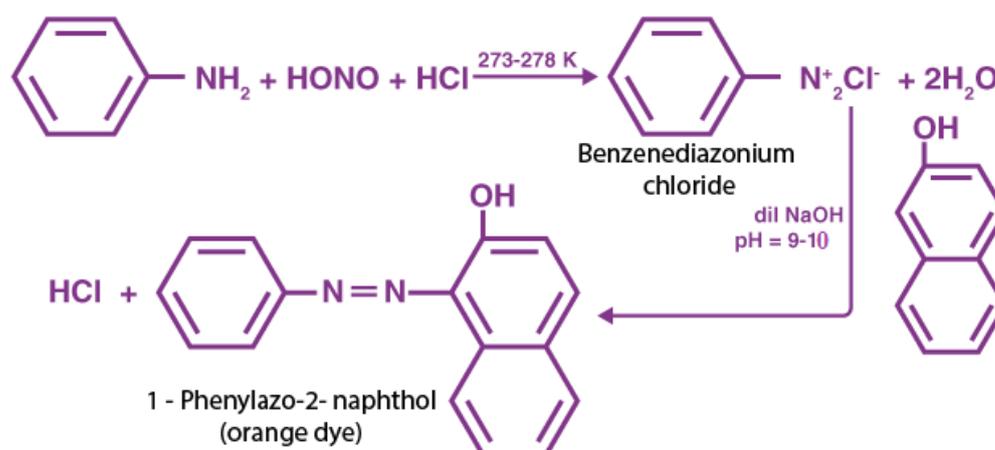
(ii) Tertiary amines and Secondary can be made notable by allowing them to react with Hinsberg's reagent (benzene sulphonyl chloride, $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$).

A product which is insoluble alkali is formed when Secondary amines react with Hinsberg's reagent to form a product that is insoluble in an alkali. For example, N, N – diethyl amine reacts with Hinsberg's reagent to form N, N – diethyl benzene sulphonamide, which is insoluble in an alkali. Tertiary amines, however, do not react with Hinsberg's reagent.

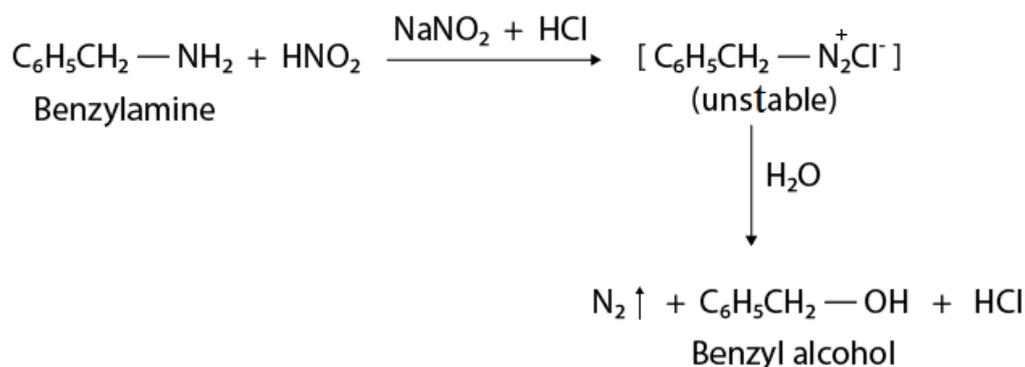


(iii) Azo-dye test can distinguish aniline & Ethylamine.

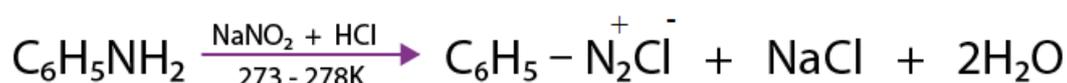
When aromatic amines are made to react with HNO_2 ($\text{NaNO}_2 + \text{dil. HCl}$) at $0 - 5^\circ\text{C}$, A dye is obtained, which is followed by making it react with the alkaline solution of 2 – naphthol. The dye is observed to be in the following colours: yellow, red, or orange in colour. A brisk effervescence is given out by Aliphatic amines due to the evolution of N_2 gas under analogous conditions.



(iv) Benzylamine and Aniline can be made notable by reacting them with nitrous acid, which is made ready in situ from sodium nitrite and mineral acid. Unstable diazonium salt is formed when nitrous acid reacts with Benzylamine, which gives a by-product as alcohol, along with the evolution of N_2 gas.

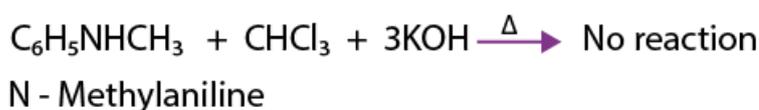
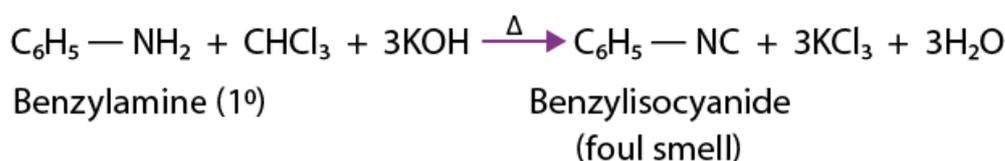


In another case, HNO_2 reacts with aniline at a very low temperature which in turn forms stable diazonium salt. Hence, the evolution of nitrogen gas does not happen.



(v) *N*-methylaniline and Aniline can be made notable by using the Carbylamine test.

On heating Primary amines with ethanolic, chloroform and potassium hydroxide, foul-smelling isocyanides or carbylamines are formed. As Aniline is a primary aromatic primary, it gives a positive carbylamines test. On the other h&, as *N*-methyl aniline is a secondary amine, it does not give a positive carbylamines test.



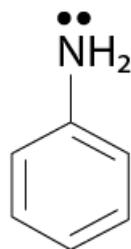
Q . 13.3 :

Account for the following.

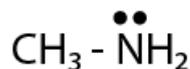
- (i) $p K_b$ of aniline is more than that of methylamine.
- (ii) Ethylamine is soluble in water, whereas aniline is not.
- (iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.
- (iv) Although the amino group is o - and p - directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of *m*-nitroaniline.
- (v) Aniline does not undergo Friedel-Crafts reaction.
- (vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.
- (vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines

Solution :

(i) $p K_b$ of methylamine is lesser than that of aniline.

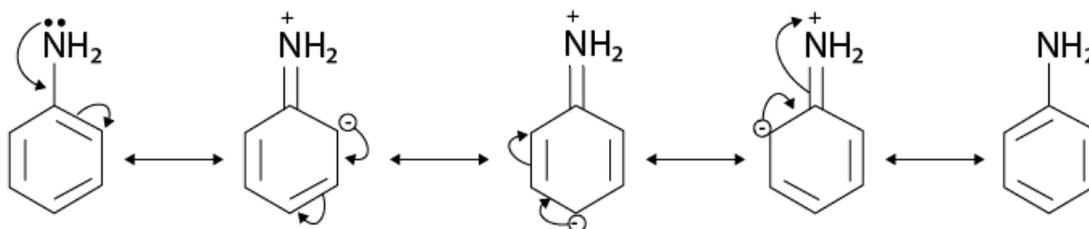


Aniline



Methylamine

When in the above process, Aniline is under resonance, the electrons available on the N – atom is delocalised over the benzene ring. Hence, the electrons on the N – atom is available in less quantity to donate.



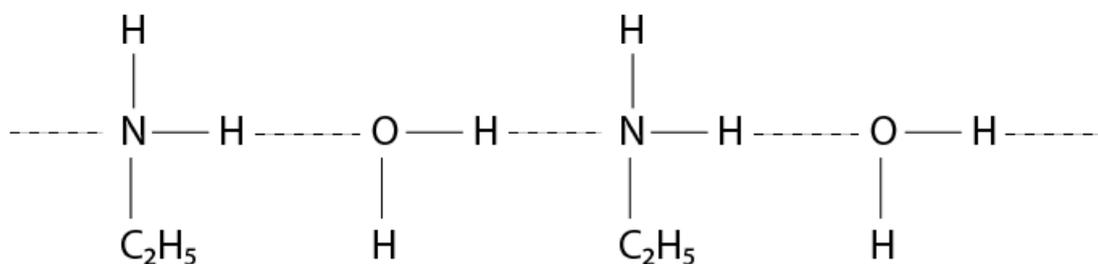
While considering the case of methylamine (due to the + I effect of methyl group), the electron density on the N – atom is improved. As an outcome, we see that methylamine is more basic than aniline.

Hence, ***p K_b of methylamine is lesser than that of aniline.***

(ii) Aniline is not soluble in water, while Ethylamine is.

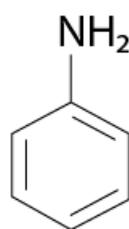
When Ethylamine is reacted with water, it tends to form intermolecular H – bonds with water.

Thus, it becomes soluble in water.



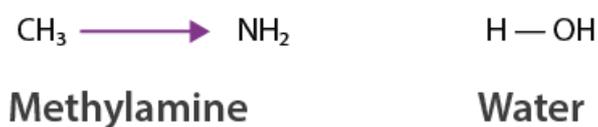
Ethylamine

However, aniline does form H – bonding with water to a very great extent reason being the presence of a large hydrophobic – C₆ H₅ group. Therefore, aniline is not soluble in water.



Aniline

(iii) Methylamine in the water, when made to react with ferric chloride, precipitates hydrated ferric oxide.



Due to the presence of $-\text{CH}_3$ group & + I effect, water is less basic than methylamine.

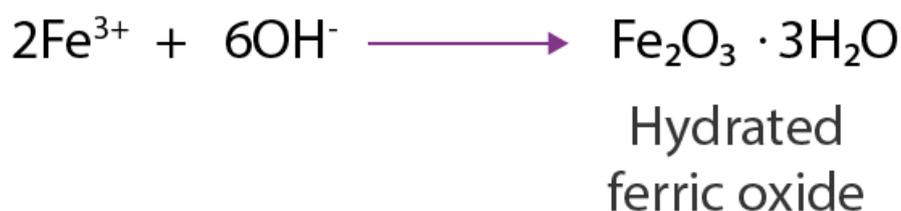
In water, thus, methylamine gives out OH^- ions by gaining H^+ ions from water.



In the above process, Ferric chloride (FeCl_3) splits, forming Fe^{3+} & Cl^- ions in water.

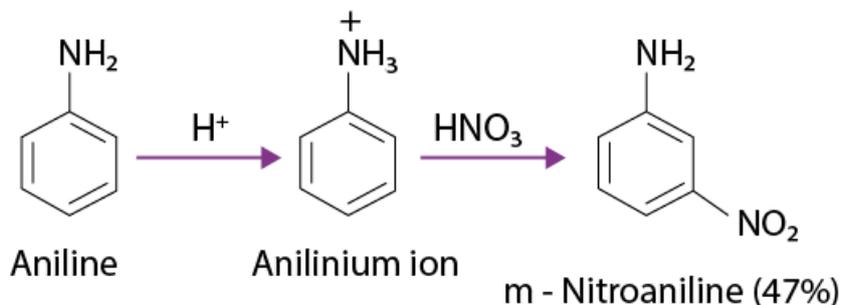


OH^- ion then combines with Fe^{3+} ion and forms an impulse of hydrated ferric oxide.



(iv) Aniline, when nitrated, gives a substantial amount of m-nitroaniline, while the amino group is o, p – directing in aromatic electrophilic substitution reactions.

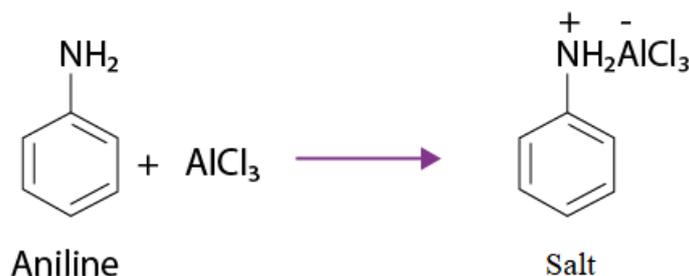
Nitration is carried out in an acidic medium. In an acidic medium, aniline is protonated to give anilinium ion (which is meta-directing).



Due to the above reason, nitration aniline gives a considerable amount of m-nitroaniline.

(v) Aniline does not take Friedel-Crafts reaction.

Friedel-Crafts reaction is performed in the presence of $AlCl_3$. But, as we know, $AlCl_3$ has an acidic nature, whereas aniline does not. Aniline is basic in nature. Therefore, aniline is then reacted with $AlCl_3$, forming a salt (this has been shown in the equation given below).

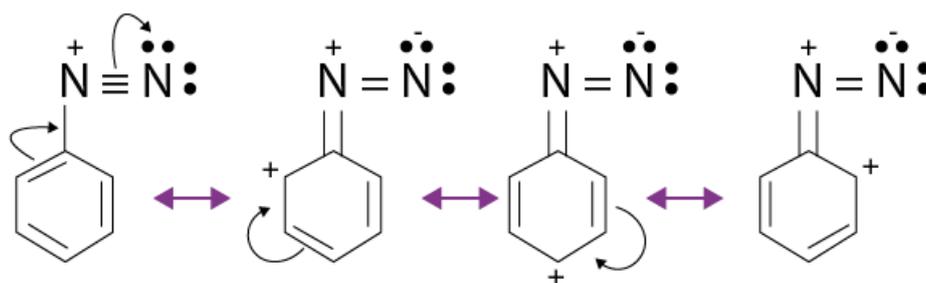


The electrophilic substitution in the benzene ring is deactivated because of the positive charge on the

N – atom. Hence, aniline does not undergo the Friedel-Crafts reaction.

(vi) On comparing the stabilities, we observe that the stability of Diazonium salts of aromatic amines is more than that of aliphatic amines.

Resonance is undergone by the diazonium ion, which is depicted in the figure given below.



The stability of the diazonium ion is accounted for by this resonance. Thus, the stability of diazonium salts of aromatic amines is higher than that of aliphatic amines.

(vii) Gabriel phthalimide synthesis is usually preferred for synthesizing primary amines.

Gabriel phthalimide synthesis is chosen because only 1° amine is formed.

This synthesis does not form 2° or 3° amines. Therefore, a pure 1° amine could be formed. Hence, Gabriel phthalimide synthesis is chosen for the synthesis of primary amines.

Q . 13.4 :

Arrange the following.

(i) In decreasing order of the pK_b values,

$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

(ii) In increasing order of basic strength,

$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2

(iii) In increasing order of basic strength,

(a) Aniline, p-nitroaniline and p-toluidine

(b) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$.

(iv) In decreasing order of basic strength in the gas phase,

$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3

(v) In increasing order of boiling point,

C_2H_5OH , $(CH_3)_2NH$, $C_2H_5NH_2$

(vi) In increasing order of solubility in water,

$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$.

Solution :

(i) $C_2H_5NH_2$ à presence of one – C_2H_5 group

$(C_2H_5)_2NH$ à presence of two – C_2H_5 groups.

Therefore, the + I effect is additional in $(C_2H_5)_2NH$ than in $C_2H_5NH_2$. Therefore, the electron density over the N-atom is more in $(C_2H_5)_2NH$ than in $C_2H_5NH_2$. Hence, $(C_2H_5)_2NH$ is more basic than $C_2H_5NH_2$.

Also, both $C_6H_5NHCH_3$ & $C_6H_5NH_2$ are less basic than $(C_2H_5)_2NH$ & $C_2H_5NH_2$ due to the delocalisation of the lone pair in the former two. Further, among $C_6H_5NHCH_3$ & $C_6H_5NH_2$, the former will be more basic due to the + T effect of – CH_3 group. Hence, the order of increasing basicity of the given compounds is as follows:

$C_6H_5NH_2 < C_6H_5NHCH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$

We know that the higher the basic strength, the lower the pK_b values.

$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

(ii) $C_6H_5N(CH_3)_2$ is more basic than $C_6H_5NH_2$ due to the presence of the + I effect of two

– CH_3 groups in $C_6H_5N(CH_3)_2$. Further, CH_3NH_2 contains one – CH_3 group while

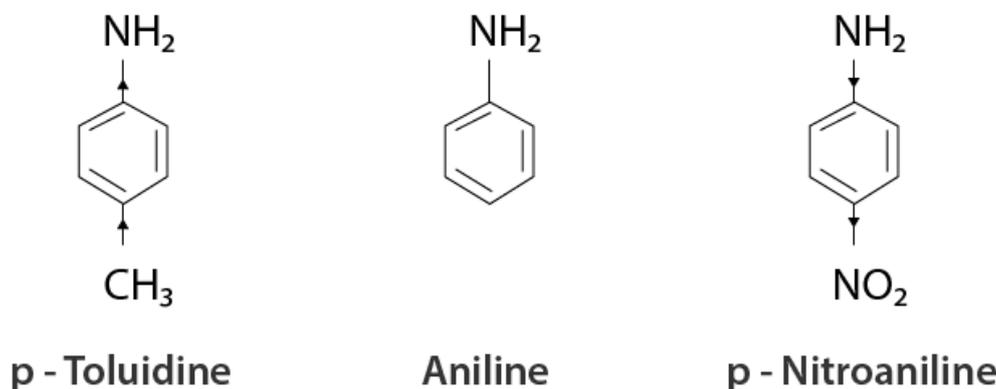
$(C_2H_5)_2NH$ contains two – C_2H_5 groups. Thus, $(C_2H_5)_2NH$ is more basic than $C_2H_5NH_2$.

Now, $C_6H_5N(CH_3)_2$ is less basic than CH_3NH_2 because of the – R effect of – C_6H_5 group.

Hence, the increasing order of the basic strengths of the given compounds is as follows:

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

(iii) (a)



In p - toluidine, the presence of the electron-donating - CH₃ group increases the electron density on the N-atom. Thus, p - toluidine is more basic than aniline. In the other case, the presence of the electron-withdrawing - NO₂ group decreases the electron density over the N - atom in p - nitroaniline. Thus, p-nitroaniline is less basic than aniline. Hence, the increasing order of the basic strengths of the given compounds is as follows: p - Nitroaniline < Aniline < p - Toluidine

(b) C₆H₅NHCH₃ is more basic than C₆H₅NH₂ due to the presence of electron-donating - CH₃ group in

C₆H₅NHCH₃. Again, in C₆H₅NHCH₃, the - C₆H₅ group is directly attached to the N - atom. However, it is not so in C₆H₅CH₂NH₂. Thus, in C₆H₅NHCH₃, the - R effect of the - C₆H₅ group decreases the electron density over the N-atom. Therefore, C₆H₅CH₂NH₂ is more basic than C₆H₅NHCH₃. Hence, the increasing order of the basic strengths of the given compounds is as follows: C₆H₅NH₂ < C₆H₅NHCH₃ < C₆H₅CH₂NH₂.

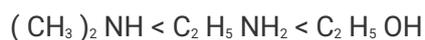
(iv) In the gas phase, there is no solvation effect. As a result, the basic strength mainly depends upon the + I effect. The higher the +I effect, the stronger the base. Also, the greater the number of alkyl groups, the higher the + I effect. Therefore, the given compounds can be arranged in the decreasing order of their basic strengths in the gas phase as follows:



(v) The extent of H-bonding existing in any compound decides the boiling point of compounds. The higher extensive the H - bonding in the compound, the higher will be the boiling point. (CH₃)₂NH has only one H - atom, while C₂H₅NH₂ has two H - atoms. Subsequently, C₂H₅NH₂ undergoes more extensive H-bonding than (CH₃)₂NH. Therefore, the boiling point of C₂H₅NH₂ is more than that of (CH₃)₂NH.

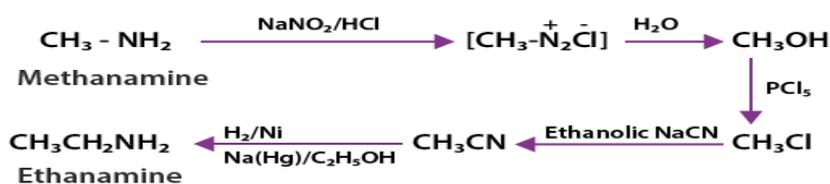
Also, O is more electronegative than N. Thus, C₂H₅OH forms stronger H - bonds than C₂H₅NH₂. As a result, the boiling point of C₂H₅OH is higher than that of C₂H₅NH₂ & (CH₃)₂NH.

Based on the above explanation, the compounds given in the question can be arranged in the ascending order of their boiling points, which is given below:

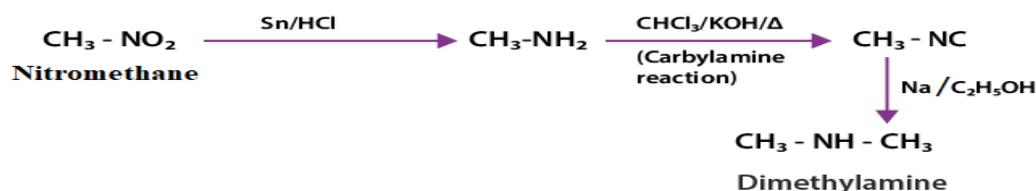


(vi) The more extensive the H - bonding, the higher the solubility. C₂H₅NH₂ contains two H - atoms, whereas (C₂H₅)₂NH contains only one H-atom. Thus, C₂H₅NH₂ undergoes more extensive H - bonding than (C₂H₅)₂NH. Hence, the solubility in water of C₂H₅NH₂ is more than that of (C₂H₅)₂NH.

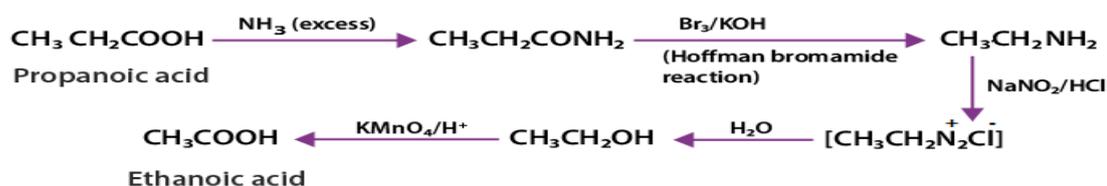
(vi)



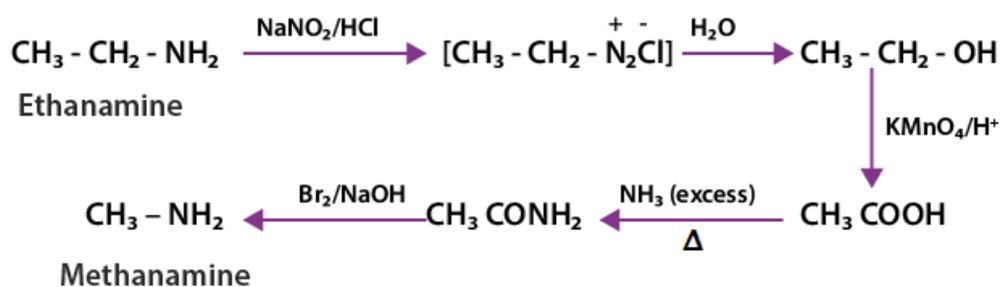
(vii)



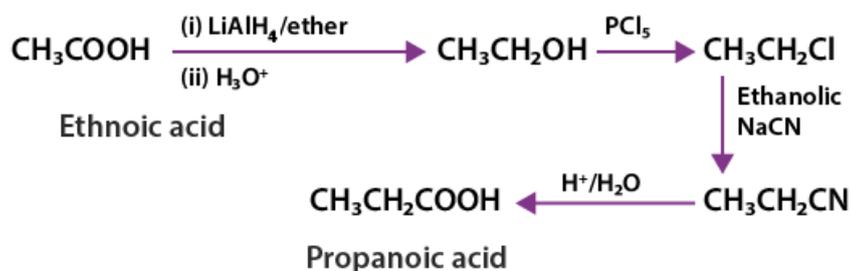
(viii)



(iv)



(v)

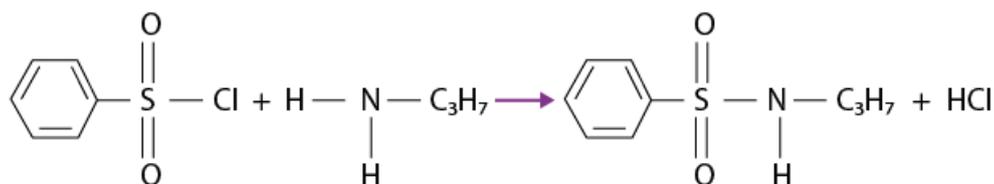


Question 13.6 :

Describe a method for the identification of primary, secondary and tertiary amines. Also, write chemical equations of the reactions involved.

Solution :

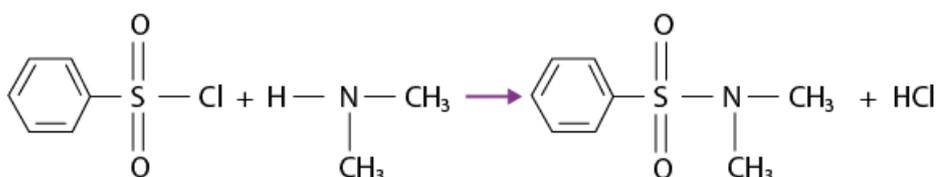
Primary, secondary and tertiary amines can be identified and distinguished by Hinsberg's test. In this test, the amines are allowed to react with Hinsberg's reagent, benzene sulphonyl chloride ($C_6H_5SO_2Cl$). The three types of amines react differently to Hinsberg's reagent. Therefore, they can be easily identified using Hinsberg's reagent. Primary amines react with benzene sulphonyl chloride to form N-alkyl benzene sulphonyl amide, which is soluble in alkali.



Benzenesulphonyl Chloride + Propanamine → N-propylbenzenesulphonamide

Due to the presence of a strong electron-withdrawing sulphonyl group in the sulphonamide, the H – atom attached to nitrogen can be easily released as a proton. So, it is acidic and dissolves in alkali.

Secondary amines react with Hinsberg's reagent to give a sulphonamide which is insoluble in alkali.



Benzenesulphonyl Chloride + Dimethylamine → N,N-Dimethylbenzenesulphonamide (insoluble in alkali)

There is no H – atom attached to the N-atom in the sulphonamide. Therefore, it is not acidic and insoluble in alkali. On the other tertiary amines do not react with Hinsberg's reagent at all.

Question 13.7:

Write short notes on the following.

(i) Carbylamine reaction

(ii) Diazotisation

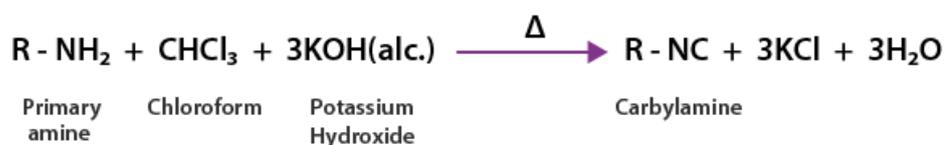
(iii) Hofmann's bromamide reaction

(iv) Coupling reaction

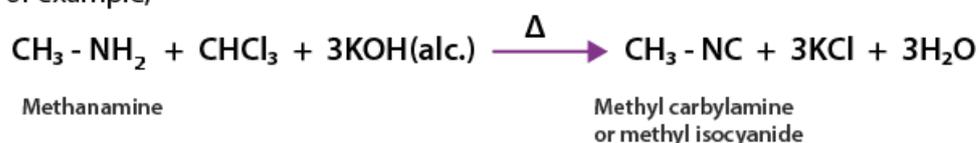
(v) Ammonolysis

(vi) Acetylation**(vii) Gabriel phthalimide synthesis.****Solution:****(i) Carbylamine reaction**

Carbylamine reaction is used as a test for the identification of primary amines. When aliphatic and aromatic primary amines are heated with chloroform and ethanolic potassium hydroxide, carbylamines (or isocyanides) are formed. These carbylamines have very unpleasant odours. Secondary and tertiary amines do not respond to this test.

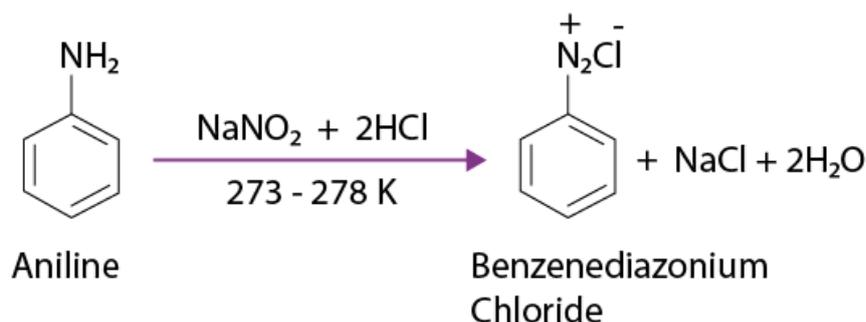


For example,

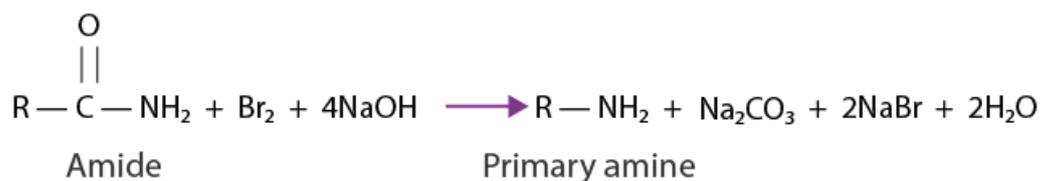
**(ii) Diazotization**

Aromatic primary amines react with nitrous acid (prepared in situ from NaNO_2 and a mineral acid such as HCl) at low temperatures (273 – 278 K) to form diazonium salts. This conversion of aromatic primary amines into diazonium salts is known as diazotization.

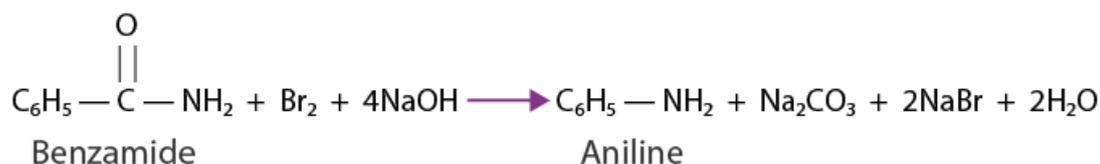
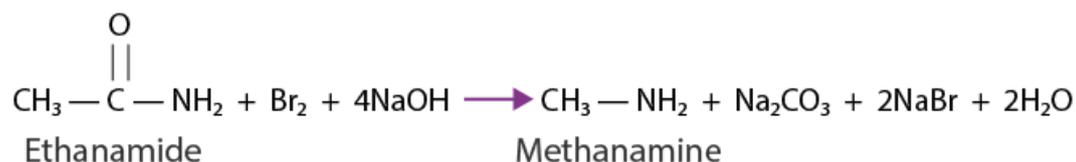
For example, on treatment with NaNO_2 & HCl at 273 – 278 K, aniline produces benzene diazonium chloride, with NaCl & H_2O as by-products.

**(iii) Hoffmann bromamide reaction**

When an amide is treated with bromine in an aqueous or ethanolic solution of sodium hydroxide, a primary amine with one carbon atom less than the original amide is produced. This degradation reaction is known as the Hoffmann bromamide reaction. This reaction involves the migration of an alkyl or aryl group from the carbonyl carbon atom of the amide to the nitrogen atom.

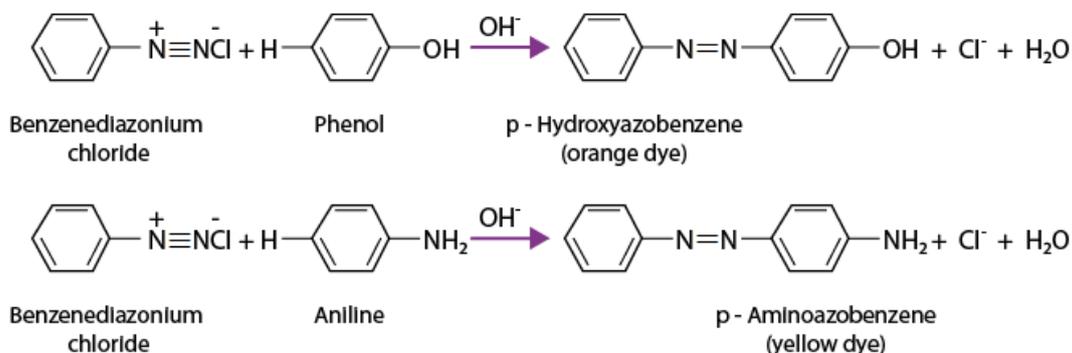


For example,



(iv) Coupling reaction

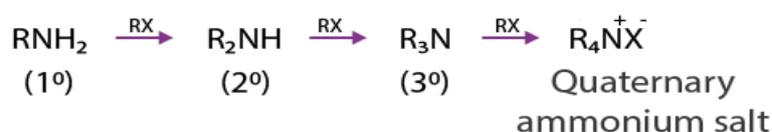
The reaction of joining two aromatic rings through the $-\text{N}=\text{N}-$ bond is known as the coupling reaction. Arene diazonium salts, such as benzene diazonium salts, react with phenol or aromatic amines to form coloured azo compounds.



It can be observed that the para-positions of phenol and aniline are coupled with the diazonium salt. This reaction proceeds through electrophilic substitution.

(v) Ammonolysis

When an alkyl or benzyl halide is allowed to react with an ethanolic solution of ammonia, it undergoes a nucleophilic substitution reaction in which the halogen atom is replaced by an amino ($-\text{NH}_2$) group. This process of cleavage of the carbon-halogen bond is known as ammonolysis.

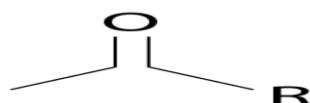


When this substituted ammonium salt is treated with a strong base, such as sodium hydroxide, the amine is obtained.



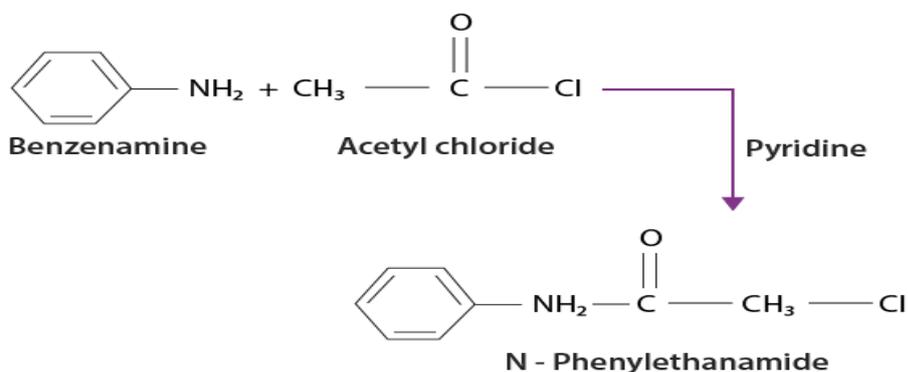
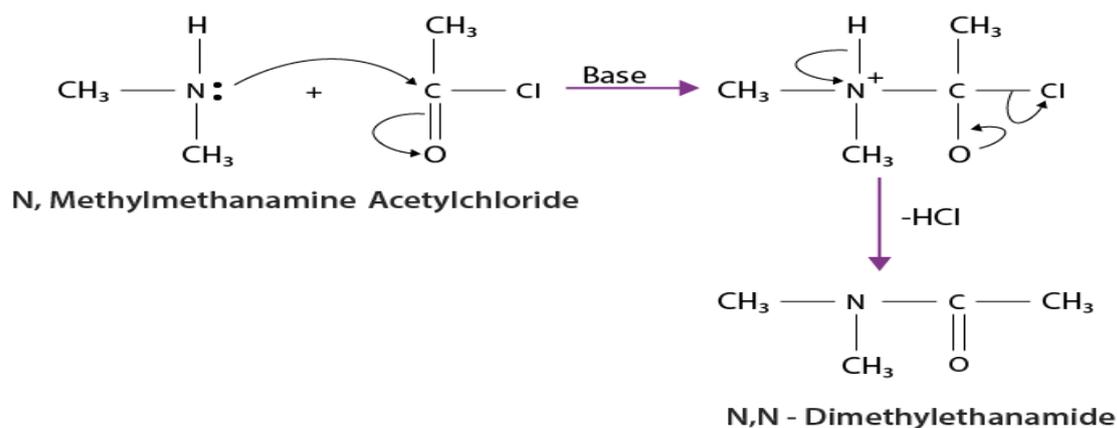
Though primary amine is produced as the major product, this process produces a mixture of primary, secondary and tertiary amines, and also a quaternary ammonium salt, as shown.

(vi) Acetylation

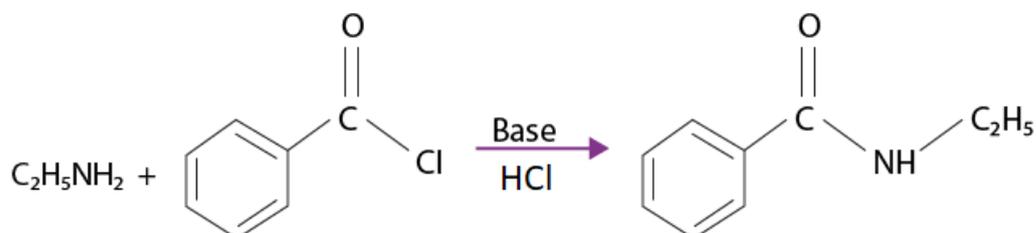


Acetylation (or ethanoylation) is the process of introducing an acetyl group into a molecule.

Aliphatic and aromatic primary & secondary amines undergo acetylation reaction by nucleophilic substitution when treated with acid chlorides, anhydrides or esters. This reaction involves the replacement of the hydrogen atom of $-\text{NH}_2$ or $>\text{NH}$ group by the acetyl group, which results in the formation of amides. In order to transfer the equilibrium to the right-hand side, the HCl that is produced while the reaction is on is removed almost immediately as it is produced. This reaction is performed in the existence of a base (such as pyridine) which is comparatively stronger than the amine.

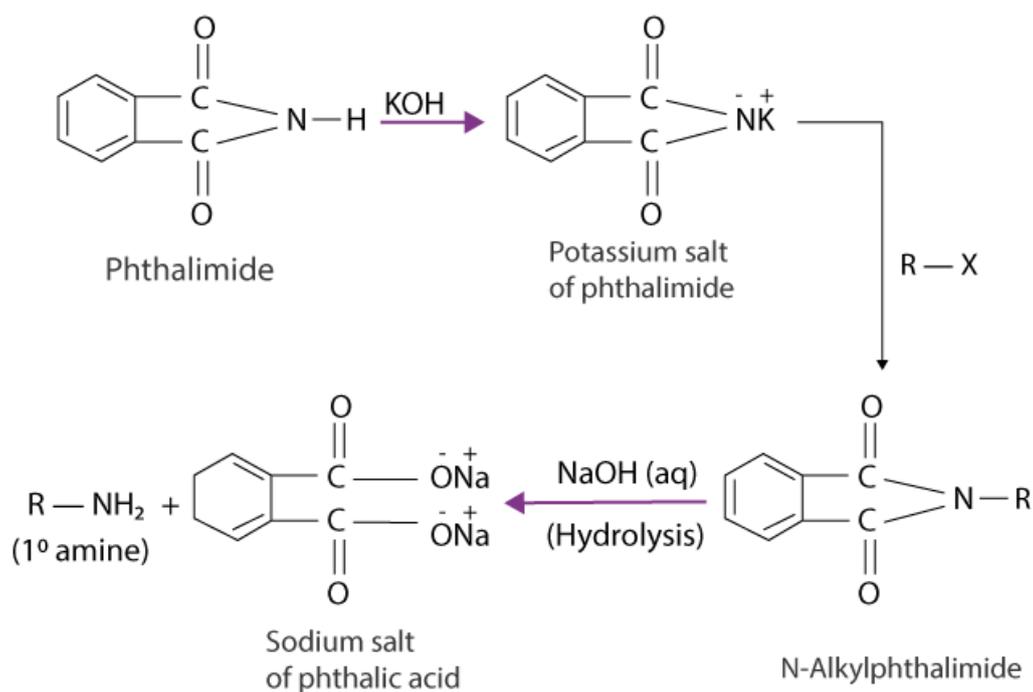


The reaction, also known as benzoylation, is the reaction that occurs when amines react with benzoyl chloride. One of the examples is illustrated below.



(vii) Gabriel phthalimide synthesis

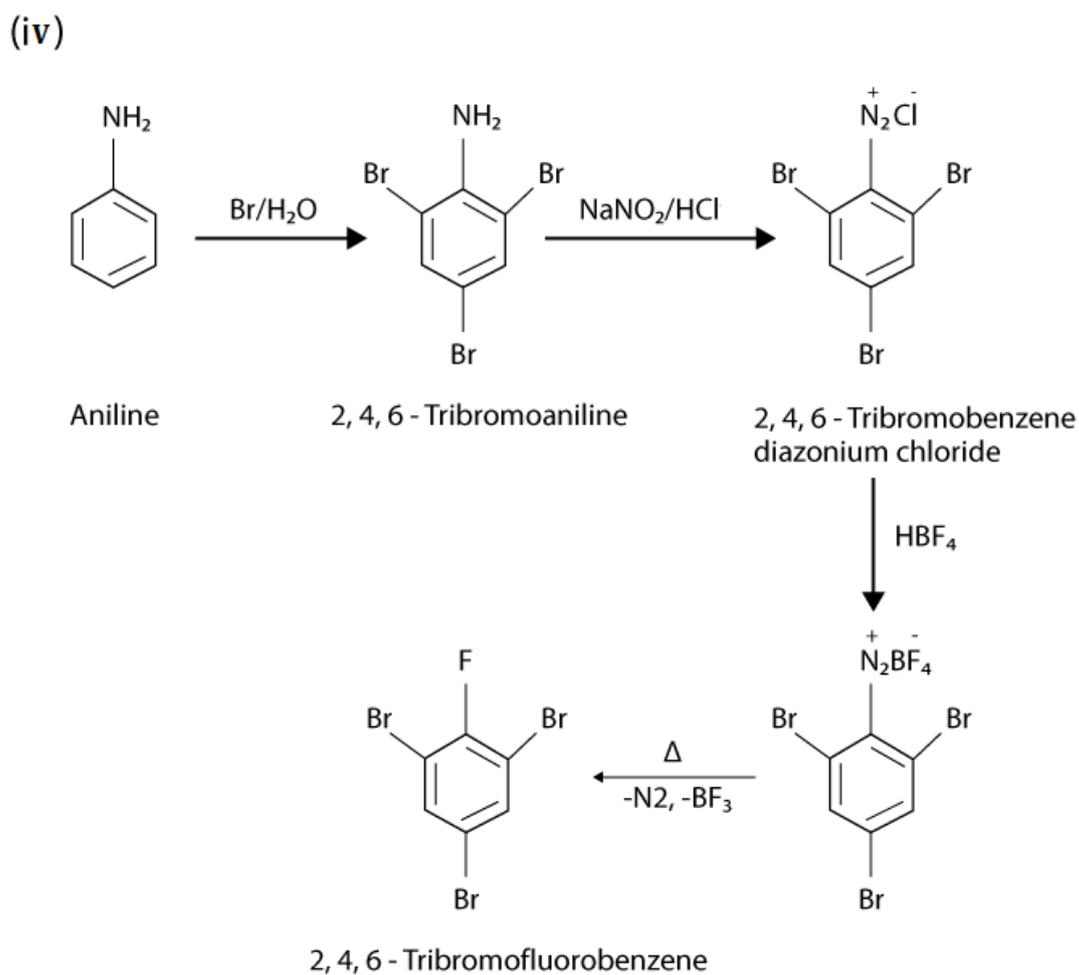
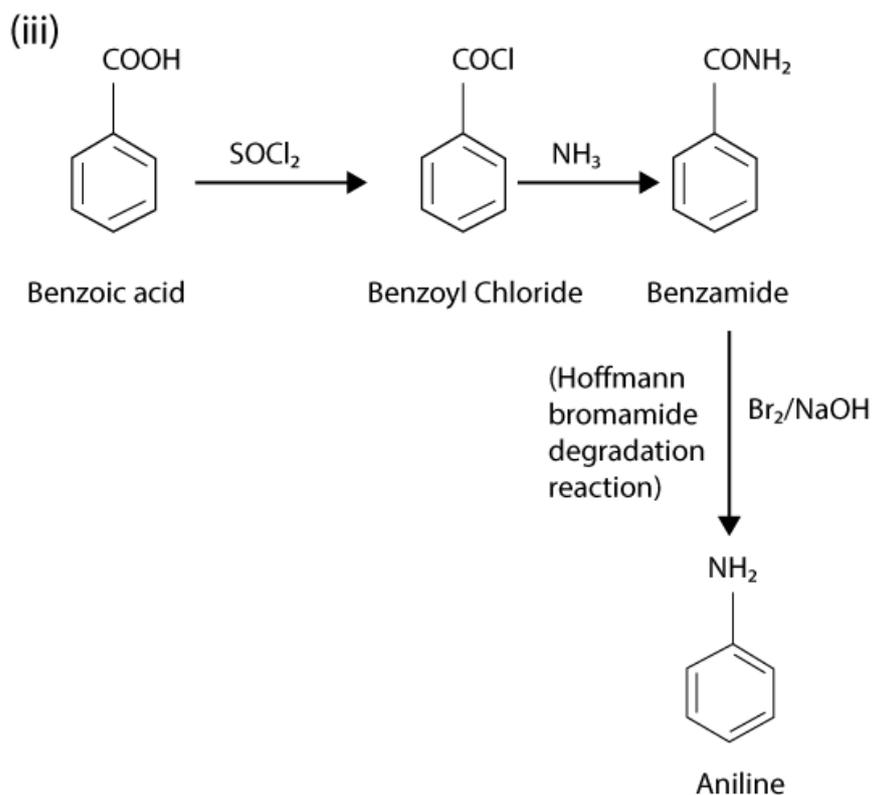
Gabriel phthalimide synthesis is a convenient and important method for the synthesis of aliphatic primary amines. It includes the reaction between phthalimide with ethanolic potassium hydroxide forming the potassium salt of phthalimide. This salt is then heated with an alkyl halide, which is succeeded by alkaline hydrolysis to give in the resultant primary amine.



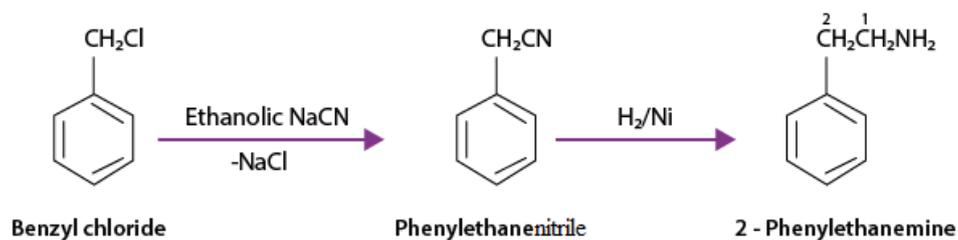
Question 13.8:

Accomplish the following conversions.

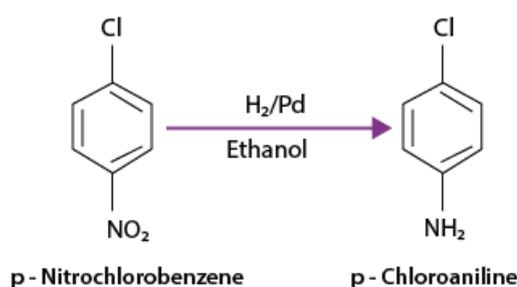
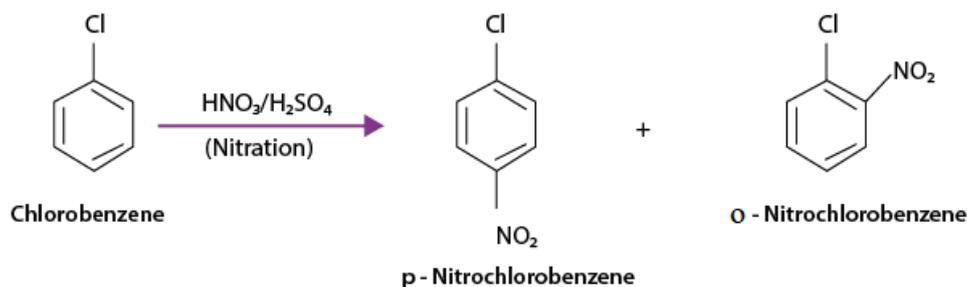
- (i) Nitrobenzene to benzoic acid
- (ii) Benzene to m-bromophenol
- (iii) Benzoic acid to aniline
- (iv) Aniline to 2, 4 ,6-tribromofluorobenzene



(v)

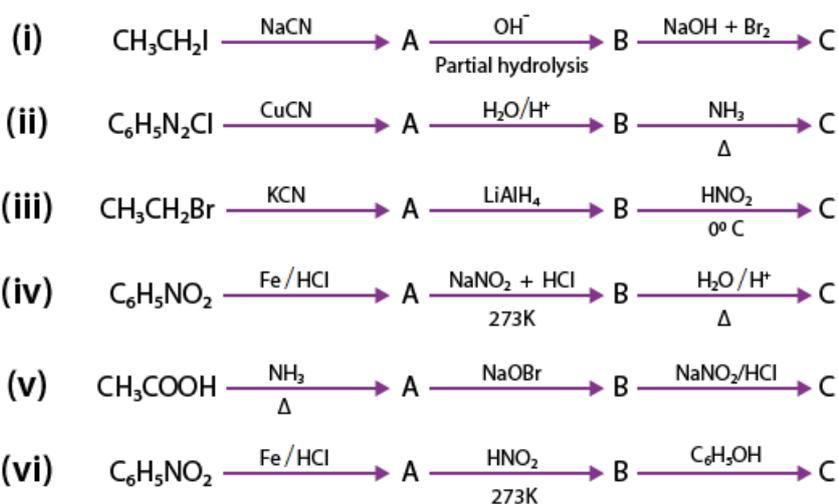


(vi)

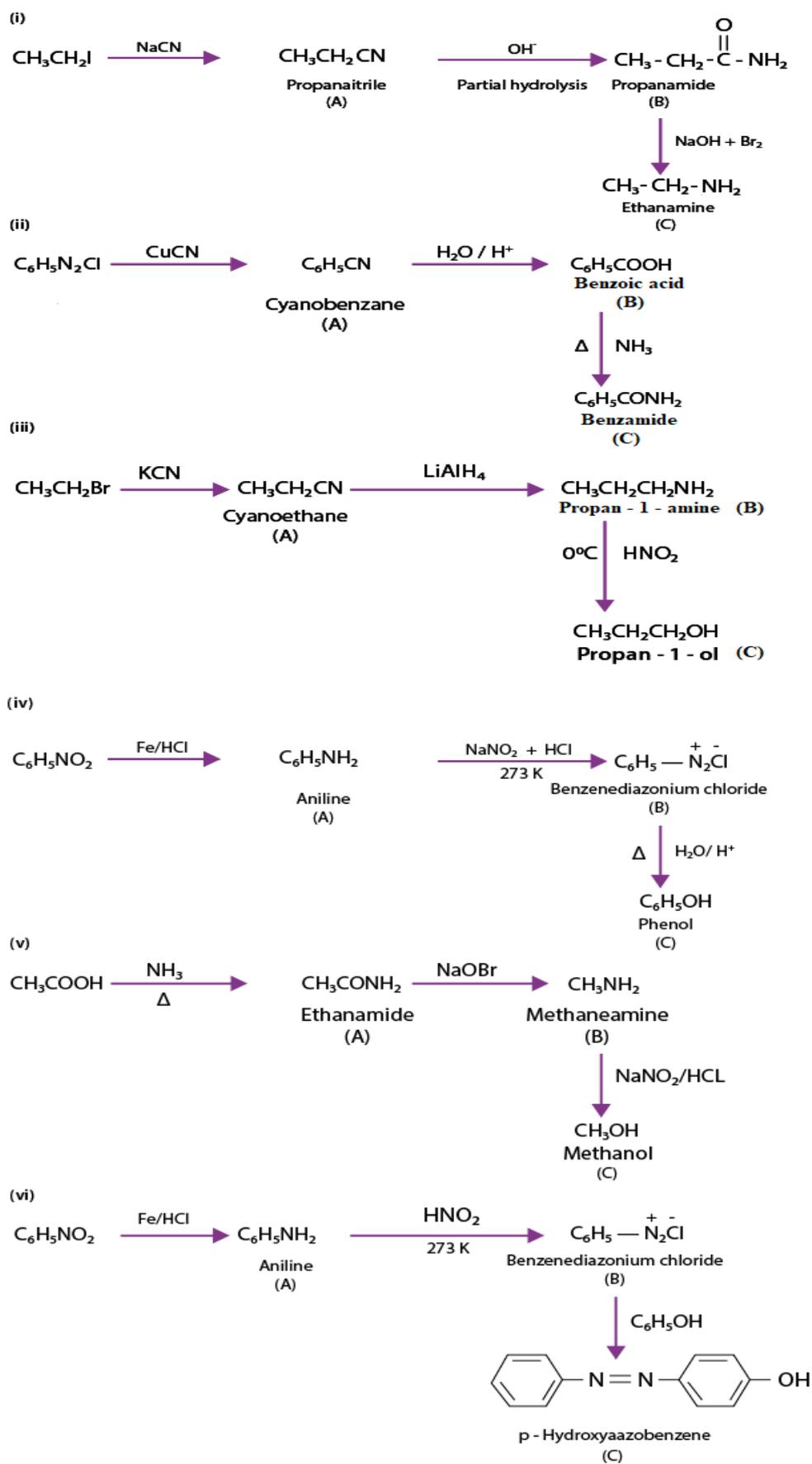


Question 13.9 :

Give the structures of A, B and C in the following reactions.



Solution:

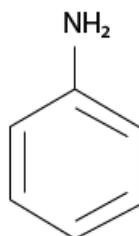


Question 13.10:

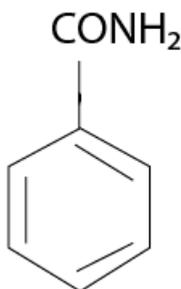
An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B', which on heating with Br_2 and KOH forms a compound 'C' of molecular formula $\text{C}_6\text{H}_7\text{N}$. Write the structures and IUPAC names of compounds A, B and C.

Solution :

It is given that compound 'C' has the molecular formula, and $\text{C}_6\text{H}_7\text{N}$ is formed by heating compound 'B' with Br_2 and KOH. This is a Hoffmann bromamide degradation reaction. Therefore, compound 'B' is an amide and compound 'C' is an amine. The only amine having the molecular formula $\text{C}_6\text{H}_7\text{N}$ is aniline ($\text{C}_6\text{H}_5\text{NH}_2$).

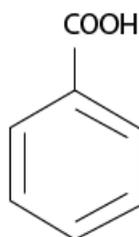
**Aniline**

Therefore, compound 'B' (from which 'C' is formed) must be benzamide ($\text{C}_6\text{H}_5\text{CO NH}_2$).

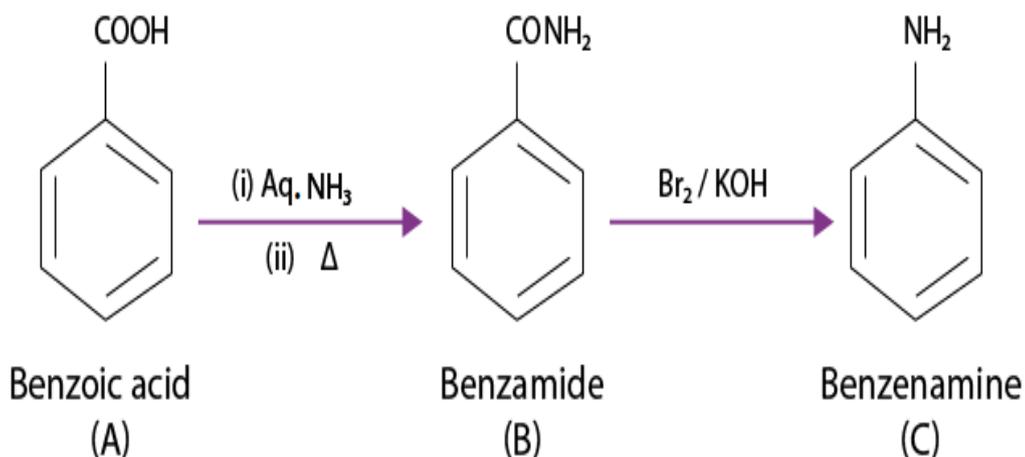
**Benzamide**

Further, benzamide is formed by heating compound 'A' with aqueous ammonia.

Therefore, compound 'A' must be benzoic acid.

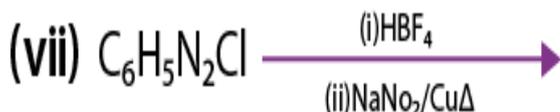
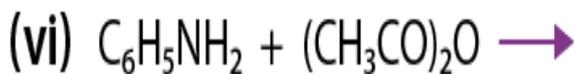
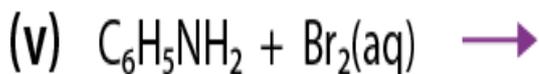
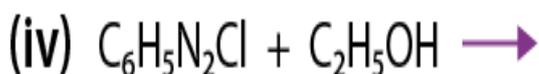
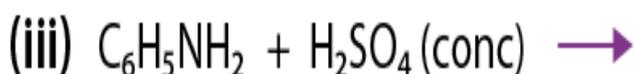
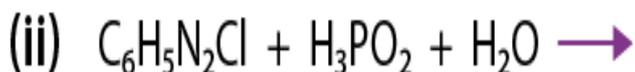
**Benzoic acid**

The given reactions can be explained with the help of the following equations:



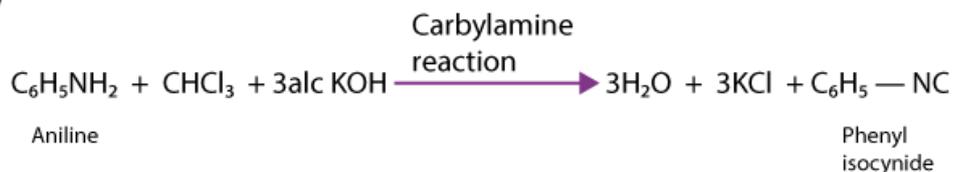
Question 13.11:

Complete the following reactions.



Solution:

(i)



(ii)



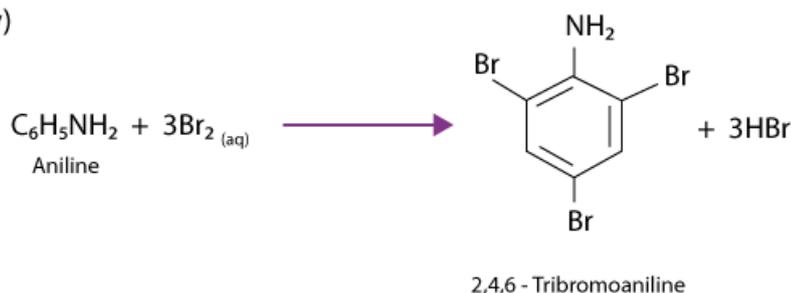
(iii)



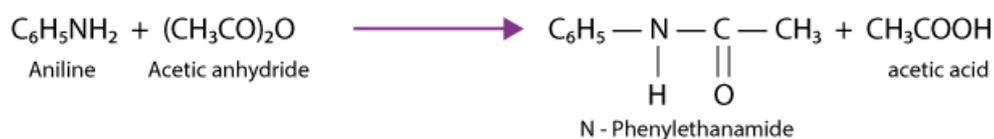
(iv)



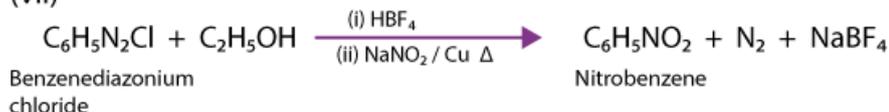
(v)



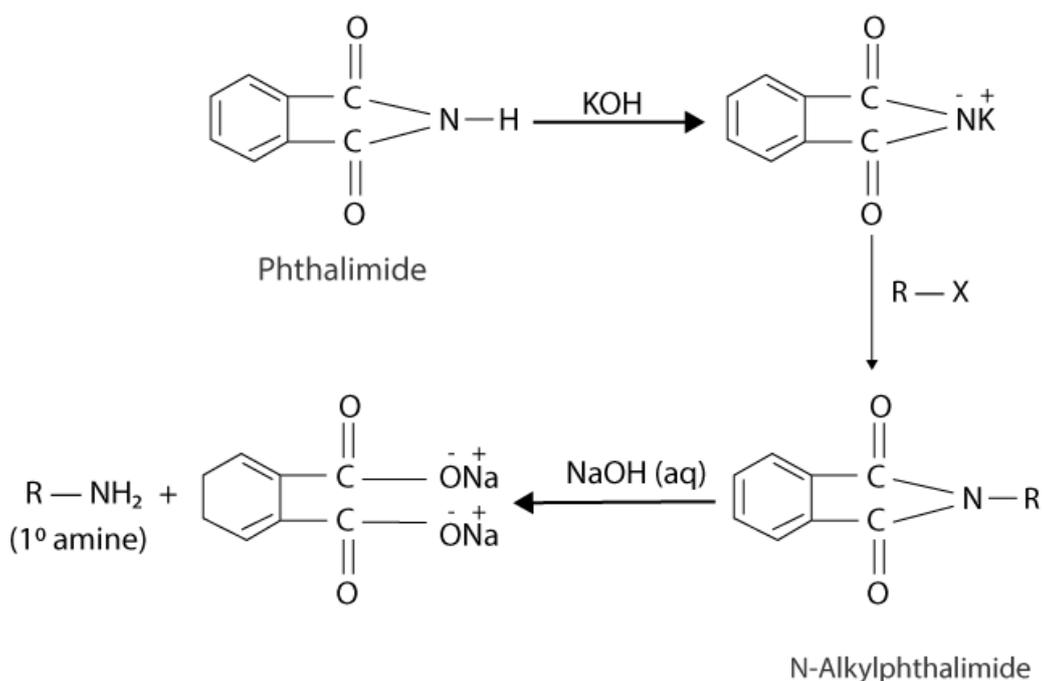
(vi)



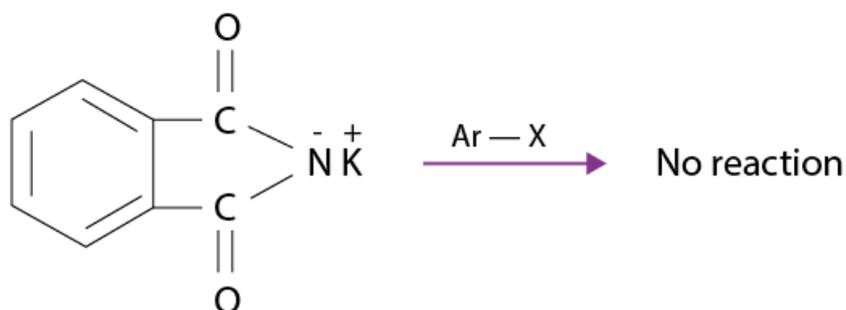
(vii)

**Question 13.12:****Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?****solution :**

Gabriel phthalimide synthesis is usually used for the formation of aliphatic primary amines. This includes nucleophilic substitution ($\text{S}_{\text{N}}2$) of alkyl halides by the anion produced by the phthalimide.



However, nucleophilic substitution with the anion formed by the phthalimide is not undergone by aryl halides.



Therefore, Gabriel phthalimide synthesis is not preferred for preparing aromatic primary amines.

Question 13.13:

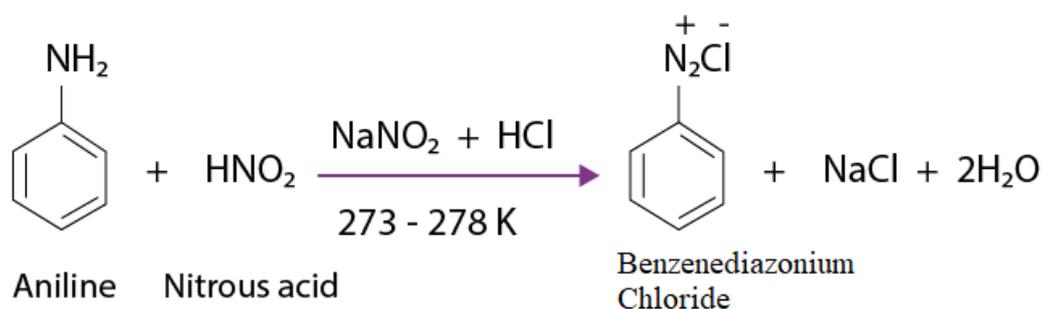
Write the reactions of

- (i) Aromatic with nitrous acid.
- (ii) Aliphatic primary amines with nitrous acid.

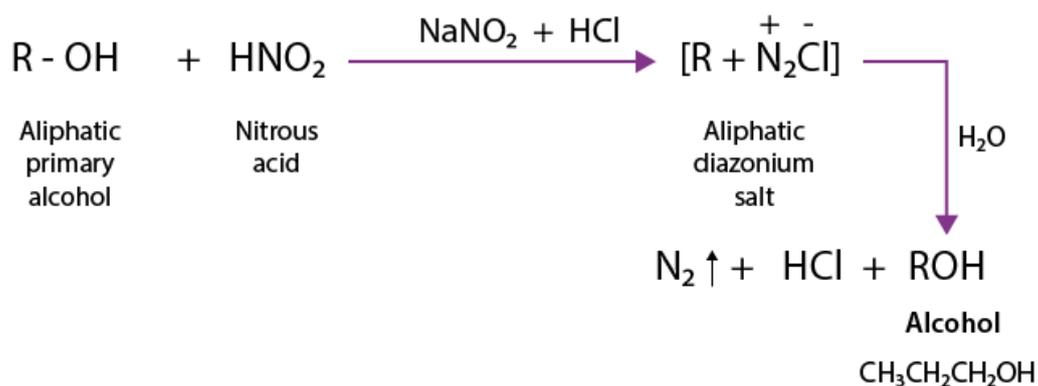
Solution:

(i) Aromatic amine when reacts with nitrous acid (which is made in situ from NaNO_2 and a mineral acid, such as

(HCl) at 273 – 278 K forming stable aromatic diazonium salts, i.e., NaCl and H_2O .



(ii) Aliphatic primary amines, when reacted with nitrous acid. (made in situ from NaNO_2 and a mineral acid, such as HCl , forming unstable aliphatic diazonium salts, which later produce alcohol and HCl , along with the evolution of N_2 gas.)



Question 13.14:

Give a plausible explanation for each of the following.

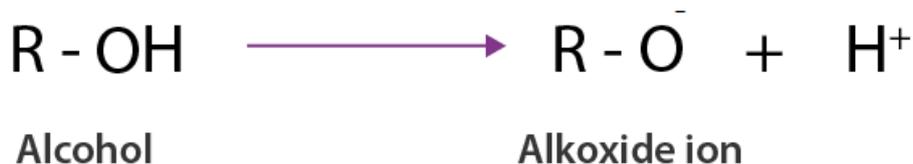
- (i) Why are alcohols more acidic than amines of comparable molecular masses?
- (ii) Why do tertiary amines have lower boiling points than primary amines?
- (iii) Why are aromatic amines weaker bases than aliphatic amines?

Solution :

- (i) Protonation of amines gives amide ions.

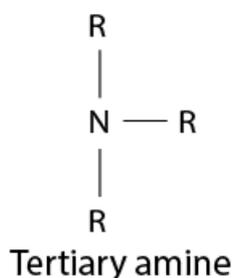
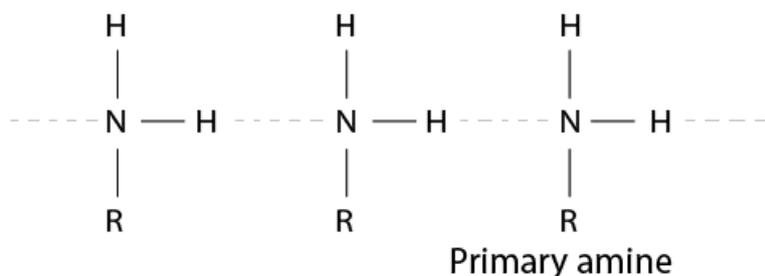


In the same way, alcohol gives away a proton which results in an alkoxide ion.



In an amide ion, N-atom has a negative charge on it, while in the alkoxide ion, the O-atom has a negative charge on it. In view of the fact that O is more electronegative than N, O has the ability to hold the negative charge more effortlessly than N. Consequently, the alkoxide ion is more stable than the amide ion. Therefore, **alcohols more acidic than amines of comparable molecular masses**

(ii) There are no H-atoms present in a molecule of a tertiary amine, while two hydrogen atoms are present in primary amines. Primary amines undergo extensive intermolecular H-bonding because of the presence of H-atoms.



Consequently, additional energy would be required to detach the molecules of primary amines. Therefore, tertiary amines have lower boiling points than primary amines.

(iii) The availability of N-atom is fewer in aromatic amines; this is because of the R effect of the benzene ring. Thus, the electrons on the N-atom in aromatic amines cannot be donated easily. This explains why aliphatic amines are stronger bases than aromatic amines.