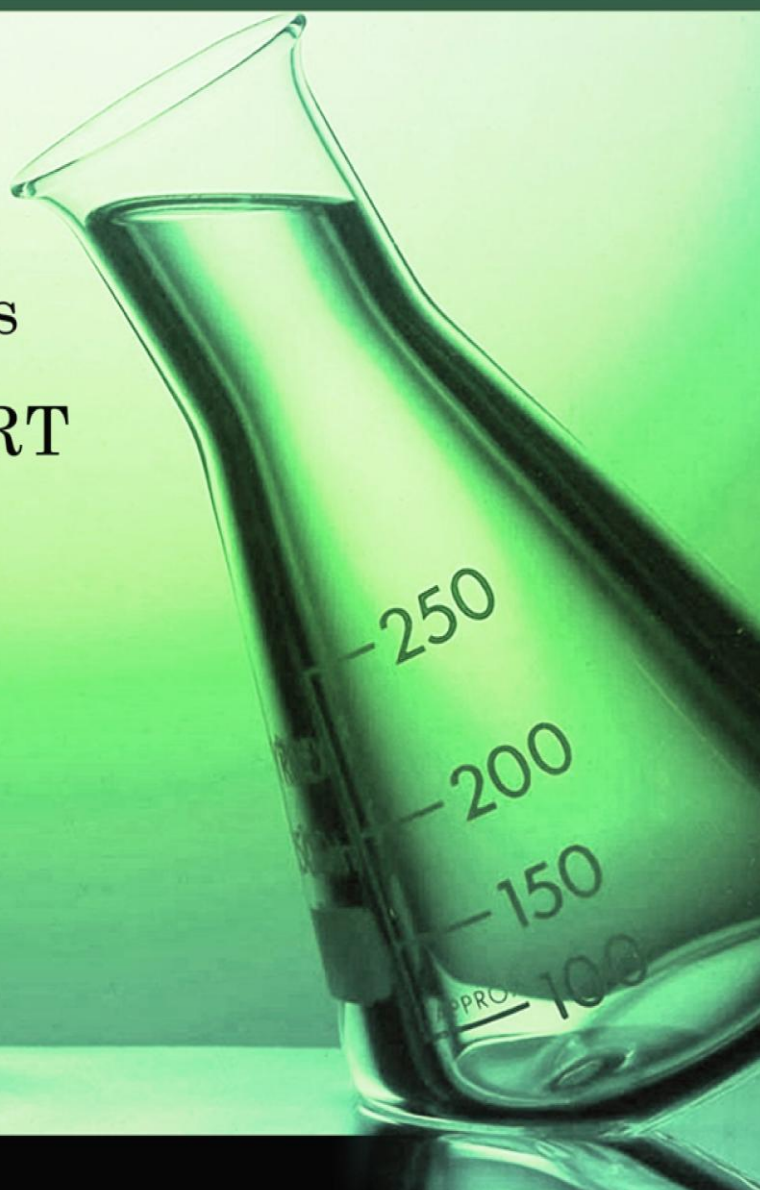




Simplifying Test Prep

CBSE Class
12 th NCERT
Chemistry
Solutions-
Chapter-13
(E BOOK)



Amines

Preface

This e-book is prepared by the CBSE board exam experts of jagranjosh.com, an online educational portal of Dainik Jagran.

The purpose of providing solutions for CBSE class 12th Science and Mathematics NCERT book is to explain the questions in an easy way and as per the CBSE marking scheme. This is a product exclusively for CBSE class 12th students which acts as a time-saver by providing a pattern for the solutions of NCERT based questions as per the CBSE curriculum. This document help to build a strong concept on the chapter mentioned in here and hence the students have been guided in the most appropriate way for their board examination

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Chapter-13
Amines
Class-XII
Subject-Chemistry

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

- (i) $(\text{CH}_3)_2\text{CHNH}_2$
- (ii) $\text{CH}_3(\text{CH}_2)_2\text{NH}_2$
- (iii) $\text{CH}_3\text{NHCH}(\text{CH}_3)_2$
- (iv) $(\text{CH}_3)_3\text{CNH}_2$
- (v) $\text{C}_6\text{H}_5\text{NHCH}_3$
- (vi) $(\text{CH}_3\text{CH}_2)_2\text{NCH}_3$
- (vii) $m\text{-BrC}_6\text{H}_4\text{NH}_2$

Answer 13.1

- (i) 1-Methylethanamine (1^0 amine)
- (ii) Propan-1-amine (1^0 amine)
- (iii) N-Methyl-2-methylethanamine (2^0 amine)
- (iv) 2-Methylpropan-2-amine (1^0 amine)
- (v) N-Methylbenzamine (2^0 amine)
- (vi) N-Ethyl-N-methylethanamine (3^0 amine)
- (vii) 3-Bromobenzenamine or 3-bromoaniline (1^0 amine)

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

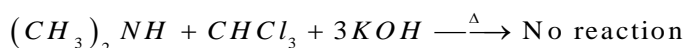
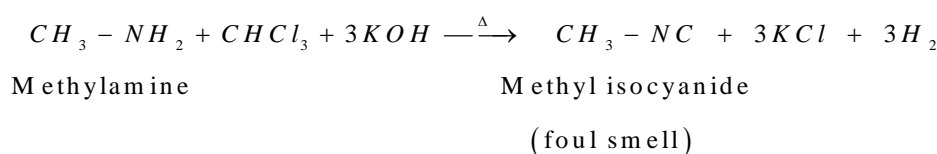
- (i) Methylamine and dimethylamine
- (ii) Secondary and tertiary amines
- (iii) Ethylamine and aniline
- (iv) Aniline and benzylamine
- (v) Aniline and N-methylaniline

Answer 13.2

- (i) Methylamine and dimethylamine can be distinguished by the carbylamine test.

Carbylamine test: When aliphatic and aromatic primary amines heated with chloroform and ethanolic potassium hydroxide, isocyanides (carbylamines) are formed.

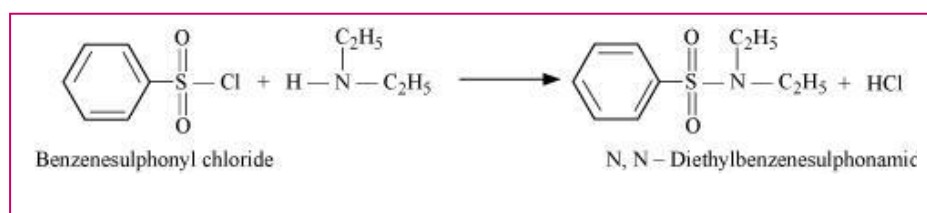
Methylamine gives a positive carbylamine test, but dimethylamine does not give this test.



- (ii) Secondary and tertiary amines can be distinguished by reacting with Hinsberg's reagent (benzenesulphonyl chloride, $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$).

Secondary amines react with Hinsberg's reagent & form a product which is insoluble in an alkali. For example- N, N-diethylamine

Tertiary amines do not react with Hinsberg's reagent.

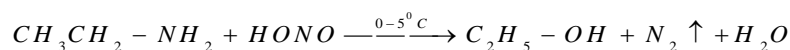
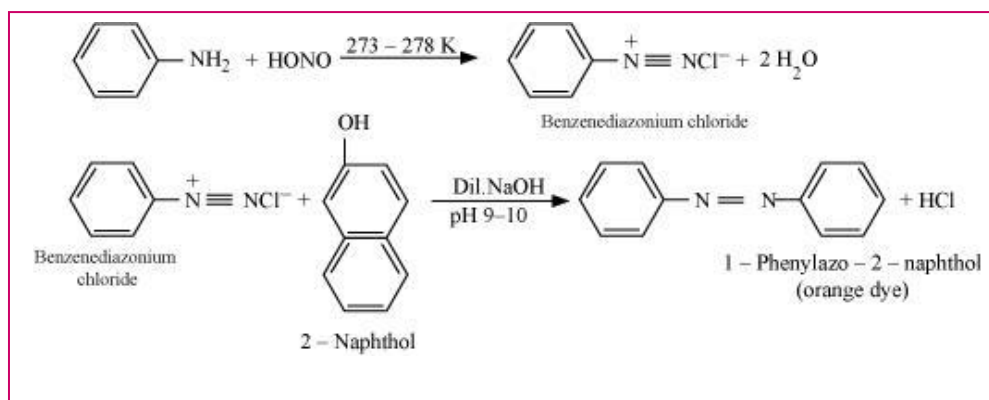


- (iii) Ethylamine and aniline can be distinguished using the azo-dye test.

Azo-dye test:

Aromatic amines react with HNO_2 ($\text{NaNO}_2 + \text{dil.HCl}$) at $0-5^\circ\text{C}$, followed by a reaction with the alkaline solution of 2-naphthol, and forms a dye. This dye is red, yellow, or orange in colour.

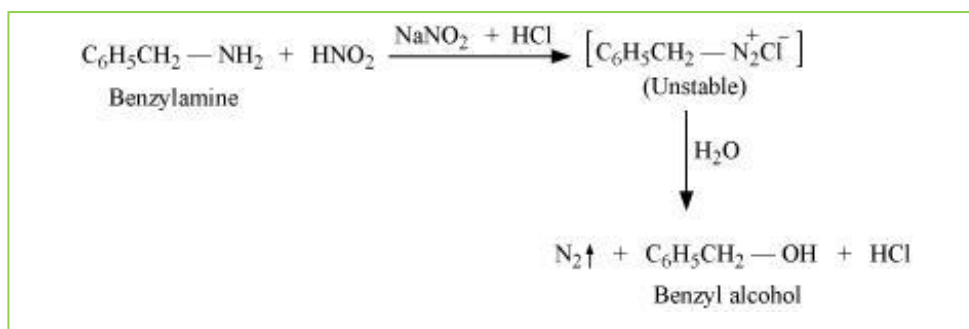
Aliphatic amines give a brisk effervescence due to the evolution of N₂ gas.



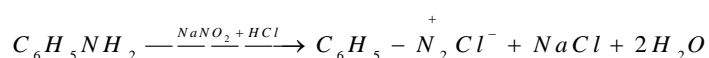
- (iv) Aniline and benzylamine can be distinguished by their reactions with the help of nitrous acid,

This nitric acid is prepared in situ from a mineral acid and sodium nitrite.

Benzylamine reacts with nitrous acid to form unstable diazonium salt, which in turn gives alcohol with the evolution of nitrogen gas.



Aniline reacts with HNO₂ at a low temperature to form stable diazonium salt. Thus, nitrogen gas is not evolved.

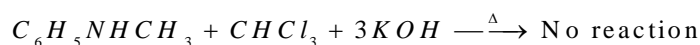
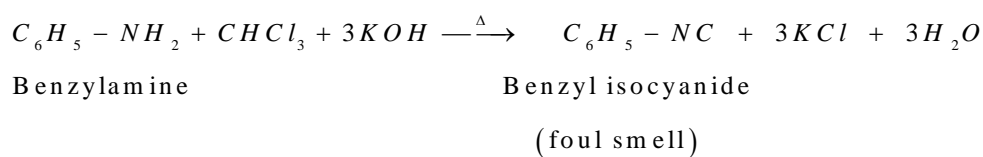


- (v) Aniline and N-methylaniline can be distinguished using the Carbylamine test.

Carbylamine test: On heating with chloroform and ethanolic potassium hydroxide, primary amines form foul-smelling isocyanides or carbylamines.

Aniline, being an aromatic primary amine, gives positive carbylamine test.

N-methylaniline, being a secondary amine does not give this test.

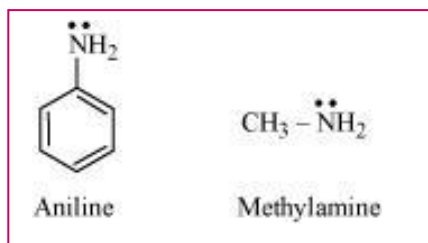


13.3 Account for the following:

- (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*, *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.**

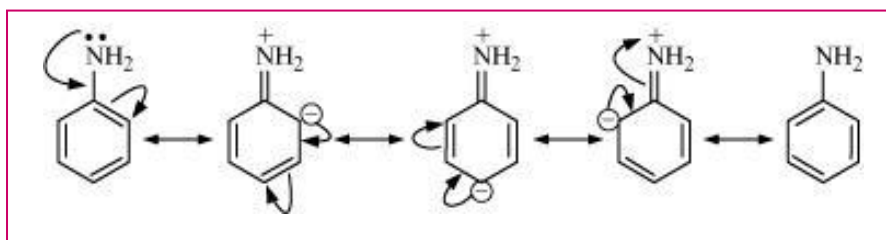
Answer 13.3

- (i) Structures of aniline & methylamine are:-



Resonating structures of aniline: -

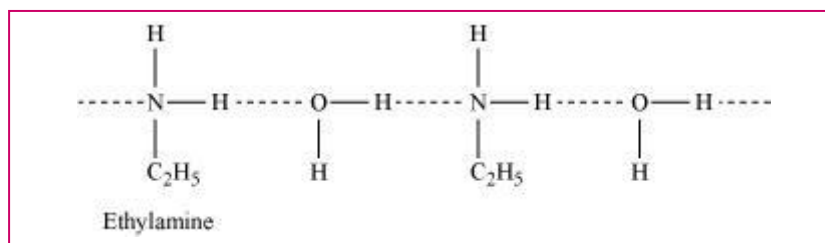
Here, electrons on the N-atom are delocalized over the benzene ring. Thus, the electrons on the N-atom are less available to donate.



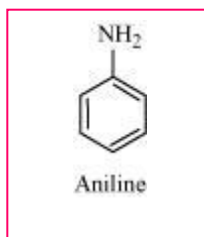
In case of methylamine, the electron density on the N-atom is increased. Thus, aniline is less basic than methylamine.

Hence, pK_b of aniline is more than that of methylamine.

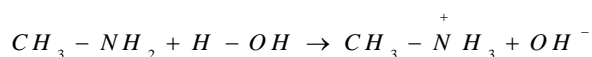
- (ii) Hydrogen bonds are formed when ethylamine is added to water. Thus, it is soluble in water.



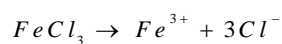
In case of aniline, large hydrophobic $-\text{C}_6\text{H}_5$ group is present. Because of which, formation of H-bonds in water is not that much prominent as it was in ethylamine. Thus, it is insoluble in water.



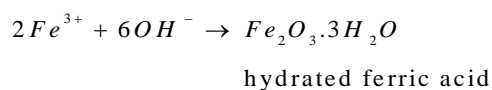
- (iii) Because of the +I effect of $-\text{CH}_3$ group in methylamine, it is more basic than water. Thus, on reaction with water, following ions are produced:



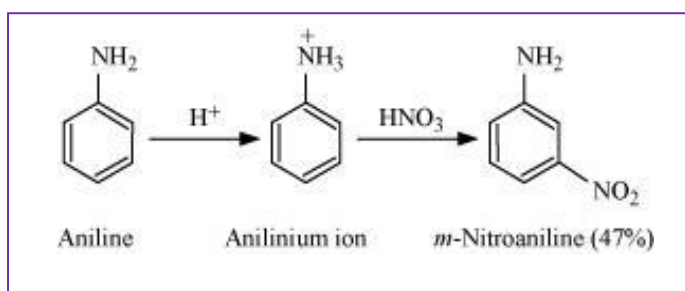
Ferric chloride (FeCl_3) dissociates in water to form Fe^{3+} and Cl^- ions.



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

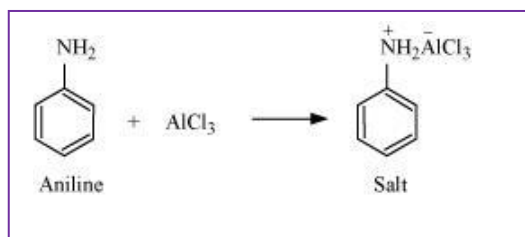


- (iv) In an acidic medium, aniline is protonated to give anilinium ion which is meta-directing.



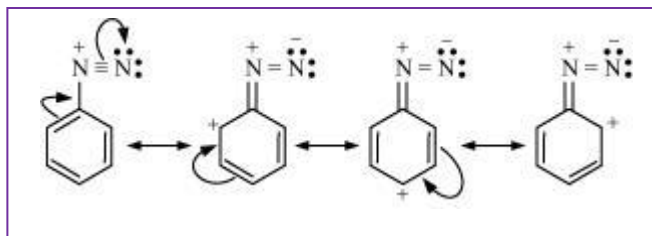
Thus, on nitration, aniline gives a substantial amount of *m*-nitroaniline.

- (v) AlCl_3 is acidic in nature & aniline is a strong base. Hence, aniline reacts with AlCl_3 to form a salt.



But it does not undergo the Friedel-Crafts reaction. It happens because of the positive charge on the N-atom. This leads to deactivation of electrophilic substitution in the benzene ring takes place.

(vi) Resonating structures of diazonium ion are:



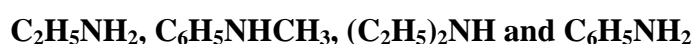
Hence, resonance is the main reason of stability of diazonium salts of aromatic amines as compared to aliphatic amines.

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

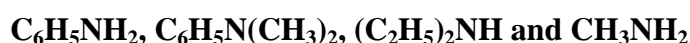
Only primary amines are formed in gabriel phthalimide synthesis. 2° or 3° amines are not formed in this synthesis. Thus, Gabriel phthalimide synthesis is preferred for synthesizing primary amines.

13.4 Arrange the following:

(i) In decreasing order of the pK_b values:



(ii) In increasing order of basic strength:



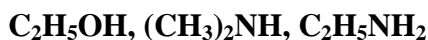
(iii) In increasing order of basic strength:



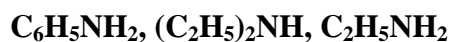
(iv) In decreasing order of basic strength in gas phase:



(v) In increasing order of boiling point:



(vi) In increasing order of solubility in water:

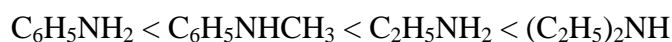


Answer 13.4

(i) The +I effect is more in $(\text{C}_2\text{H}_5)_2\text{NH}$ than in $\text{C}_2\text{H}_5\text{NH}_2$. Therefore, the electron density over the N-atom is more in $(\text{C}_2\text{H}_5)_2\text{NH}$ than in $\text{C}_2\text{H}_5\text{NH}_2$.

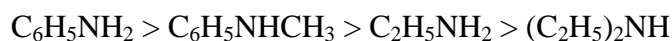
Due to the delocalization of the lone pair in $\text{C}_6\text{H}_5\text{NHCH}_3$ and $\text{C}_6\text{H}_5\text{NH}_2$, they are less basic than $(\text{C}_2\text{H}_5)_2\text{NH}$ and $\text{C}_2\text{H}_5\text{NH}_2$.

Thus, the order of increasing basicity of the given compounds is:



Higher the basic strength, lower the pK_b value.

Thus, the increasing order of pK_b values:

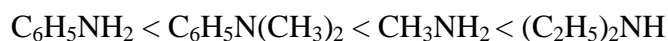


(ii) $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ is less basic than CH_3NH_2 because of the -R effect of $-\text{C}_6\text{H}_5$ group.

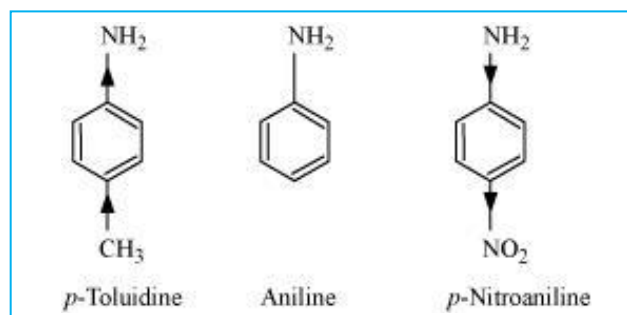
Now, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ is more basic than $\text{C}_6\text{H}_5\text{NH}_2$ due to the presence of the +I effect of two $-\text{CH}_3$ groups in $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$.

In CH_3NH_2 , one $-\text{CH}_3$ group is present whereas in $(\text{C}_2\text{H}_5)_2\text{NH}$, two $-\text{C}_2\text{H}_5$ groups are present. Thus, $(\text{C}_2\text{H}_5)_2\text{NH}$ is more basic than $\text{C}_2\text{H}_5\text{NH}_2$.

Thus, the increasing order of the basic strengths is:



(iii) (a)



p-toluidine is more basic than aniline as $-\text{CH}_3$ group present in *p*-toluidine increases the electron density on the N-atom.

In *p*-nitroaniline, $-\text{NO}_2$ group decreases the electron density over the N-atom. Thus, it is less basic than aniline.

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



- (b) In $\text{C}_6\text{H}_5\text{NHCH}_3$, $-\text{CH}_3$ group (electron-donating group) is present. Because of which $\text{C}_6\text{H}_5\text{NHCH}_3$ is more basic than $\text{C}_6\text{H}_5\text{NH}_2$. Also, $-\text{C}_6\text{H}_5$ group is directly attached to the N-atom which is not present in $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$.

$-\text{R}$ effect of $-\text{C}_6\text{H}_5$ group decreases the electron density over the N-atom in $\text{C}_6\text{H}_5\text{NHCH}_3$.

Thus, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ is more basic than $\text{C}_6\text{H}_5\text{NHCH}_3$.

Thus, the increasing order of the basic strengths of the given compounds is:



- (iv) Here, the basic strength mainly depends upon the $+\text{I}$ effect. Higher the $+\text{I}$ effect, the stronger is the base. Number of alkyl groups decides the intensity of $+\text{I}$ effect.

Thus, the order of decreasing basic strengths in the gas phase is:

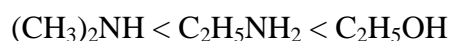


- (v) We know that, Oxygen is more electronegative than Nitrogen. Thus, $\text{C}_2\text{H}_5\text{OH}$ forms stronger H-bonds than $\text{C}_2\text{H}_5\text{NH}_2$.

Also, one hydrogen bond is present in $(\text{CH}_3)_2\text{NH}$ whereas in $\text{C}_2\text{H}_5\text{NH}_2$, 2 hydrogen bonds are present. Boiling points of compounds depend on the extent of H-bonding present in that compound.

Hence, the boiling point of $\text{C}_2\text{H}_5\text{NH}_2$ is higher than that of $(\text{CH}_3)_2\text{NH}$.

Thus, the increasing order of their boiling points is:

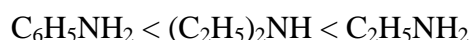


- (vi) Boiling points of compounds depend on the extent of H-bonding present in that compound. The more extensive the H-bonding, the higher is the solubility.

One hydrogen bond is present in $(\text{C}_2\text{H}_5)_2\text{NH}$ whereas in $\text{C}_2\text{H}_5\text{NH}_2$, 2 hydrogen bonds are present.

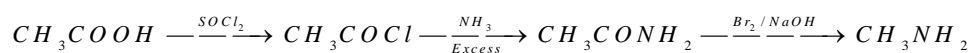
Thus, the solubility of $\text{C}_2\text{H}_5\text{NH}_2$ in water is more than that of $(\text{C}_2\text{H}_5)_2\text{NH}$.

Hence, the increasing order of their solubility in water is:



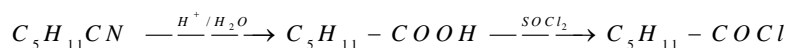
13.5 How will you convert?

- (i) Ethanoic acid into methanamine
- (ii) Hexanenitrile into 1-aminopentane
- (iii) Methanol to ethanoic acid
- (iv) Ethanamine into methanamine
- (v) Ethanoic acid into propanoic acid
- (vi) Methanamine into ethanamine
- (vii) Nitromethane into dimethylamine
- (viii) Propanoic acid into ethanoic acid

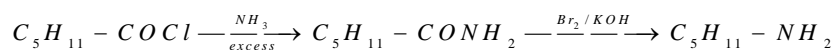
Answer 13.5**(i)**

Ethanoic
acid

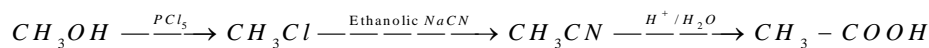
Methanamine

(ii)

Hexanenitrile

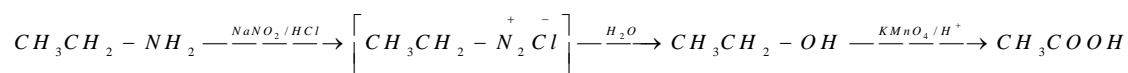


1-Aminopentane

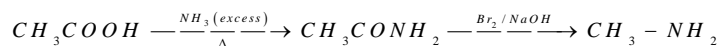
(iii)

Methanol

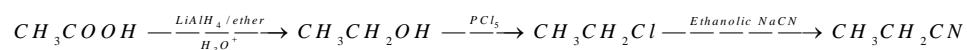
Ethanoic acid

(iv)

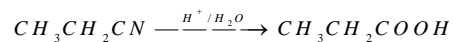
Ethanamine



Methanamine

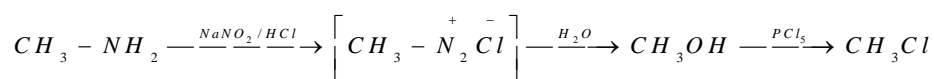
(v)

Ethanoic acid

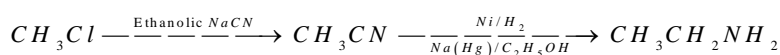


Propanoic acid

(vi)

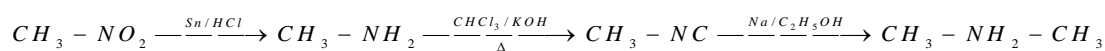


Methanamine



Ethanamine

(vii)



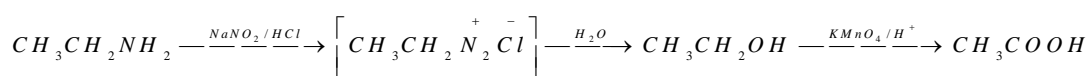
Nitromethane

Dimethylamine

(viii)



Propanoic acid



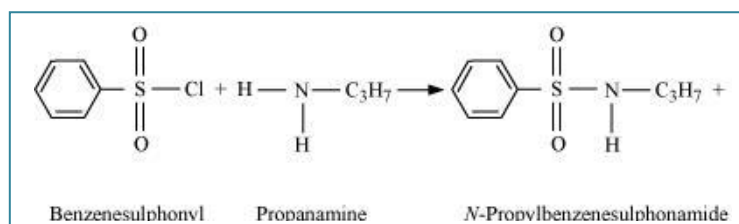
Ethanoic acid

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

Answer 13.6 **Hinsberg's test:**

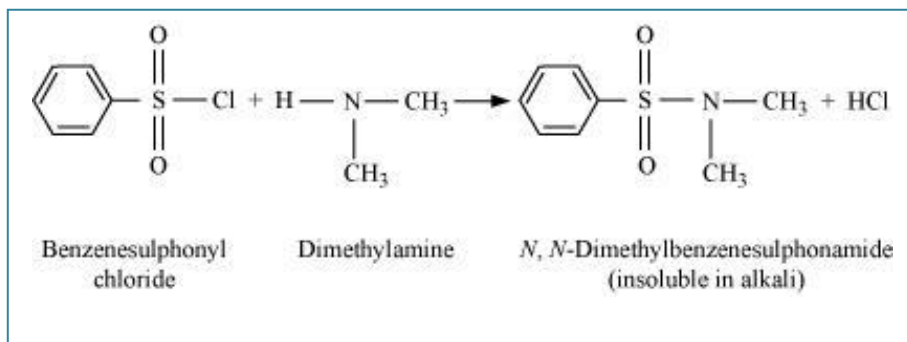
In this test, the amines are reacted with Hinsberg's reagent, benzenesulphonyl chloride ($C_6H_5SO_2Cl$).

Primary amines on reacting with hinsberg's reagent, forms N-alkylbenzenesulphonyl amide which is soluble in alkali.



Because of 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 behaves as acidic and dissolves in alkali.

Secondary amines form a sulphonamide on reacting with Hinsberg's reagent. This product is insoluble in alkali.



H-atom attached to the N-atom is absent in the sulphonamide. Thus, it is not acidic and insoluble in alkali.

Tertiary amines do not react with Hinsberg's reagent at all.

13.7 Write short notes on the following:

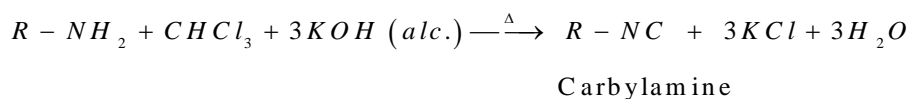
- (i) Carbylamine reaction
- (ii) Diazotisation
- (iii) Hofmann's bromamide reaction
- (iv) Coupling reaction
- (v) Ammonolysis
- (vi) Acetylation
- (vii) Gabriel phthalimide synthesis

Answer 13.6**(i) Carbylamine reaction:**

When aliphatic and aromatic primary amines are heated with chloroform and ethanolic potassium hydroxide, carbylamines are formed. Secondary and tertiary amines do not respond to this test.

Carbylamines have very unpleasant odours.

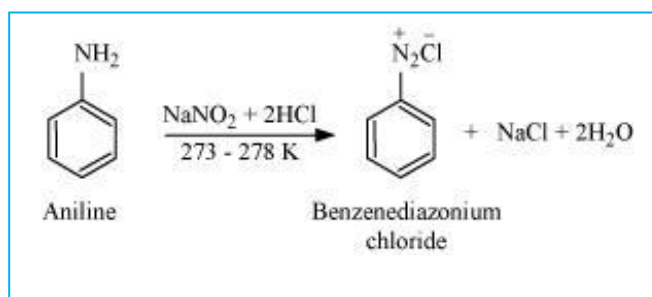
This is used as a test for the identification of primary amines.

**(ii) Diazotisation:**

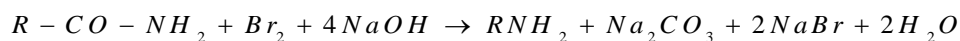
In this reaction, nitrous acid used is prepared in situ from $NaNO_2$ and a mineral acid.

Here, aromatic primary amines react with nitrous acid at low temperatures to form diazonium salts. This reaction is known as diazotization.

For example:

**(iii) Hoffmann bromamide reaction:**

This is a degradation reaction. In this reaction, 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 reaction is known as Hoffmann bromamide reaction.



Amide

1° amine

For example:

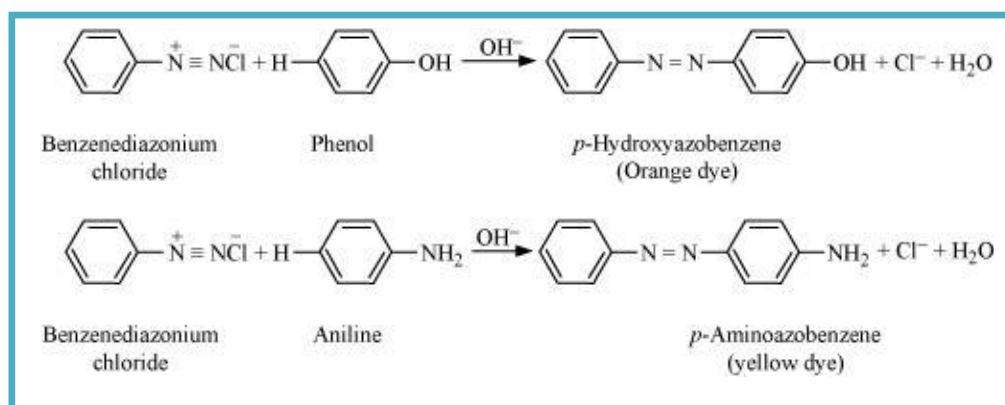


Ethanamide

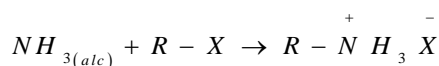
Methanamine

(iv) **Coupling reaction:**

In this reaction, two aromatic rings joined through the $-N=N-$ bond. This reaction is known as coupling reaction. For example-

(v) **Ammonolysis:**

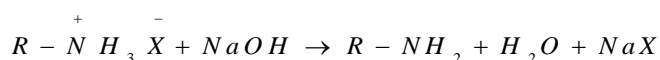
In this reaction, an alkyl or benzyl halide is treated with an ethanolic solution of ammonia, which undergoes nucleophilic substitution reaction. In this, the halogen atom is replaced by an amino ($-NH_2$) group. This is known as ammonolysis.



Ammonia

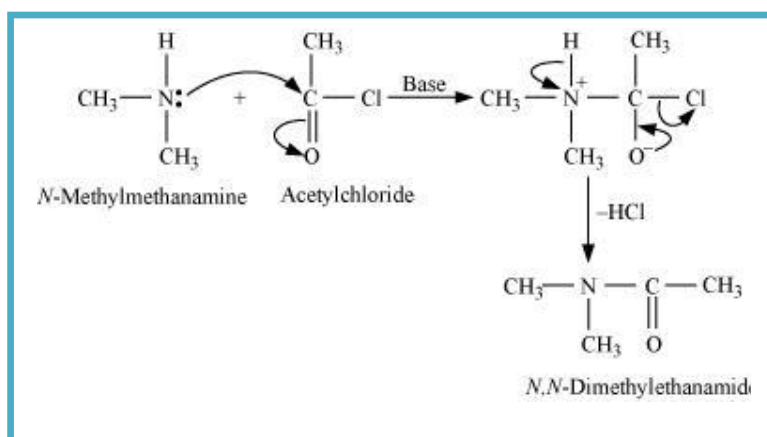
Substituted ammonium salt

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

(vi) **Acetylation:**

By this reaction, an acetyl group is introduced into a molecule.

To carry acetylation in aliphatic and aromatic amines, they are treated with acid chlorides, anhydrides or esters. It involves the replacement of the hydrogen atom of $-NH_2$ or $>NH$ group by the acetyl group.

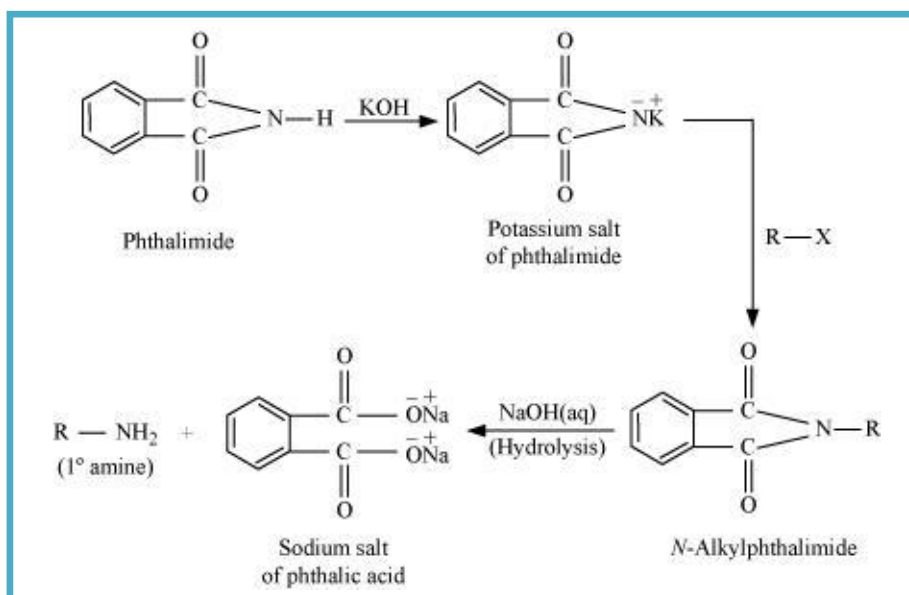


(vii) **Gabriel phthalimide synthesis:**

This method is a very useful for the preparation of aliphatic primary amines.

This reaction takes place in 3 steps:

- First, phthalimide is treated with ethanolic potassium hydroxide to form potassium salt of phthalimide
- This salt of phthalimide is further heated with alkyl halide
- This reaction is followed by alkaline hydrolysis to yield the corresponding primary amine.

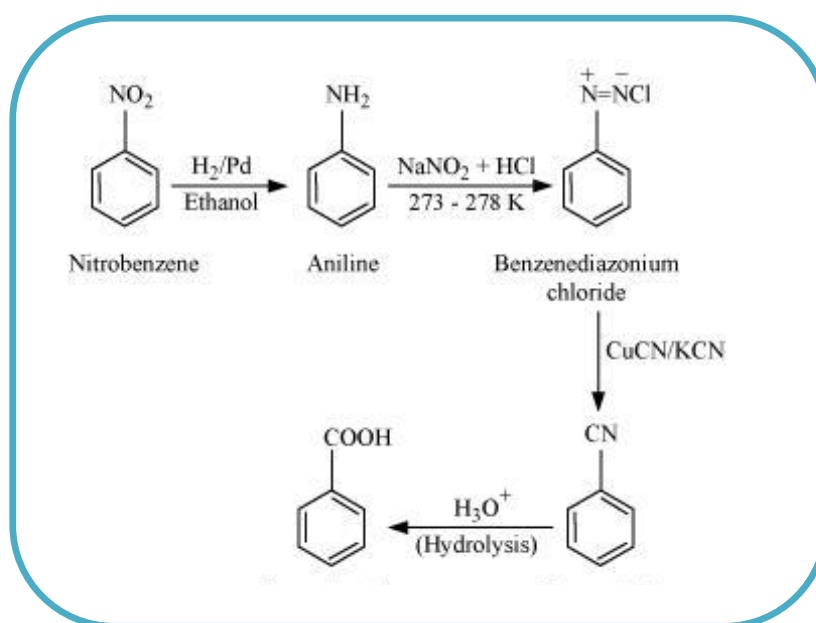


13.8 Accomplish the following conversions:

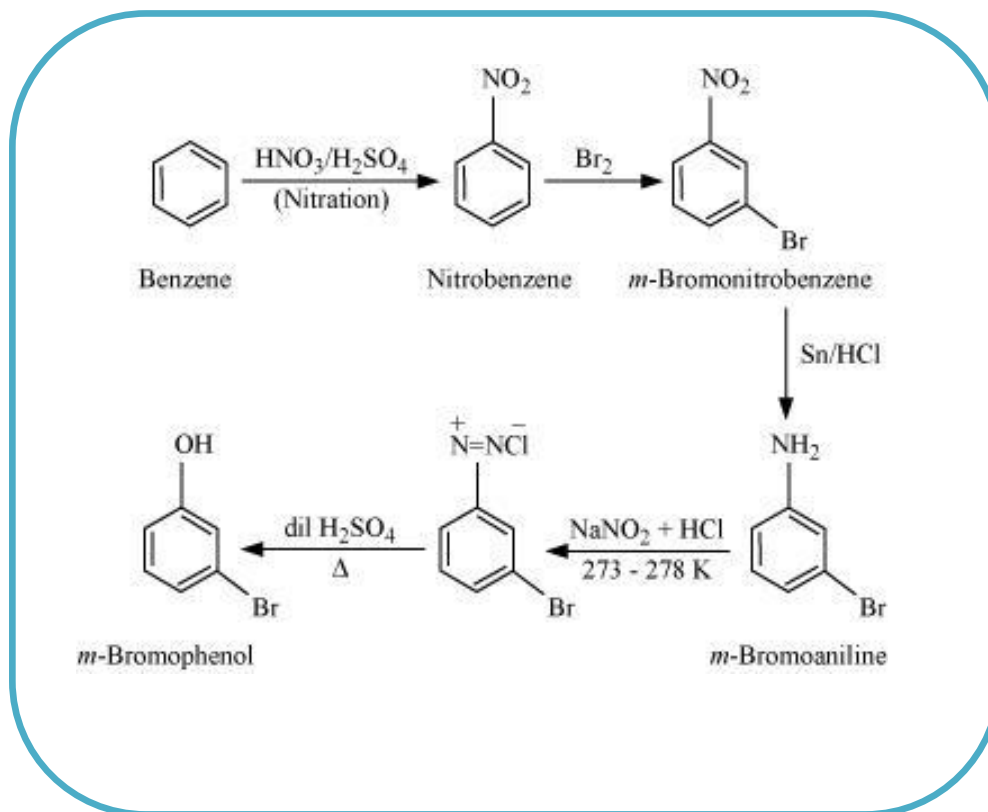
- (i) Nitrobenzene to benzoic acid
- (ii) Benzene to *m*-bromophenol
- (iii) Benzoic acid to aniline
- (iv) Aniline to 2,4,6-tribromofluorobenzene
- (v) Benzyl chloride to 2-phenylethanamine
- (vi) Chlorobenzene to *p*-chloroaniline
- (vii) Aniline to *p*-bromoaniline
- (viii) Benzamide to toluene
-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

Answer 13.6

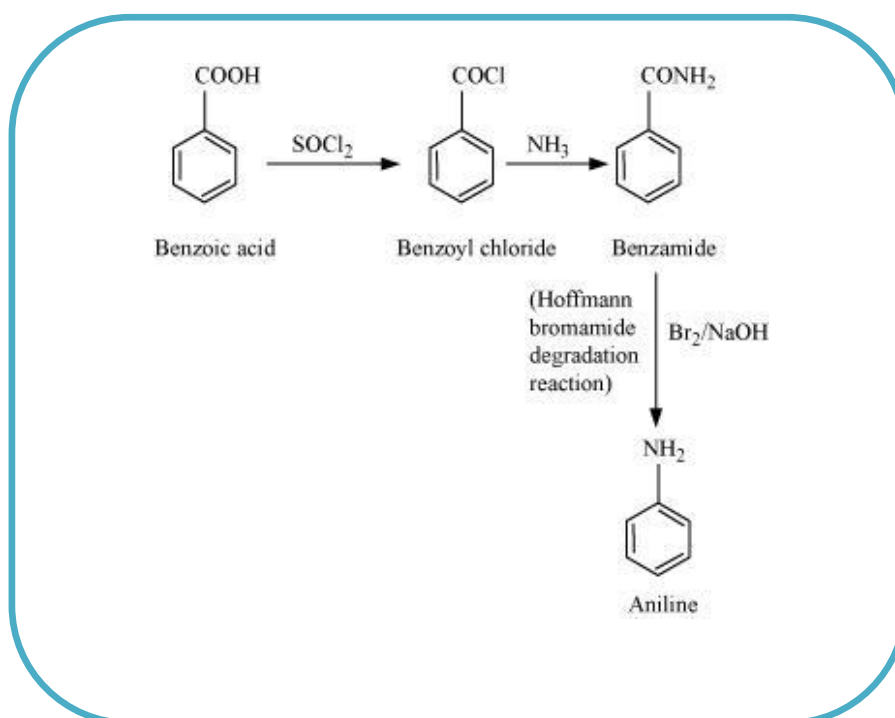
(i)



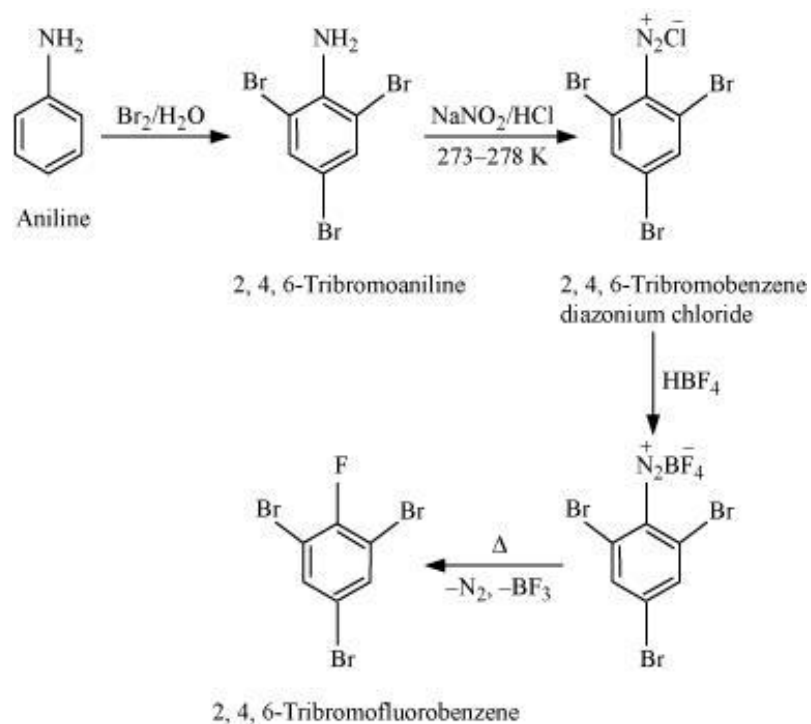
(ii)



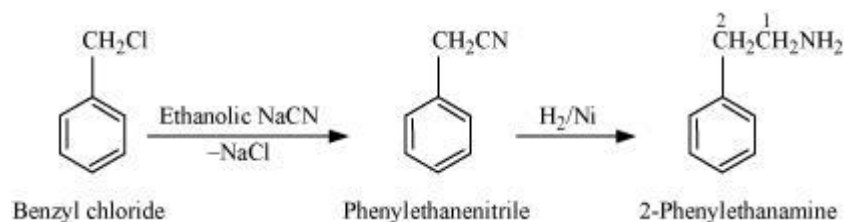
(iii)



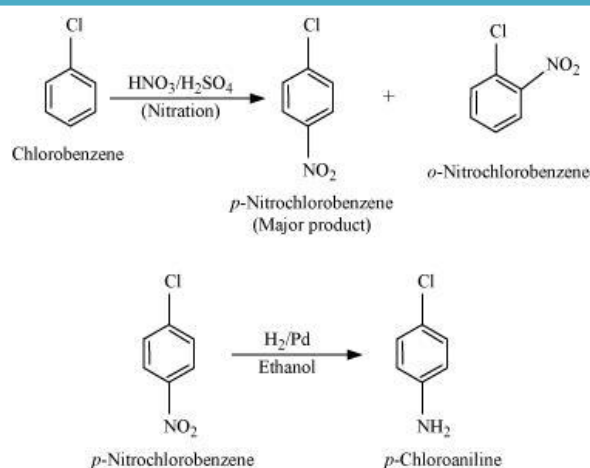
(iv)



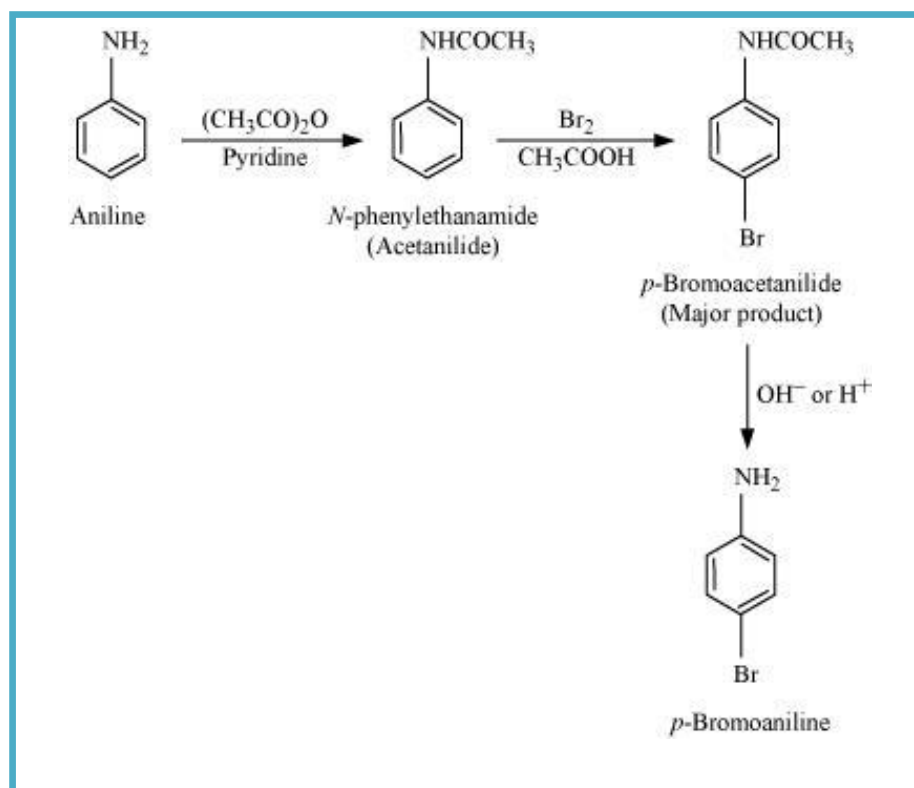
(v)



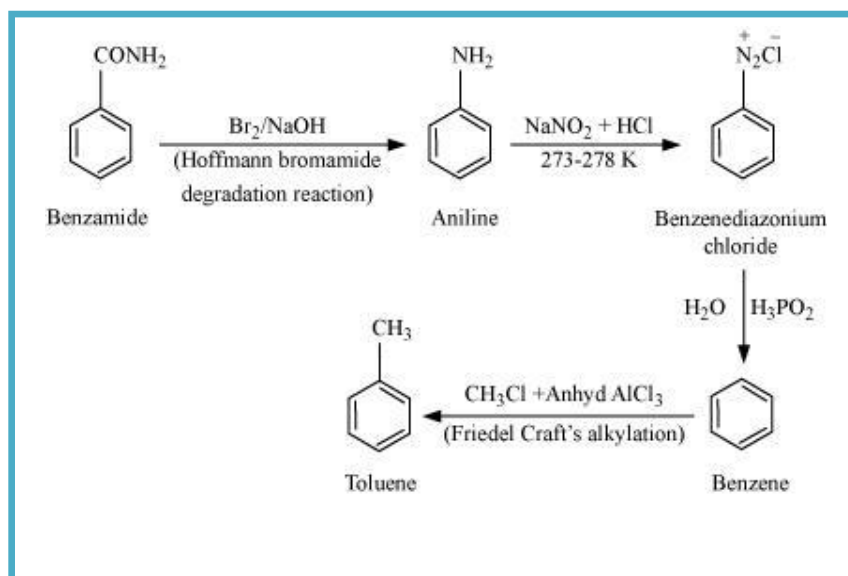
(vi)



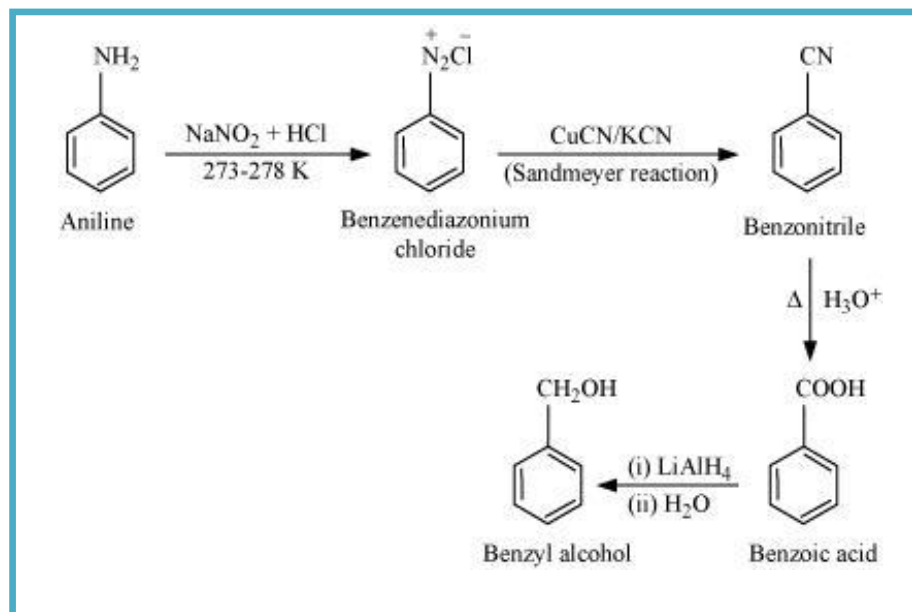
(vii)



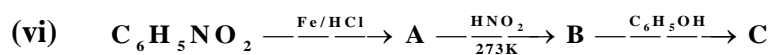
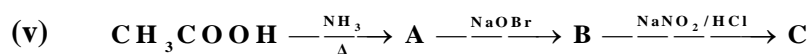
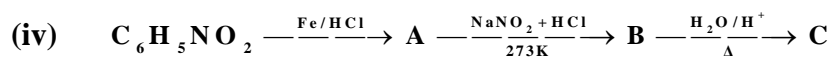
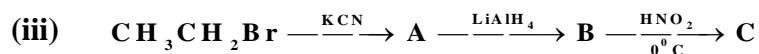
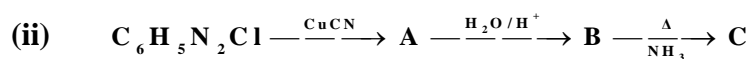
(viii)



(ix)

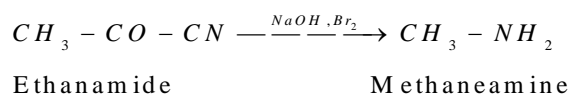
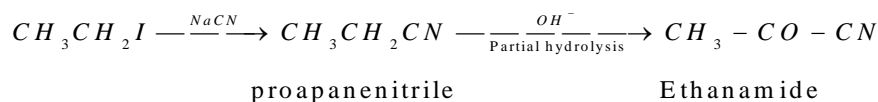


13.9 Give the structures of A, B and C in the following reactions:

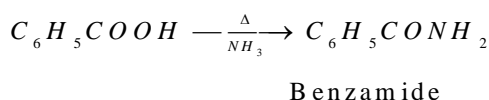
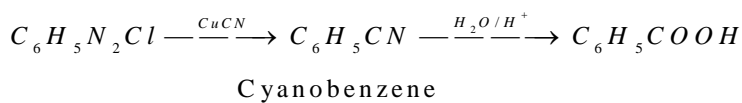


Answer 13.6

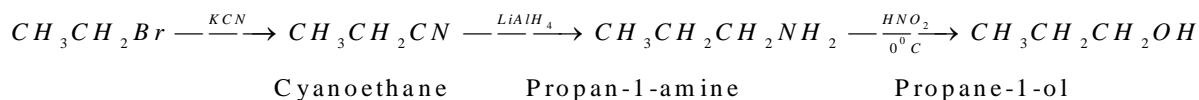
(i)



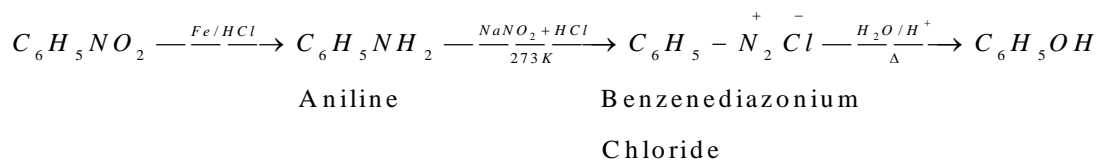
(ii)



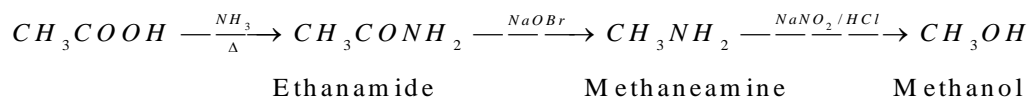
(iii)



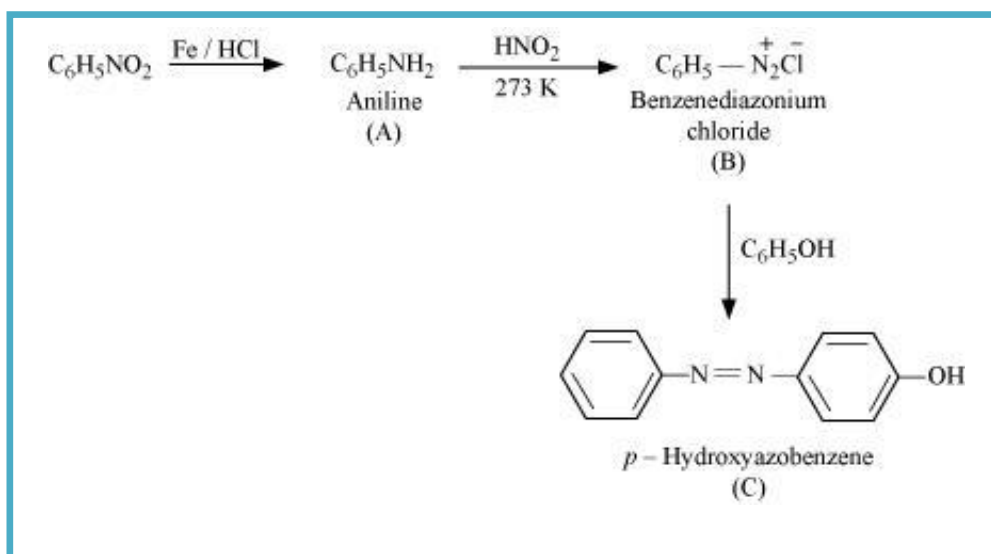
(iv)



(v)



(vi)



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 C_6H_7N . Write the structures and IUPAC names of compounds A, B and C.

Answer 13.6

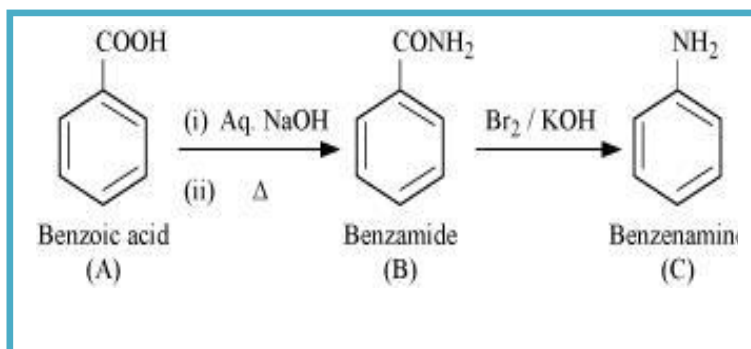
Compound 'C' is formed from compound 'B' by heating with Br_2 and KOH . This reaction is a Hoffmann bromamide degradation reaction.

Thus, compound 'B' should be an amide and compound 'C' is an amine.

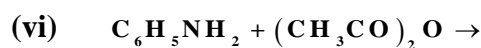
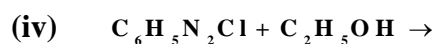
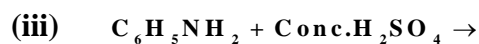
Therefore, compound 'B' is benzamide, ($C_6H_5CONH_2$).

Benzamide is formed by heating compound 'A' with aqueous ammonia. Thus, compound 'A' is a benzoic acid.

Reactions involved are:

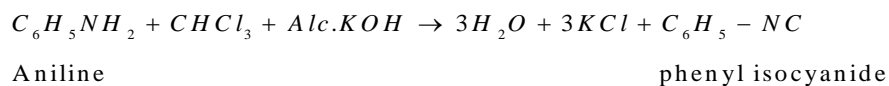


13.11 Complete the following reactions:

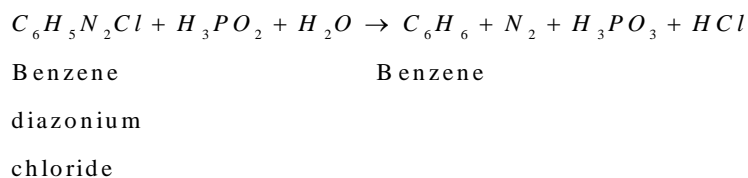


Answer 13.6

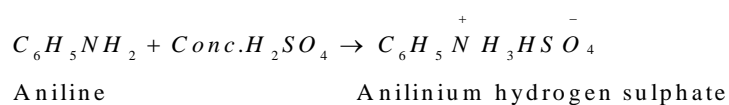
(i)



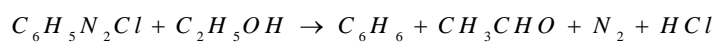
(ii)



(iii)



(iv)



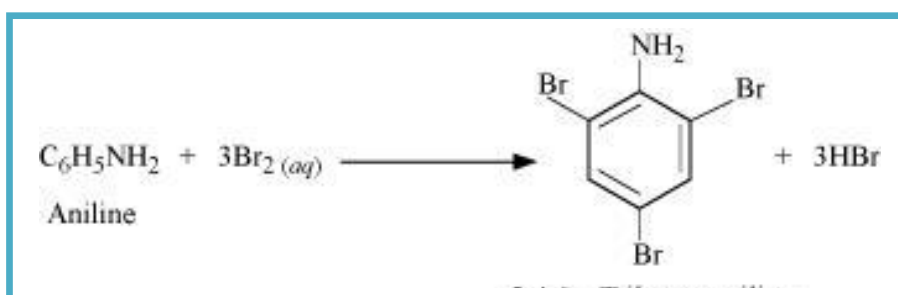
Benzene

Benzene

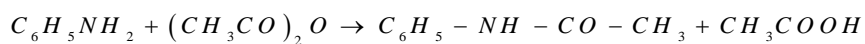
diazonium

chloride

(v)



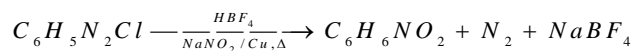
(vi)



Aniline

N-phenylethanamide

(vii)



Benzene

Nitrobenzene

diazonium

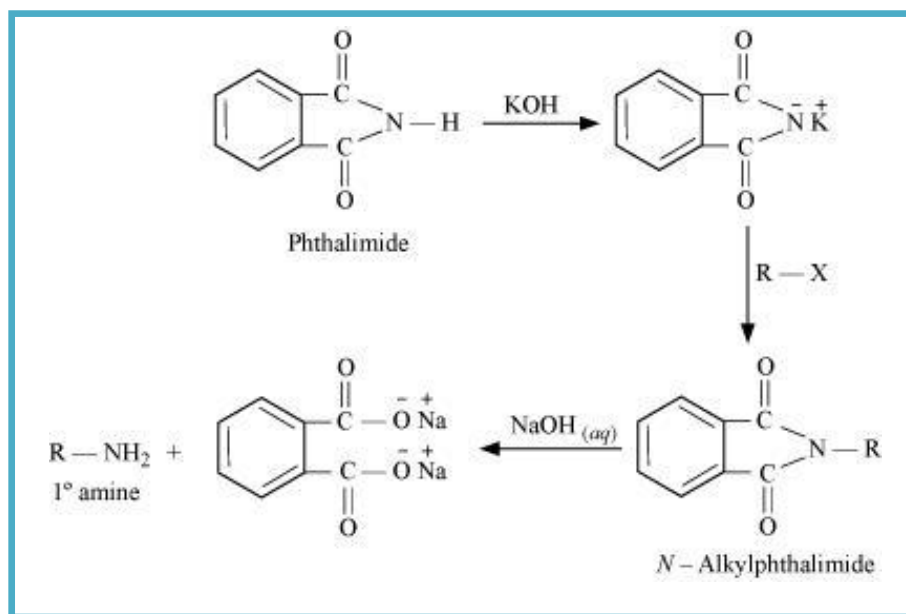
chloride

13.12 Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?

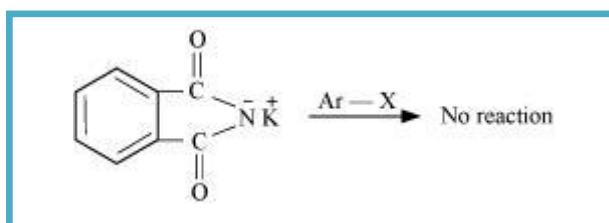
Answer 13.6

Gabriel phthalimide synthesis:

It is used for the preparation of aliphatic primary amines.



On the other hand, aryl halides do not undergo nucleophilic substitution reaction with the anion formed by the phthalimide.



Hence, aromatic primary amines cannot be prepared by this process.

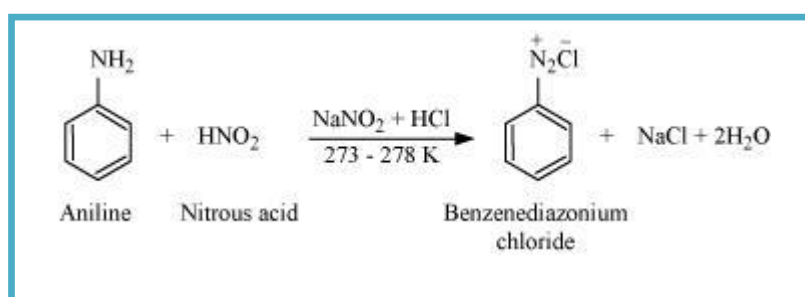
13.13 Write the reactions of**(i) Aromatic and**

(ii) Aliphatic primary amines with nitrous acid.

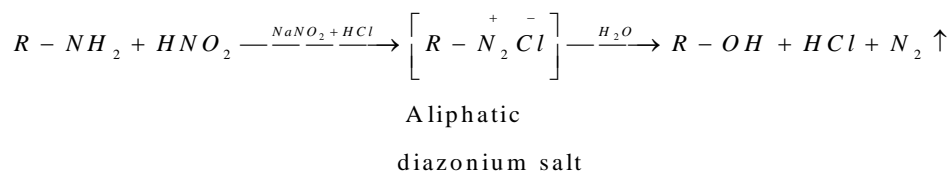
Answer 13.6

(i) Reaction of aromatic amines with nitrous acid:

In this reaction, nitric acid is prepared in situ from NaNO_2 and a mineral acid at $273 - 278 \text{ K}$.



(ii) Reaction of Aliphatic primary amines with nitrous acid: -



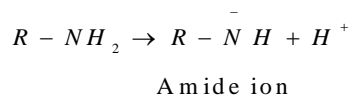
13.14 Give plausible explanation for each of the following:

- (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 aliphatic amines are stronger bases than aromatic amines?

Answer 13.6

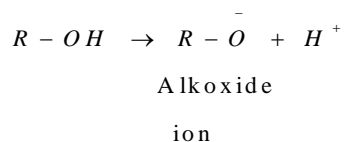
(i)

Amines undergo protonation to give amide ion.



In this ion, the negative charge is on the N-atom

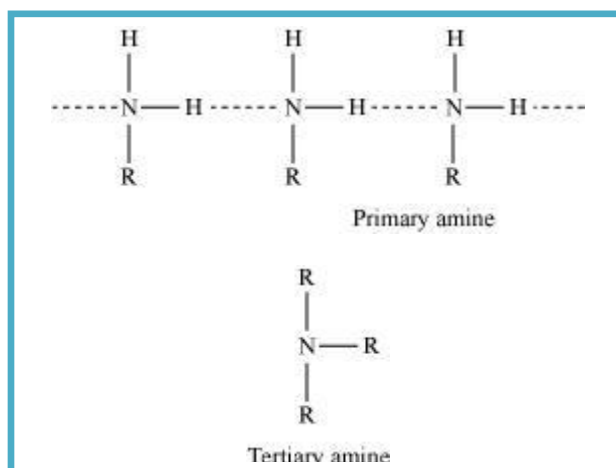
Alcohol loses a proton to give alkoxide ion.



Here, the negative charge is on the O-atom.

O is more electronegative than N, O can accommodate the negative charge more easily than N. Thus, the amide ion is less stable than the alkoxide ion. Hence, amines are less acidic than alcohols of comparable molecular masses.

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



As a result, extra energy is required to break the hydrogen bonds of primary amines. Thus, primary amines have higher boiling points than tertiary amines.

- (iii) The electrons on the N-atom in aromatic amines cannot be donated easily because of the $-R$ effect of the benzene ring. Thus, the electrons on the N- atom are less available. Thus, aliphatic amines are stronger bases than aromatic amines.

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