

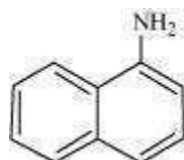
Chapter 9 - Amines XII

Intext Questions

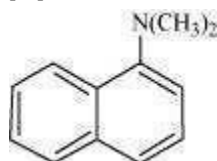
Question 9.1:

Classify the following amines as primary, secondary or tertiary:

(i)



(ii)



(iii) $(\text{C}_2\text{H}_5)_2\text{CHNH}_2$

(iv) $(\text{C}_2\text{H}_5)_2\text{NH}$

Answer

Primary: (i) and (iii)

Secondary: (iv)

Tertiary: (ii)

Question 9.2:

(i) Write structures of different isomeric amines corresponding to the molecular formula,

$\text{C}_4\text{H}_{11}\text{N}$

(ii) Write IUPAC names of all the isomers.

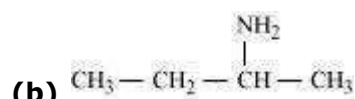
(iii) What type of isomerism is exhibited by different pairs of amines?

Answer

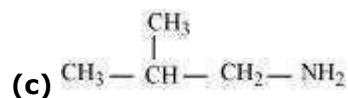
(i), (ii) The structures and their IUPAC names of different isomeric amines corresponding to the molecular formula, $\text{C}_4\text{H}_{11}\text{N}$ are given below:

(a) $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$

Butanamine (1°)

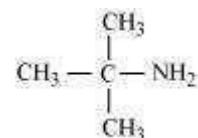


Butan-2-amine (1°)

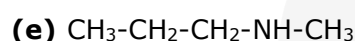


2-Methylpropanamine (1°)

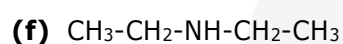
(d)



2-Methylpropan-2-amine (1°)

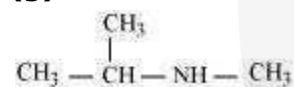


N-Methylpropanamine (2°)



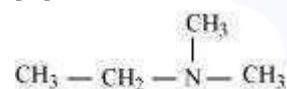
N-Ethylethanamine (2°)

(g)



N-Methylpropan-2-amine (2°)

(h)



N,N-Dimethylethanamine (3°)

(iii) The pairs (a) and (b) and (e) and (g) exhibit position isomerism.

The pairs (a) and (c); (a) and (d); (b) and (c); (b) and (d) exhibit chain isomerism.

The pairs (e) and (f) and (f) and (g) exhibit metamerism.

All primary amines exhibit functional isomerism with secondary and tertiary amines and vice-versa.

Question 9.3:

How will you convert?

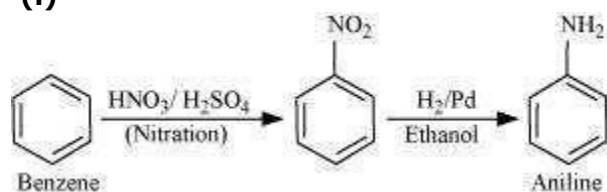
(i) Benzene into aniline

(ii) Benzene into N, N-dimethylaniline

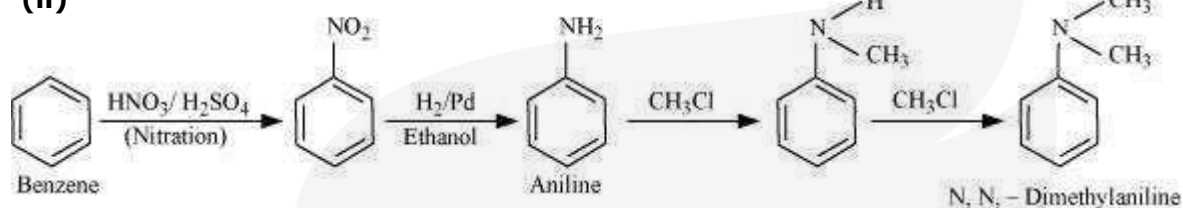
(iii) $\text{Cl} - (\text{CH}_2)_4 - \text{Cl}$ into hexan-1, 6-diamine?

Answer

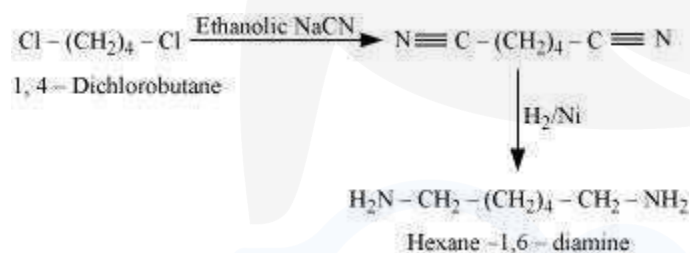
(i)



(ii)



(iii)



Question 9.4:

Arrange the following in increasing order of their basic strength:

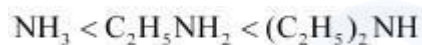
(i) $\text{C}_2\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{NH}_2$, NH_3 , $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ and $(\text{C}_2\text{H}_5)_2\text{NH}$

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

(iii) CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, $(\text{CH}_3)_3\text{N}$, $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$.

Answer

(i) Considering the inductive effect of alkyl groups, NH_3 , $\text{C}_2\text{H}_5\text{NH}_2$, and $(\text{C}_2\text{H}_5)_2\text{NH}$ can be arranged in the increasing order of their basic strengths as:



Again, $\text{C}_6\text{H}_5\text{NH}_2$ has proton acceptability less than NH_3 . Thus, we have:



Due to the $-I$ effect of C_6H_5 group, the electron density on the N-atom in $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ is lower than that on the N-atom in $\text{C}_2\text{H}_5\text{NH}_2$, but more than that in NH_3 . Therefore, the given compounds can be arranged in the order of their basic strengths as:

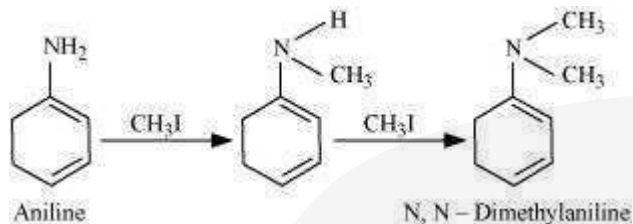


Question 9.6:

Write reactions of the final alkylation product of aniline with excess of methyl iodide in the presence of sodium carbonate solution.

Answer

Aniline reacts with methyl iodide to produce N, N-dimethylaniline.

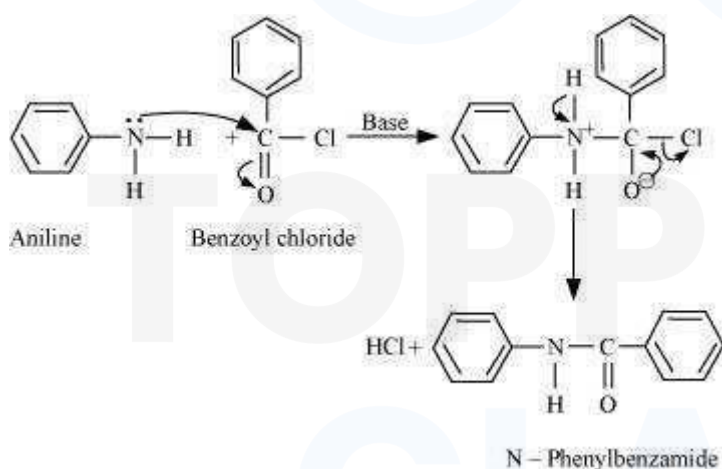


With excess methyl iodide, in the presence of Na₂CO₃ solution, N, N-dimethylaniline produces N, N, N-trimethylanilinium carbonate.

**Question 9.7:**

Write chemical reaction of aniline with benzoyl chloride and write the name of the product obtained.

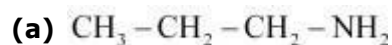
Answer

**Question 9.8:**

Write structures of different isomers corresponding to the molecular formula, C₃H₉N. Write IUPAC names of the isomers which will liberate nitrogen gas on treatment with nitrous acid.

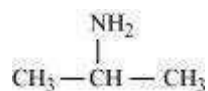
Answer

The structures of different isomers corresponding to the molecular formula, C₃H₉N are given below:



Propan-1-amine (1°)

(b)



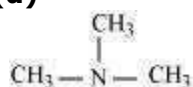
Propan-2-amine (1°)

(c)



N-Methylethanamine (2°)

(d)



N,N-Dimethylmethanamine (3°)

1° amines, (a) propan-1-amine, and (b) Propan-2-amine will liberate nitrogen gas on treatment with nitrous acid.



Propan-1-amine

Propan-1-ol



Propan-2-amine

Propan-2-ol

Question 9.9:

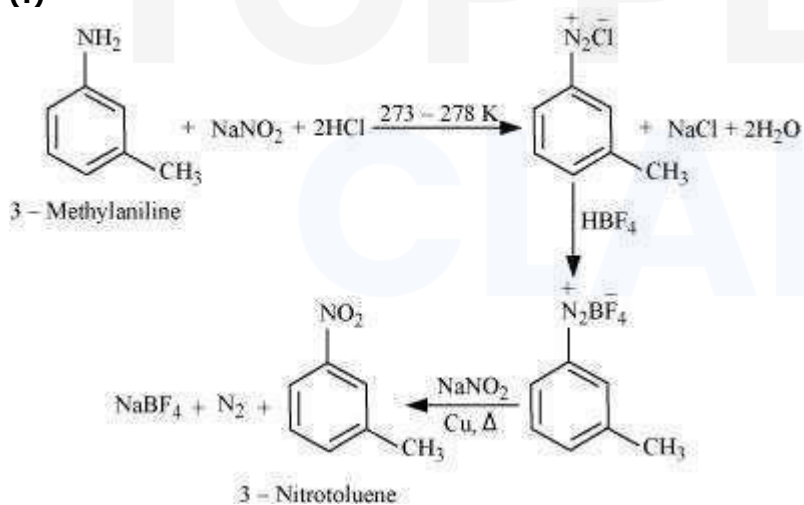
Convert

(i) 3-Methylaniline into 3-nitrotoluene.

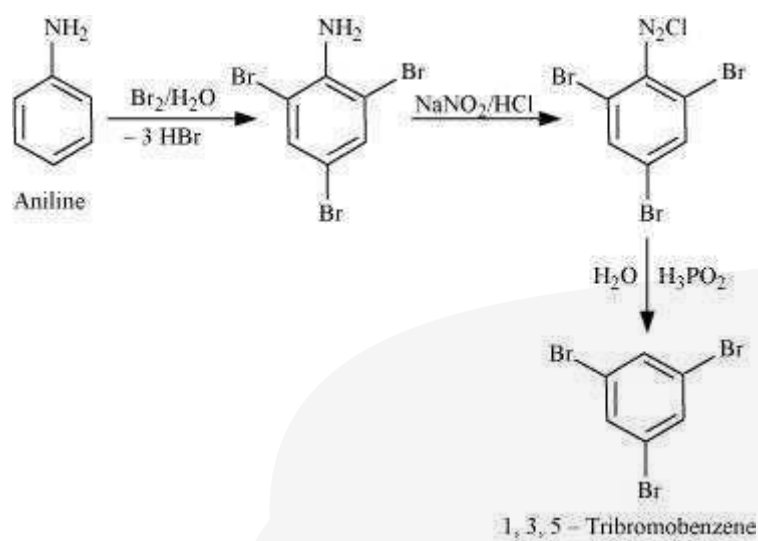
(ii) Aniline into 1,3,5-tribromobenzene.

Answer

(i)

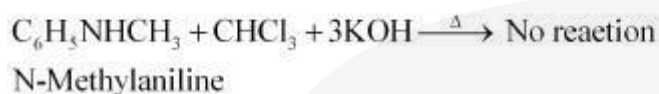
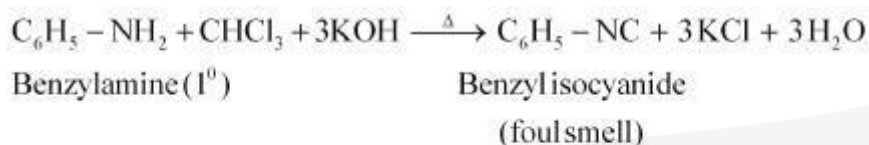


(ii)



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(v) Aniline and N-methylaniline can be distinguished using the Carbylamine test. Primary amines, on heating with chloroform and ethanolic potassium hydroxide, form foulsmelling isocyanides or carbylamines. Aniline, being an aromatic primary amine, gives positive carbylamine test. However, N-methylaniline, being a secondary amine does not.



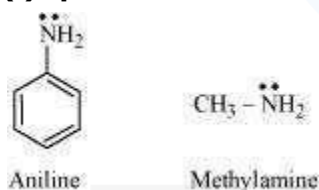
Question 9.3:

Account for the following:

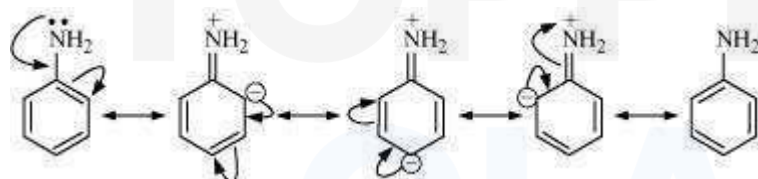
- (i) pK_b of aniline is more than that of methylamine.
- (ii) Ethylamine is soluble in water whereas aniline is not.
- (iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.
- (iv) Although amino group is o - and p - directing in aromatic electrophilic substitution 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.

Answer

(i) **pK_b of aniline is more than that of methylamine:**



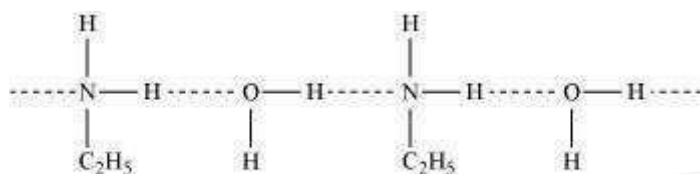
Aniline undergoes resonance and as a result, the electrons on the N-atom are delocalized over the benzene ring. Therefore, the electrons on the N-atom are less available to donate.



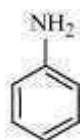
On the other hand, in case of methylamine (due to the +I effect of methyl group), the electron density on the N-atom is increased. As a result, aniline is less basic than methylamine. Thus, pK_b of aniline is more than that of methylamine.

(ii) Ethylamine is soluble in water whereas aniline is not:

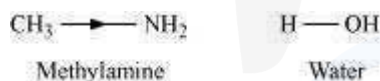
Ethylamine when added to water forms intermolecular H-bonds with water. Hence, it is soluble in water.



But aniline does not undergo H-bonding with water to a very large extent due to the presence of a large hydrophobic $-C_6H_5$ group. Hence, aniline is insoluble in water.



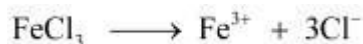
(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide:



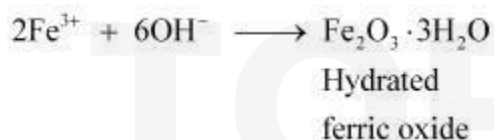
Due to the +I effect of $-CH_3$ group, methylamine is more basic than water. Therefore, in water, methylamine produces OH^- ions by accepting H^+ ions from water.



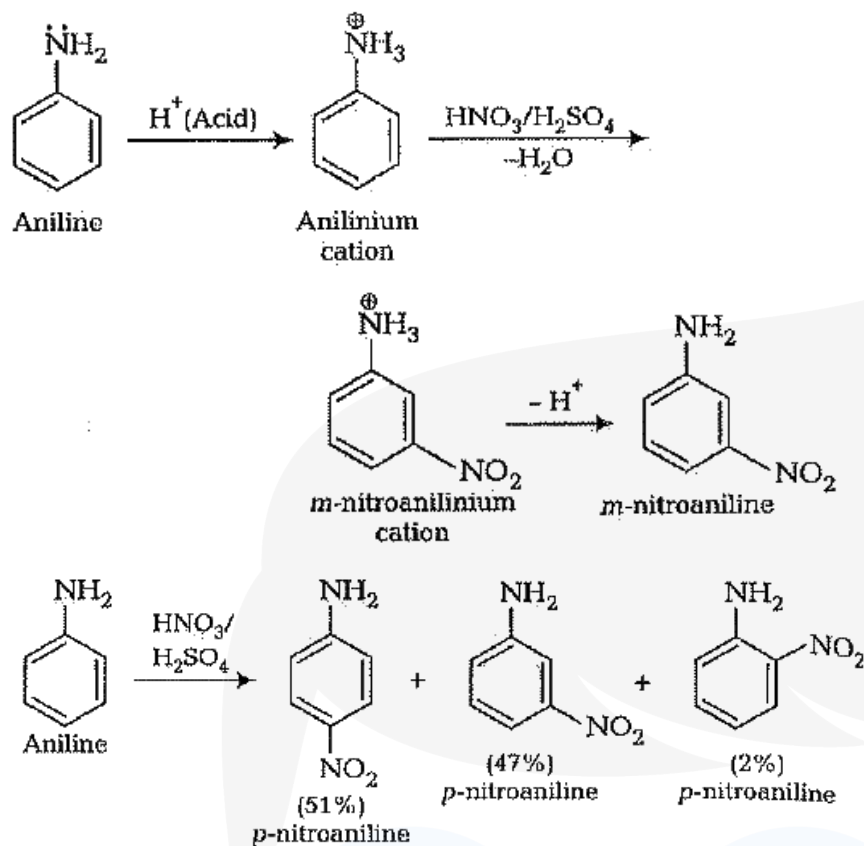
Ferric chloride ($FeCl_3$) dissociates in water to form Fe^{3+} and Cl^- ions.



Then, OH^- ion reacts with Fe^{3+} ion to form a precipitate of hydrated ferric oxide.



(iv) In presence of conc. HNO_3 and conc. H_2SO_4 , most of aniline gets protonated to form anilinium ion. Now aniline and anilinium ions both are present in the reaction mixture. In aniline $-NH_2$ group is o- and p-directing but anilinium ion is m-directing. Because of more amount of anilinium ion, a lot of m-nitroaniline is formed.



(v) Aniline does not undergo Friedel-Crafts reaction:

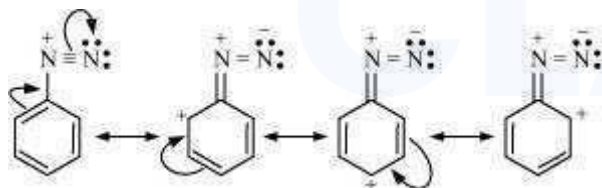
A Friedel-Crafts reaction is carried out in the presence of $AlCl_3$. But $AlCl_3$ is acidic in nature, while aniline is a strong base. Thus, aniline reacts with $AlCl_3$ to form a salt (as shown in the following equation).



Due to the positive charge on the N-atom, electrophilic substitution in the benzene ring is deactivated. Hence, aniline does not undergo the Friedel-Crafts reaction.

(vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines:

The diazonium ion undergoes resonance as shown below:



This resonance accounts for the stability of the diazonium ion. Hence, diazonium salts of aromatic amines are more stable than those of aliphatic amines.

(vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines:

Gabriel phthalimide synthesis results in the formation of 1° amine only. 2° or 3° amines are not formed in this synthesis. Thus, a pure 1° amine can be obtained. Therefore, Gabriel phthalimide synthesis is preferred for synthesizing primary amines.

Question 9.4:

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 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:

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

Answer

(i) In $C_2H_5NH_2$, only one $-C_2H_5$ group is present while in $(C_2H_5)_2NH$, two $-C_2H_5$ groups are present. Thus, the +I effect is more 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 $C_6H_5NHCH_3$ and $C_6H_5NH_2$ are less basic than $(C_2H_5)_2NH$ and $C_2H_5NH_2$ due to the delocalization of the lone pair in the former two. Further, among $C_6H_5NHCH_3$ and $C_6H_5NH_2$, 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:

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

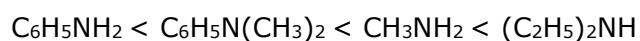
We know that the higher the basic strength, the lower is the pK_b values.

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

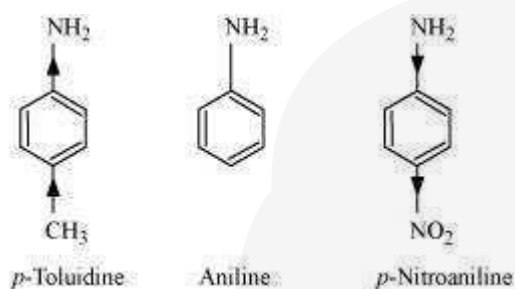
(ii) $C_6H_5N(CH_3)_2$ is more basic than $C_6H_5NH_2$ due to the presence of the +I effect of two $-CH_3$ groups in $C_6H_5N(CH_3)_2$. Further, CH_3NH_2 contains one $-CH_3$ group while $(C_2H_5)_2NH$ contains two $-C_2H_5$ groups. Thus, $(C_2H_5)_2NH$ is more basic than $C_2H_5NH_2$.

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:



(iii) (a)



In p -toluidine, the presence of electron-donating $-CH_3$ group increases the electron density on the N-atom.

Thus, p -toluidine is more basic than aniline.

On the other hand, the presence of electron-withdrawing $-NO_2$ 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:



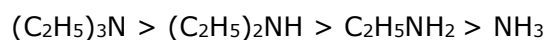
(b) $C_6H_5NHCH_3$ is more basic than $C_6H_5NH_2$ due to the presence of electron-donating $-CH_3$ group in $C_6H_5NHCH_3$.

Again, in $C_6H_5NHCH_3$, $-C_6H_5$ group is directly attached to the N-atom. However, it is not so in $C_6H_5CH_2NH_2$. Thus, in $C_6H_5NHCH_3$, the $-R$ effect of $-C_6H_5$ group decreases the electron density over the N-atom. Therefore, $C_6H_5CH_2NH_2$ is more basic than $C_6H_5NHCH_3$.

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

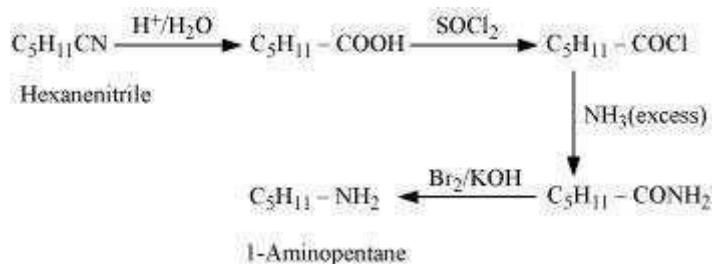


(iv) In the gas phase, there is no solvation effect. As a result, the basic strength mainly depends upon the +I effect. The higher the +I effect, the stronger is the base. Also, the greater the number of alkyl groups, the higher is the +I effect. Therefore, the given compounds can be arranged in the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

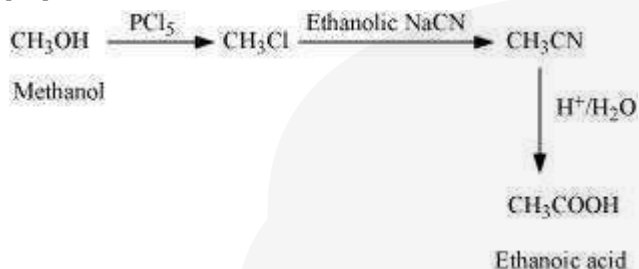


(v) The boiling points of compounds depend on the extent of H-bonding present in that compound. The more extensive the H-bonding in the compound, the higher is the boiling point. $(CH_3)_2NH$ contains only one H-atom whereas $C_2H_5NH_2$ contains two H-atoms. Then,

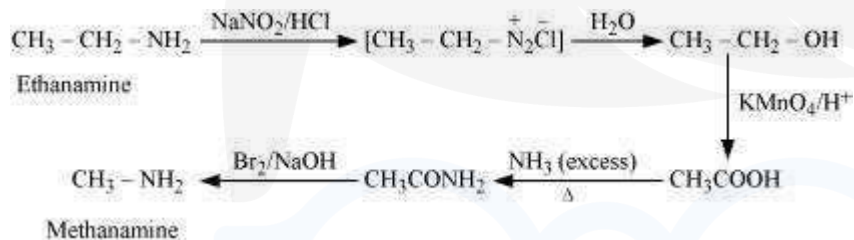
(ii)



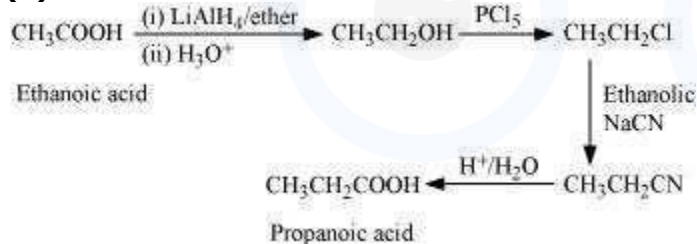
(iii)



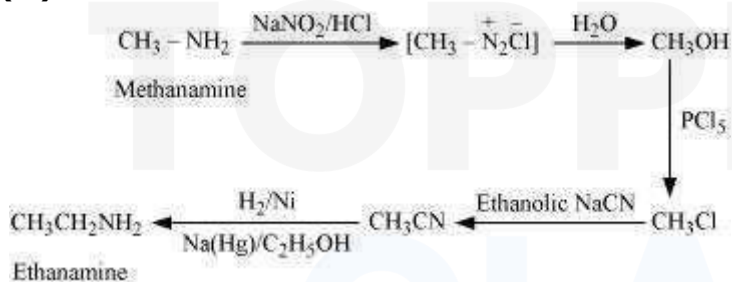
(iv)



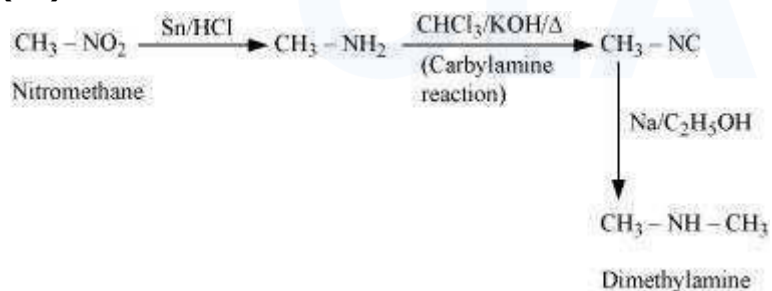
(v)



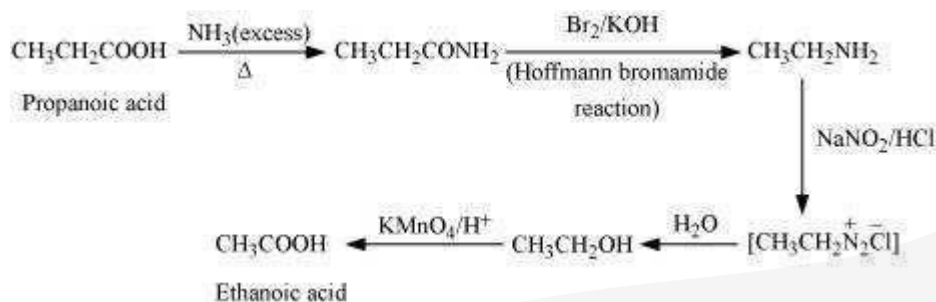
(vi)



(vii)



(viii)

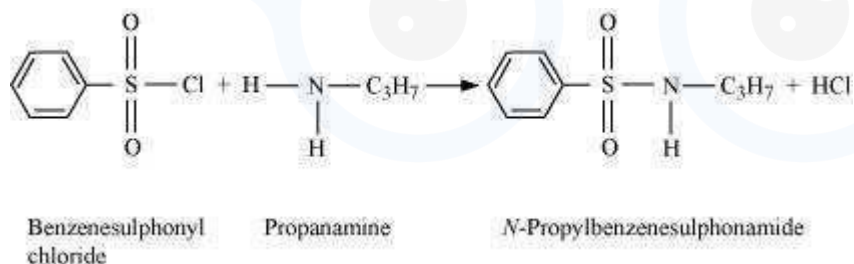


Question 9.6:

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

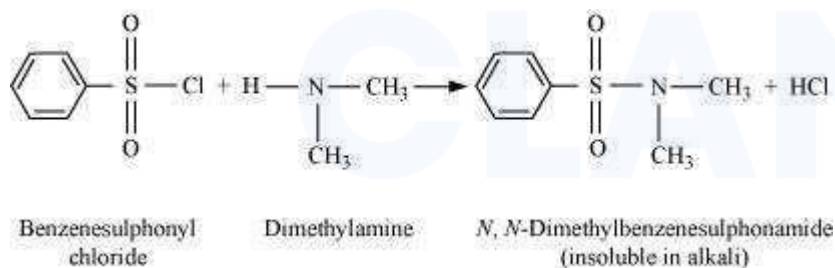
Answer

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, benzenesulphonyl chloride ($\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$). The three types of amines react differently with Hinsberg's reagent. Therefore, they can be easily identified using Hinsberg's reagent. Primary amines react with benzenesulphonyl chloride to form N-alkylbenzenesulphonyl amide which is soluble in alkali.



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 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.



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 hand, tertiary amines do not react with Hinsberg's reagent at all.

Question 9.7:

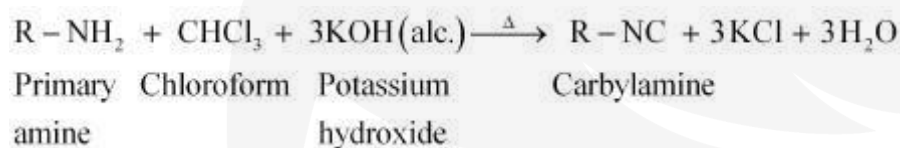
Write short notes on the following:

- (i) Carbylamine reaction
- (ii) Diazotisation
- (iii) Hofmann's bromamide reaction
- (iv) Coupling reaction
- (v) Ammonolysis
- (vi) Acetylation
- (vii) Gabriel phthalimide synthesis.

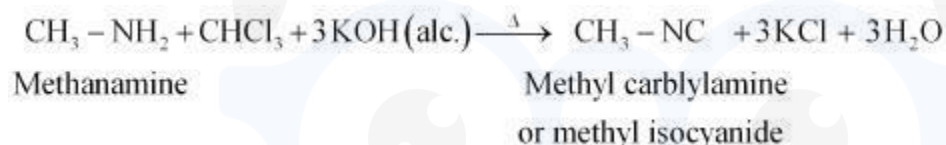
Answer

(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) Diazotisation

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.

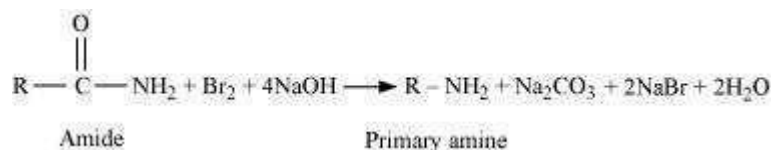
For example, on treatment with NaNO_2 and HCl at 273–278 K, aniline produces benzenediazonium chloride, with NaCl and H_2O as by-products.



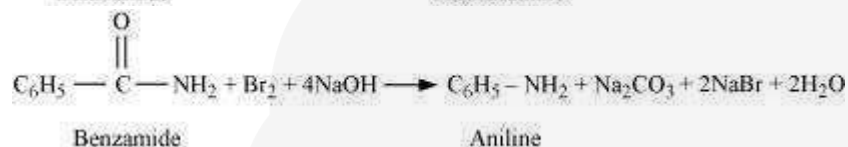
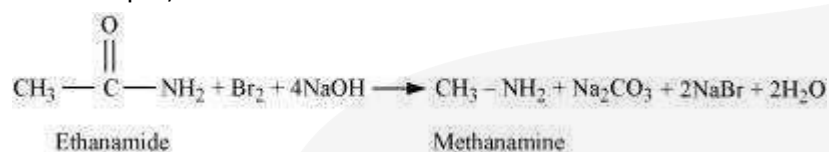
(iii) Hoffmann bromamide reaction

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 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.

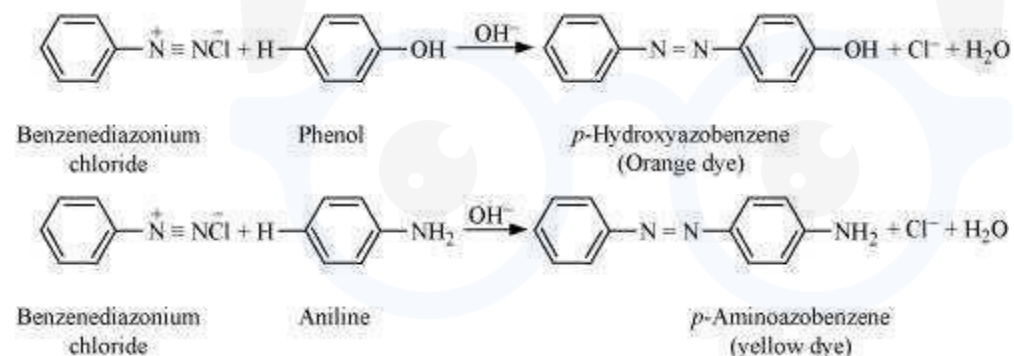


For example,



(iv) Coupling reaction

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



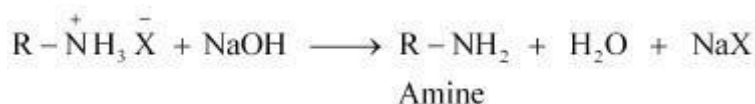
It can be observed that, the para-positions of phenol and aniline are coupled with the diazonium salt. This reaction proceeds through electrophilic substitution.

(v) Ammonolysis

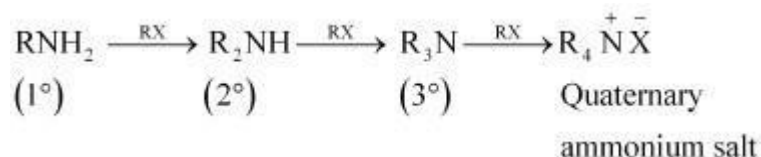
When an alkyl or benzyl halide is allowed to react with an ethanolic solution of ammonia, it undergoes nucleophilic substitution reaction in which the halogen atom is replaced by an amino (-NH₂) group. This process of cleavage of the carbon-halogen bond is known as ammonolysis.



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

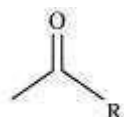


Though primary amine is produced as the major product, this process produces a mixture of primary, secondary and tertiary amines, and also a quaternary ammonium salt as shown.



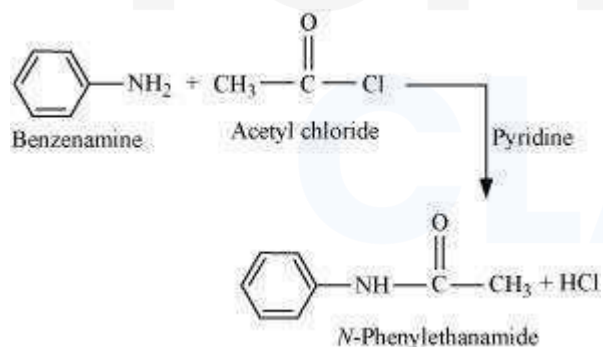
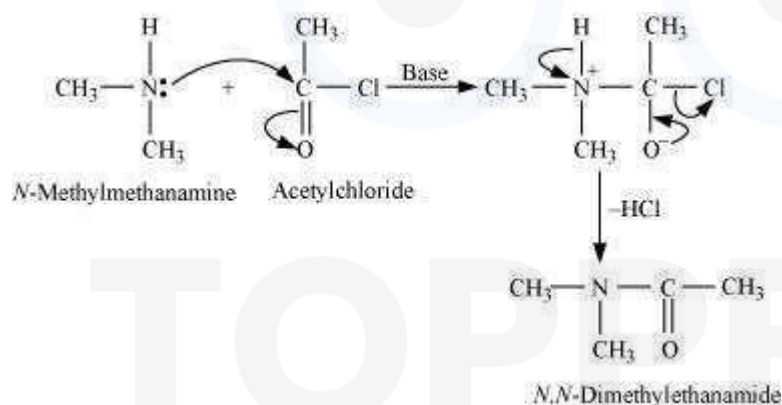
(vi) Acetylation

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

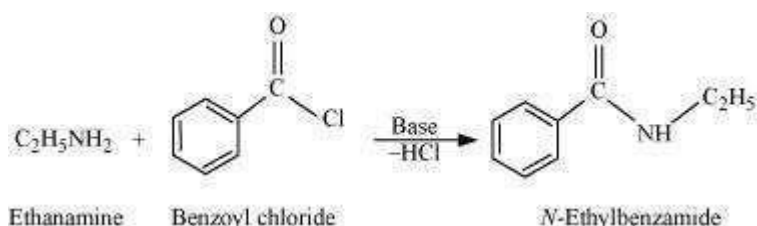


Acetyl group

Aliphatic and aromatic primary and 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 in turn leads to the production of amides. To shift the equilibrium to the right hand side, the HCl formed during the reaction is removed as soon as it is formed. This reaction is carried out in the presence of a base (such as pyridine) which is stronger than the amine.

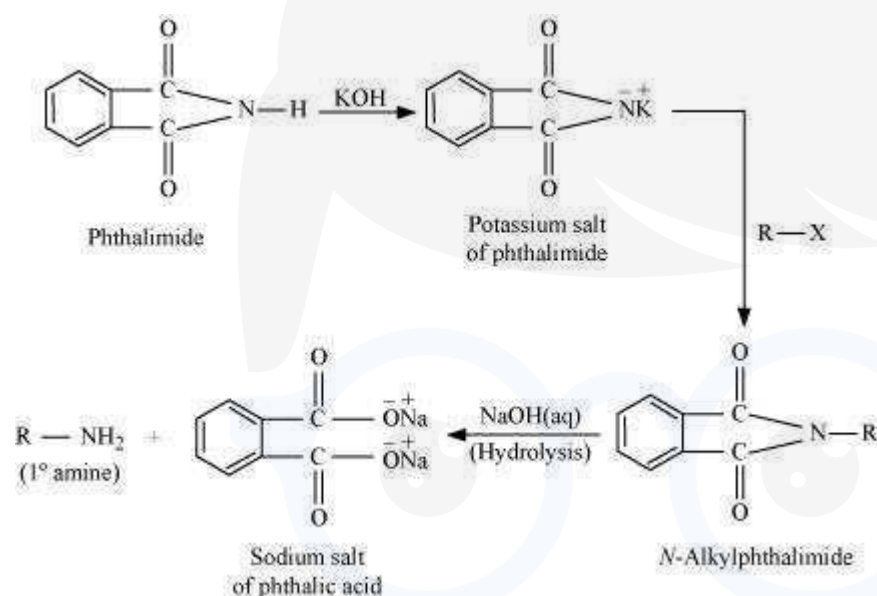


When amines react with benzoyl chloride, the reaction is also known as benzoylation. For example,



(vii) Gabriel phthalimide synthesis

Gabriel phthalimide synthesis is a very useful method for the preparation of aliphatic primary amines. It involves the treatment of phthalimide with ethanolic potassium hydroxide to form potassium salt of phthalimide. This salt is further heated with alkyl halide, followed by alkaline hydrolysis to yield the corresponding primary amine.



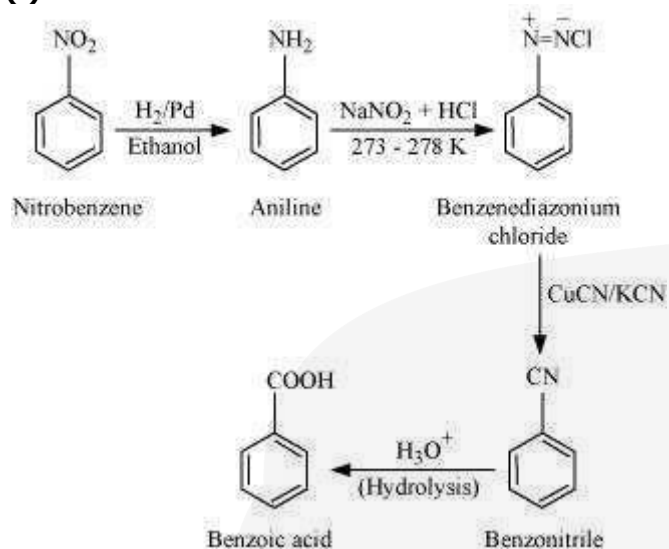
Question 9.8:

Accomplish the following conversions:

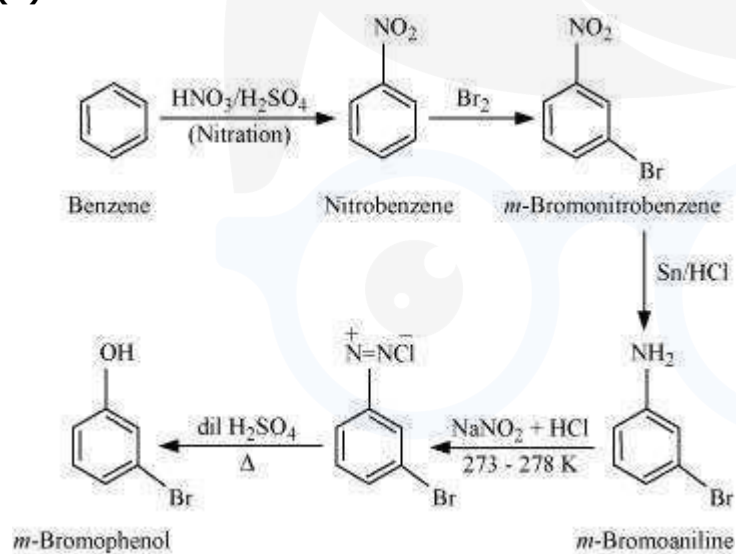
- (i) Nitrobenzene to benzoic acid
- (ii) Benzene to *m*-bromophenol
- (iii) Benzoic acid to aniline
- (iv) Aniline to 2,4,6-tribromofluorobenzene
- (v) Benzyl chloride to 2-phenylethanamine
- (vi) Chlorobenzene to *p*-chloroaniline
- (vii) Aniline to *p*-bromoaniline
- (viii) Benzamide to toluene
- (ix) Aniline to benzyl alcohol.

Answer

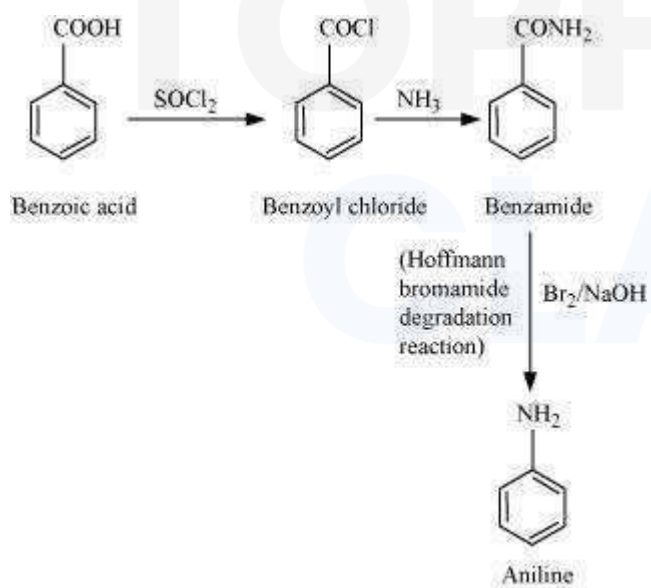
(i)



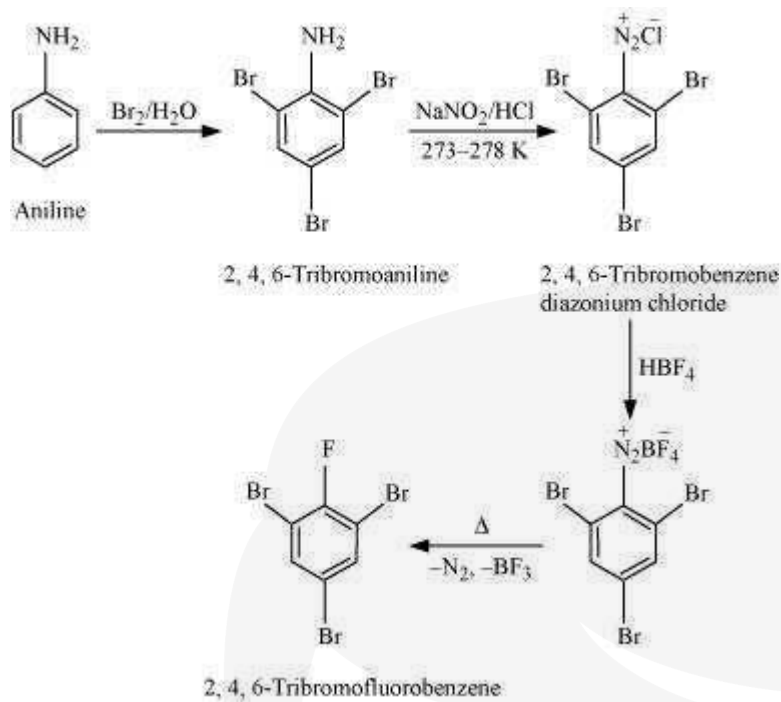
(ii)



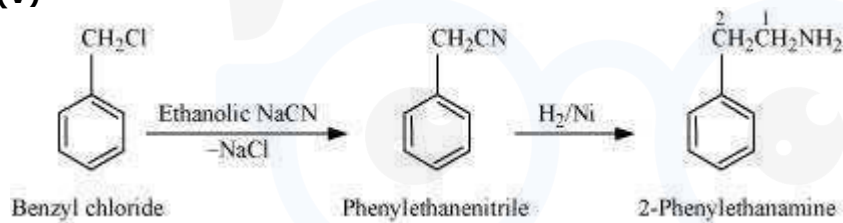
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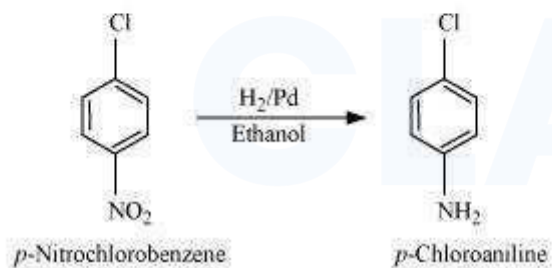
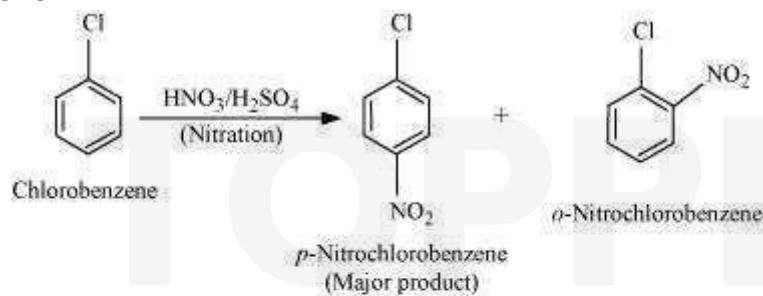
(iv)



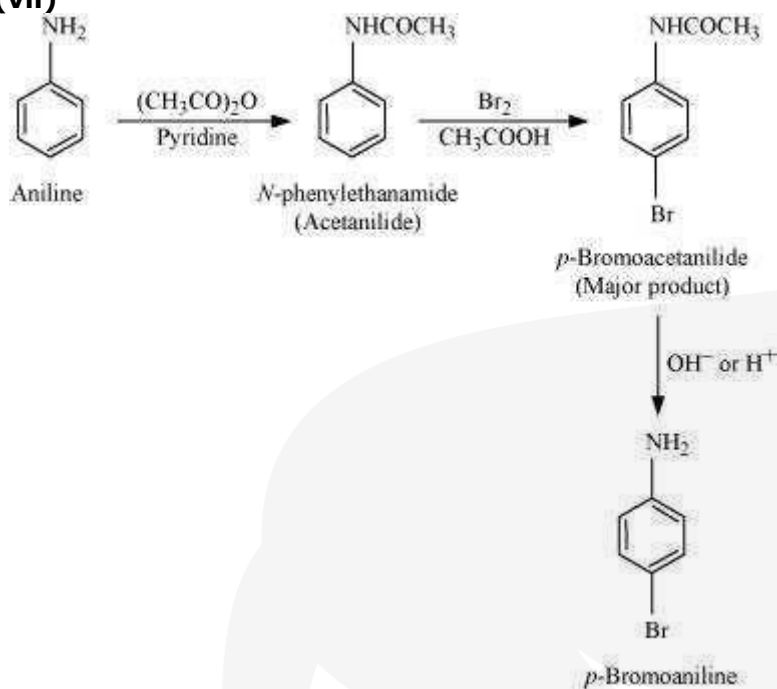
(v)



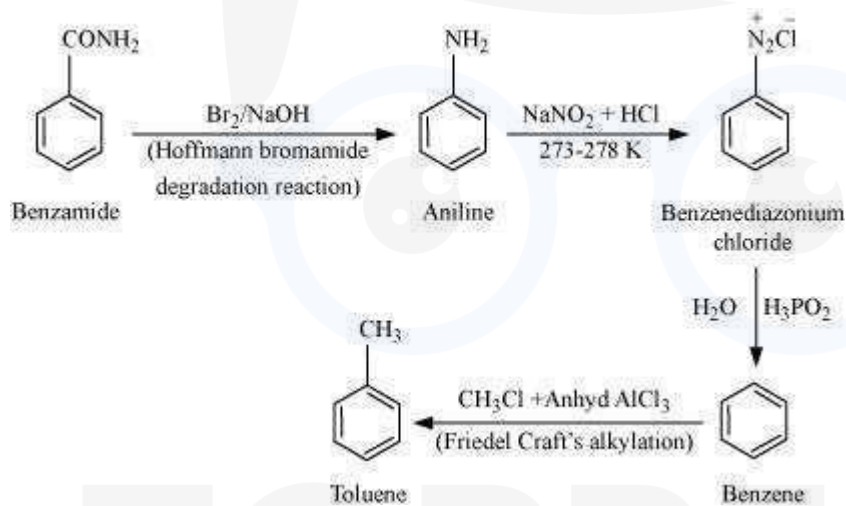
(vi)



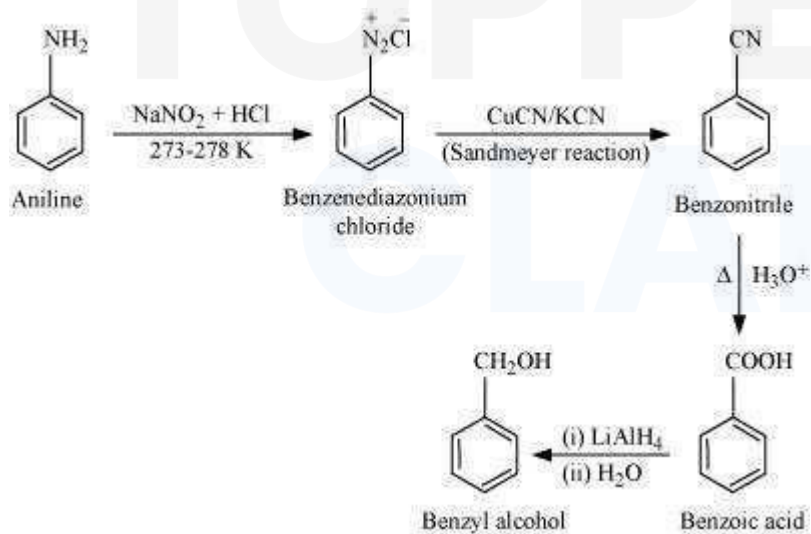
(vii)



(viii)

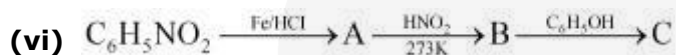
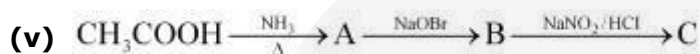
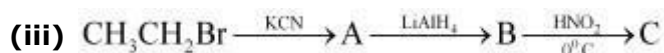
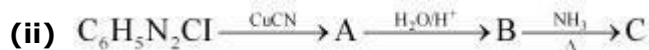


(ix)



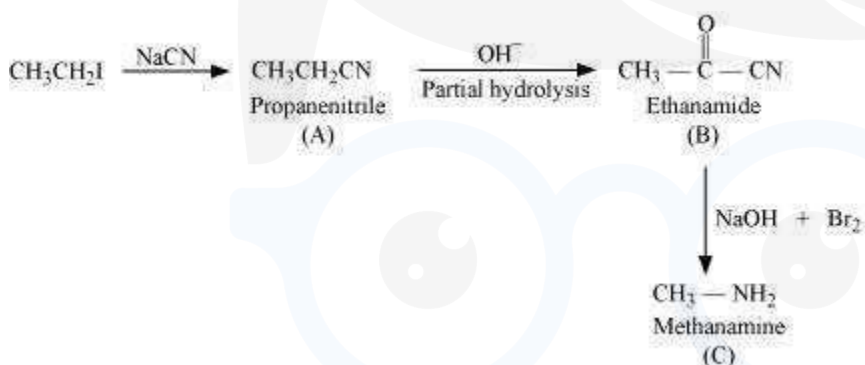
Question 9.9:

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

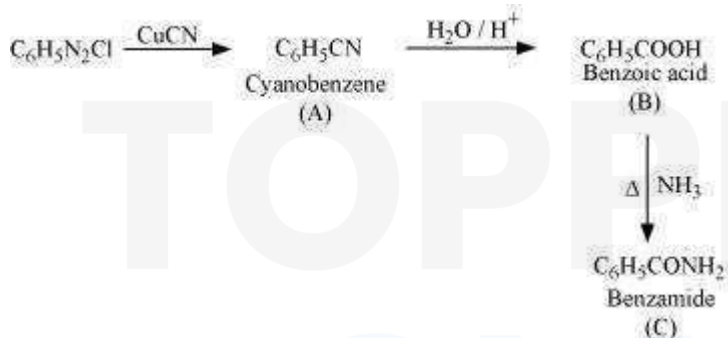


Answer

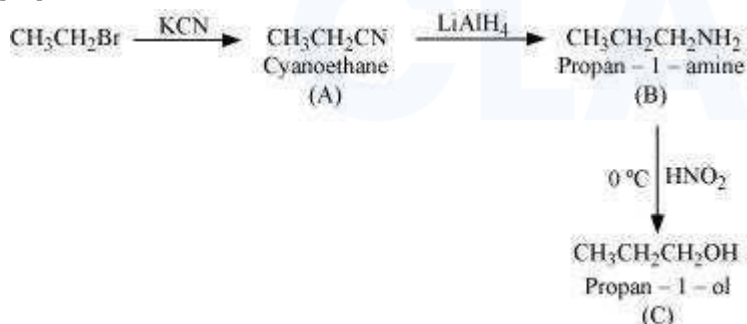
(i)



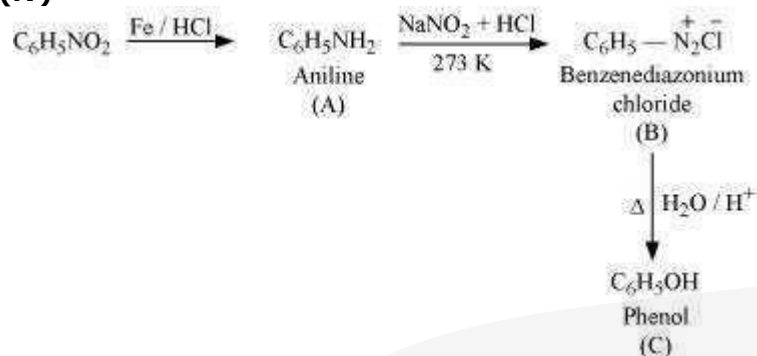
(ii)



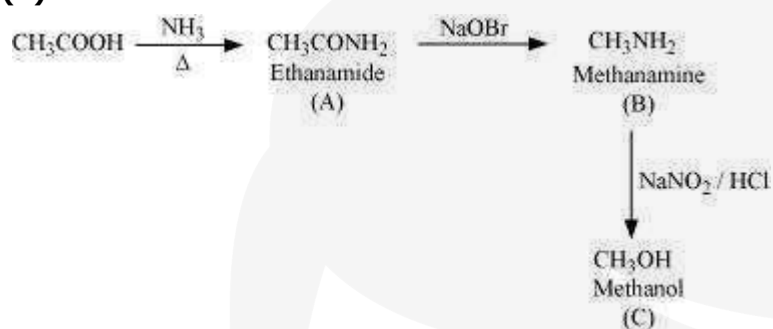
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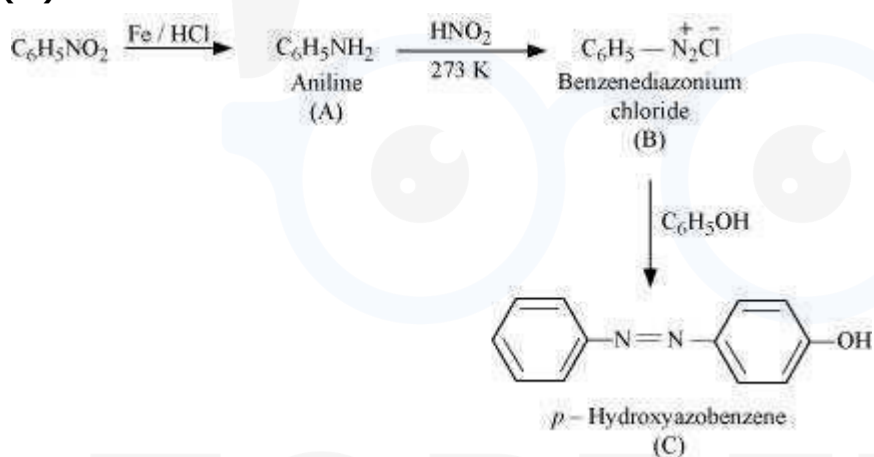
(iv)



(v)



(vi)

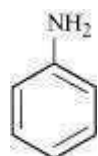


Question 9.10:

An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br₂ and KOH forms a compound 'C' of molecular formula C₆H₇N. Write the structures and IUPAC names of compounds A, B and C.

Answer

It is given that compound 'C' having the molecular formula, C_6H_7N 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, C_6H_7N is aniline, ($C_6H_5NH_2$).



Aniline

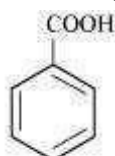
Therefore, compound 'B' (from which 'C' is formed) must be benzamide, ($C_6H_5CONH_2$).



Benzamide

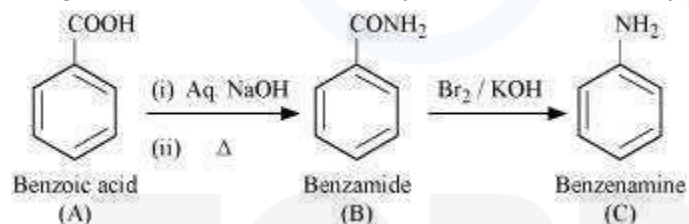
Further, benzamide is formed by heating compound 'A' with aqueous ammonia.

Therefore, compound 'A' must be benzoic acid.



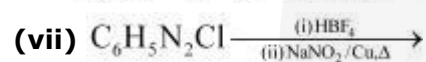
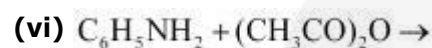
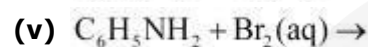
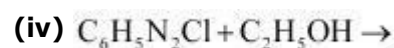
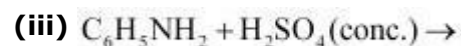
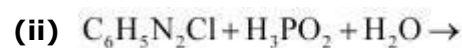
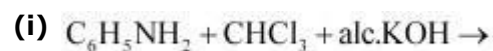
Benzoic acid

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



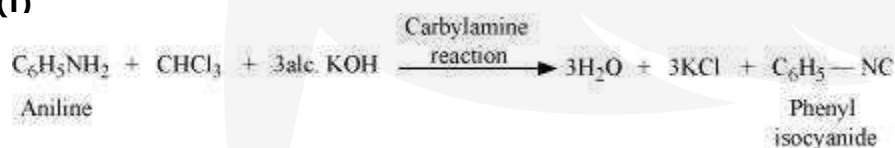
Question 9.11:

Complete the following reactions:

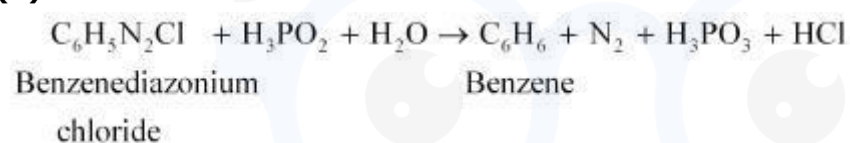


Answer

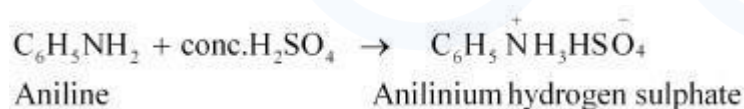
(i)



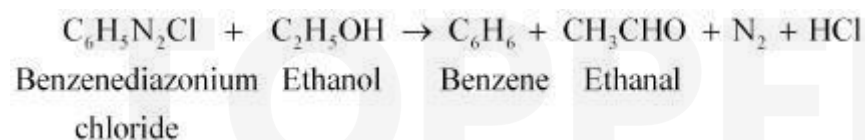
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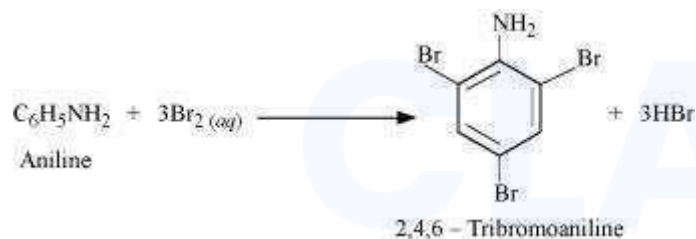
(iii)

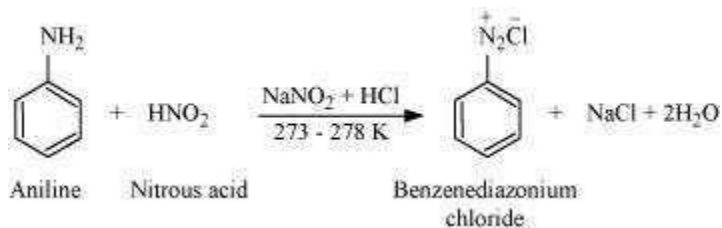


(iv)

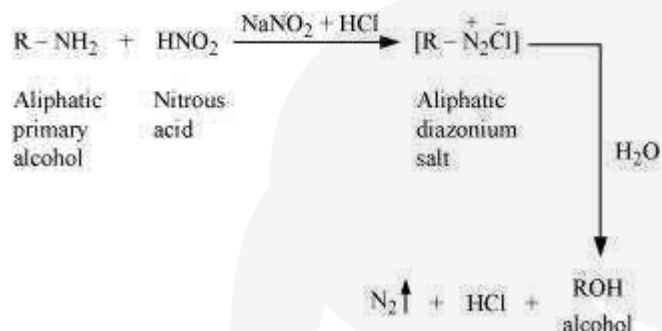


(v)





(ii) Aliphatic primary amines react with nitrous acid (prepared in situ from NaNO₂ and a mineral acid such as HCl) to form unstable aliphatic diazonium salts, which further produce alcohol and HCl with the evolution of N₂ gas.



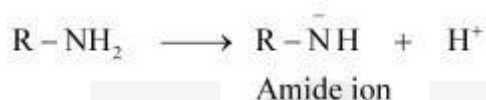
Question 9.14:

Give plausible explanation for each of the following:

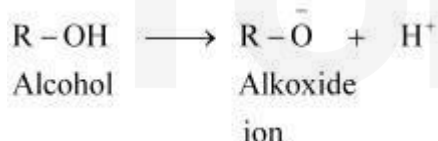
- (i)** Why are amines less acidic than alcohols of comparable molecular masses?
- (ii)** Why do primary amines have higher boiling point than tertiary amines?
- (iii)** Why are aliphatic amines stronger bases than aromatic amines?

Answer

(i) Amines undergo protonation to give amide ion.

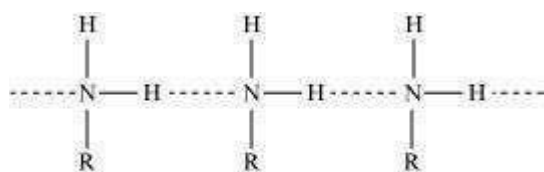


Similarly, alcohol loses a proton to give alkoxide ion.

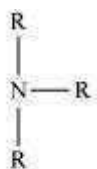


In an amide ion, the negative charge is on the N-atom whereas in alkoxide ion, the negative charge is on the O-atom. Since O is more electronegative than N, O can accommodate the negative charge more easily than N. As a result, the amide ion is less stable than the alkoxide ion. Hence, amines are less acidic than alcohols of comparable molecular masses.

(ii) In a molecule of tertiary amine, there are no H-atoms whereas in primary amines, two hydrogen atoms are present. Due to the presence of H-atoms, primary amines undergo extensive intermolecular H-bonding.



Primary amine



Tertiary amine

As a result, extra energy is required to separate the molecules of primary amines. Hence, primary amines have higher boiling points than tertiary amines.

- (iii)** Due to the $-R$ effect of the benzene ring, the electrons on the N-atom are less available in case of aromatic amines. Therefore, the electrons on the N-atom in aromatic amines cannot be donated easily. This explains why aliphatic amines are stronger bases than aromatic amines.

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