

NCERT Solution for Class 12 Chemistry Chapter 13 Amines

Q. 13.1:

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

- (i) (CH3)2 CH NH 2
- (ii) CH3 (CH2)2 NH 2
- (iii) CH3 NH CH (CH3)2
- (iv) (CH3)3 CNH 2
- (v) C₆ H₅ NH CH ₃
- (vi) (CH3 CH2)2 N CH3
- (vii) m Br C6 H4 NH2

Solution:

- (i) 1 Methylethanamine (10 amine)
- (ii) Propan 1 amine (10 amine)
- (iii) N Methyl 2 methyl ethanamine (20 amine)
- (iv) 2 Methylpropan 2 amine (10 amine)
- (v) N Methyl benzamine or N methylaniline (20 amine)
- (vi) N Ethyl N methyl ethanamine (30 amine)
- (vii) 3 Bromobenzenamine or 3 bromoaniline (10 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 & Methylamine can be made notable by the carbylamine test.

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

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

$$CH_{3} = NH_{2} + CHCl_{3} + 3KOH \xrightarrow{s} CH_{3} - NC + 3KCl + 3H_{2}$$
Methylamine(I*)

Methylisocyanide

(foul smell)

(CH₃)₂ NH+CHCl₃+3KOH \xrightarrow{s} No reaction

(ii) Tertiary amines & Secondary can be made notable by allowing them to react with Hinsberg's reagent (benzene sulphonyl chloride, $C_6 H_5 SO_2 CI$).

A product which is insoluble in 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 $_2$ (NaNO $_2$ + dil. HCl) at 0 – 5 ° 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 color. A brisk effervescence is given out by Aliphatic amines due to the evolution of N_2 gas under analogous conditions.

$$NH_2 + HONO \xrightarrow{273 - 278 \text{ K}} \qquad \bigwedge_{N} \equiv \text{NCT} + 2 \text{ H}_2\text{O}$$

$$OH \qquad \qquad \text{Determediate minume chloride}$$

$$N = NCT + \frac{1}{2} + HCI$$

$$1 - \text{Phenylazo} - 2 - \text{naphthol}$$

$$CH_3CH_2 - NH_2 + HONO \xrightarrow{-0.5^{\circ}C} + C_2H_3OH + N_2 \uparrow + H_2O$$

(iv) benzylamine & Aniline can be made notable by reacting them with nitrous acid, which is made ready in situ from a sodium nitrite & 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

$$\begin{array}{c} C_6H_5CH_2-NH_2+HNO_2 & \underbrace{NaNO_2+HCI}_{C_6H_5CH_2}-N_2^{+}CI \\ \\ Benzylamine & \\ & H_2O \\ \\ & N_2\uparrow+C_6H_5CH_2-OH+HCI \\ \\ Benzyl alcohol & \\ \end{array}$$

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.

$$C_{_{6}}H_{_{5}}NH_{2} \xrightarrow{\quad NaNO_{2}+IKT) \\ 273-278K} C_{_{6}}H_{_{5}} - \stackrel{+}{N_{_{2}}}C_{1} + NaCI + 2H_{_{2}}O$$

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

On heating Primary amines with ethanolic, chloroform & 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.

$$\begin{array}{ccc} C_6H_5-NH_2+CHCI_3+3KOH & \xrightarrow{\Delta} & C_6H_5-NC+3KCI+3H_2O \\ Benzylamine(I^0) & Benzyl isocyanide \\ & & & & & & & & & & \\ C_6H_3NHCH_3+CHCI_3+3KOH & \xrightarrow{\Delta} & No \ reaction \\ N-Methylaniline & & & & & & & & \\ \end{array}$$

Q. 13.3:

Account for the following:

- (i) pKb 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

Solution:

(i) p K b of methylamine is lesser than that of aniline :





When, in the above process, Aniline is under resonance, the electrons available on the N- atom are delocalized 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 forms intermolecular H - bonds with water.

Thus, it becomes soluble in water.

However, aniline does form H – bonding with water to a very great extent reason being the presence of a large hydrophobic – C_6 H₅ group. Therefore, aniline is not soluble in water.



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

$CH_3 \longrightarrow NH_2$	н-он
Methylamine	Water

Due to the presence of – CH₃ group & + I effect of, water is less basic than methylamine.

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

$$CH_3 - NH_2 + H - OH \longrightarrow CH_3 - NH_3 + OH^-$$

In the above process, Ferric chloride (FeCl₃) splits forming Fe³⁺ & Cl⁻ ions in water.

$$FeCl_3 \longrightarrow Fe^{3+} + 3Cl^-$$

OH ion then combines with Fe³⁺ ion and forms an impulsive of hydrated ferric oxide.

$$\begin{array}{ccc} 2Fe^{3+} & + & 6OH^- & \longrightarrow & Fe_2O_3 \cdot 3H_2O \\ & & & Hydrated \\ & & ferric \ oxide \end{array}$$

(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.

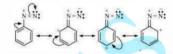
(v) Aniline does not take Friedel - Crafts reaction.

Friedel – Crafts reaction is performed in the presence of Al Cl $_3$. But, as we know that, Al Cl $_3$ has a acidic nature, whereas aniline does not. Aniline is basic in nature. Therefore, aniline is then reacted with Al Cl $_3$ 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 are 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 pKb values:
- C2H5NH2, C6H5NHCH3, (C2H5)2NH and C6H5NH2
- (ii) In increasing order of basic strength:
- C6H5NH2, C6H5N(CH3)2, (C2H5)2NH and CH3NH2
- (iii) In increasing order of basic strength:
- (a) Aniline, p-nitroaniline and p-toluidine
- (b) C6H5NH2, C6H5NHCH3, C6H5CH2NH2.
- (iv) In decreasing order of basic strength in gas phase:
- C2H5NH2, (C2H5)2NH, (C2H5)3N and NH3
- (v) In increasing order of boiling point:
- C2H5OH, (CH3)2NH, C2H5NH2
- (vi) In increasing order of solubility in water:
- C6H5NH2, (C2H5)2NH, C2H5NH2.

Solution:

(i) C₂ H₅ NH₂ à presence of one - C₂ H₅ group

 $(C_2 H_5)_2$ NH à presence of two – $C_2 H_5$ groups.

Therefore, the + I effect is additional in (C $_2$ H $_5$) $_2$ NH than in C $_2$ H $_5$ NH $_2$. Therefore, the electron density over the N-atom is more in (C $_2$ H $_5$) $_2$ NH than in C $_2$ H $_5$ NH $_2$. Hence, (C $_2$ H $_5$) $_2$ NH is more basic than C $_2$



H₅ NH₂.

Also, both $C_6 H_5 NH CH_3 \& C_6 H_5 NH_2$ are less basic than ($C_2 H_5$)₂ NH & $C_2 H_5 NH_2$ due to the delocalization of the lone pair in the former two. Further, among $C_6 H_5 NH CH_3 \& C_6 H_5 NH_2$, 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:

 $C_6 H_5 NH_2 < C_6 H_5 NHCH_3 < C_2 H_5 NH_2 < (C_2 H_5)_2 NH$

We know that the higher the basic strength, the lower is the p K b values.

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

(ii) $C_6 H_5 N(CH_3)_2$ is more basic than $C_6 H_5 NH_2$ due to the presence of the +1 effect of two

- CH₃ groups in C₆ H₅ N(CH₃)₂. Further, CH ₃NH ₂ contains one - CH₃ group while

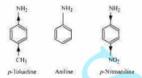
 $(C_2H_5)_2NH$ contains two $-C_2H_5$ groups. Thus, $(C_2H_5)_2NH$ is more basic than $C_2H_5NH_2$.

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:

 $C_6 H_5 NH_2 < C_6 H_5 N(CH_3)_2 < CH_3 NH_2 < (C_2 H_5)_2 NH_3 + (C_3 H_5)_2 NH_3 + (C$

(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. In the other case, 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: p – Nitroaniline < Aniline < p – Toluidine

- (b) $C_6 H_5 NHCH_3$ is more basic than $C_6 H_5 NH_2$ due to the presence of electron-donating CH_3 group in
- C_6H_5 NHCH₃. Again, in C_6H_5 NHCH₃, $-C_6H_5$ group is directly attached to the N atom. However, it is not so in C_6H_5 CH₂ NH₂. Thus, in C_6H_5 NHCH₃, the R effect of $-C_6H_5$ group decreases the electron density over the N-atom. Therefore, C_6H_5 CH₂ NH₂ is more basic than C_6H_5 NHCH₃. Hence, the increasing order of the basic strengths of the given compounds is as follows: C_6H_5 NH₂ < C_6H_5 NHCH₃ < C_6H_5 CH₂ NH₂.
- (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:

 $(C_2 H_5)_3 N > (C_2 H_5)_2 NH > C_2 H_5 NH_2 > NH_3$

(v) The extent of H-bonding existing in any compound decides the boiling point of compounds. The higher extensive the H \sim bonding in the compound, the higher will be the boiling point. (CH₃)₂ NH has only one H \sim atom while C₂ H₅NH₂ has two H \sim atoms. Subsequently, C₂ H₅ NH₂ undergoes more extensive H-bonding than (CH₃)₂NH. Therefore, the boiling point of C₂ H₅ NH₂ is more than that of (CH₃)₂ NH.

Also, O is more electronegative than N. Thus, $C_2 H_5 OH$ forms stronger H – bonds than $C_2 H_5 NH_2$. As a result, the boiling point of $C_2 H_5 OH$ is higher than that of $C_2 H_5 NH_2$ & $(CH_3)_2 NH$.

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:

(CH₃)₂ NH < C₂ H₅ NH₂ < C₂ H₅ OH



NH. Hence, the solubility in water of $C_2 H_5 NH_2$ is more than that of $(C_2 H_5)_2 NH$.

Further, the solubility of amines decreases with an increase in the molecular mass. This is because the molecular mass of amines increases with an increase in the size of the hydrophobic part. The molecular mass of $C_6H_5NH_2$ is greater than that of $C_2H_5NH_2$ & (C_2H_5) $_2NH$.

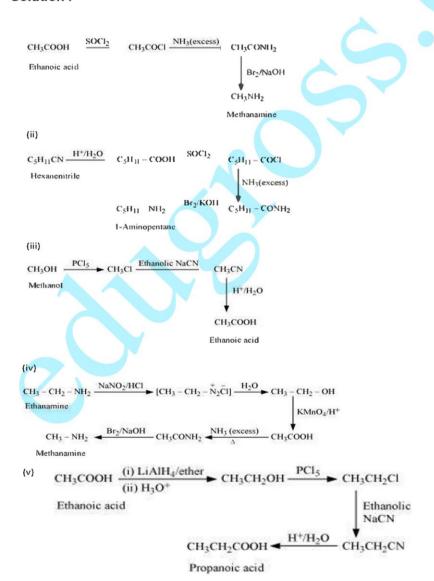
Hence, the increasing order of their solubility in water is as follows:

 $C_6 H_5 NH_2 < (C_2 H_5)_2 NH < C_2 H_5 NH_2$

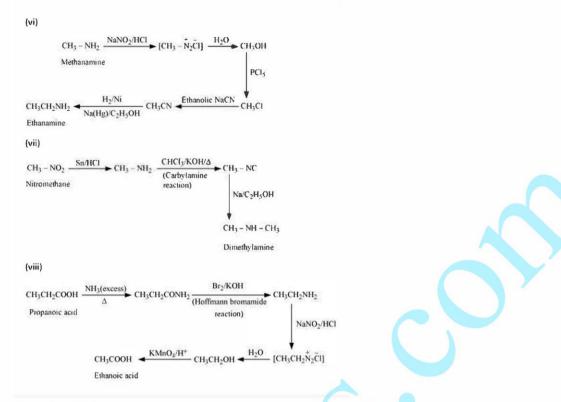
Q. 13.5:

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 Solution :







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 & tertiary amines can be identified & distinguished by Hinsberg's test. In this test, the amines are allowed to react with Hinsberg's reagent, benzene sulphonyl chloride ($C_6 H_5 SO_2 CI$). 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.

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 & 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 & 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 & aromatic primary amines are heated with chloroform & ethanolic potassium hydroxide, carbylamines (or isocyanides) are formed. These carbylamines have very unpleasant odours. Secondary & tertiary amines do not respond to this test.

R = NII + CHCI, + 3KOII(alc.)
$$\xrightarrow{a}$$
 R = NC + 3KCI + 3H₂O

Primary Chloroform Potassium Carbylamine
amine hydroxide

For example,

CH NII + CHCI, + 3KOII(alc.) \xrightarrow{a} CH, NC + 3KCI + 3H₂O

Methyl carbylamine
or methyl socyanide

(ii) Diazotization

Aromatic primary amines react with nitrous acid (prepared in situ from NaNO₂ & 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_2 O 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.

$$|| R - C - NH_2 + Br_2 + 4NaOH - \bullet R - NH_2 + Na_2CO_1 + 2NaBr - 2H_2O$$
Armde Primary aroune

For example,
$$|| CH_1 - C - NH_2 + Br_2 + 4NaOH - CH_1 - NH_2 + Na_2CO_1 - 2NaBr + 2H_2O$$
Ethaniamide - Methaniamire
$$|| C_6H_5 - C - NH_2 + Br_2 + 4NaOH - C_6H_5 - NH_2 + Na_2CO_1 + 2NaBr - 2H_2O$$
Benzamide - Aniline

(iv) Coupling reaction

The reaction of joining two aromatic rings through the -N=N- bond is known as 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 & 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

(- NH ₂) group. This process of cleavage of the carbon-halogen bond is known as ammonolysis.

$$R - NH X + NaOH \longrightarrow R - NH_2 + H_2O + NaX$$
Amine

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 & tertiary amines, & also a quaternary ammonium salt as shown.

(vi) Acetylation

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

Aliphatic & 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 $-NH_2$ or >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 is also known as benzoylation is the reaction that occurs when amines react with benzoyl chloride. One of the examples is illustrated below :



Gapriei primaiimide 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 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) Benzyl chloride to 2 phenylethanamine
- (vi) Chlorobenzene to p chloroaniline
- (vii) Aniline to p bromoaniline
- (viii) Benzamide to toluene
- (ix) Aniline to benzyl alcohol.

Solution:

(i)

(iii)



(v)

Question 13.9:

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

(ii)
$$C_6H_5$$
 CI CUEN A $\xrightarrow{H_5OM'}$ B NH C

(iii)
$$CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LABH_4} B \xrightarrow{BMJ_5} C$$

(iv)
$$C_6\Pi_5$$
 $^{\circ}O_2$ Fe HCL A $^{N_0NO_3+HCL}_{273K}$ B H_3O_3H_3 C

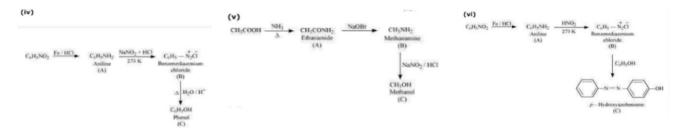
(v)
$$CH_3COOH \xrightarrow{NH_1} A \xrightarrow{NatBM} B \xrightarrow{NaNO_3 HCT} C$$

(vi)
$$C_6\Pi_5NO_2 \xrightarrow{\text{LetK1}} A \xrightarrow{\text{HNO.}} B \xrightarrow{\text{C.H.OH}} C$$

Solution:

(i)





Ouestion 13.10:

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.

Solution:

It is given that compound 'C' having the molecular formula, C_6H_7N is formed by heating compound 'B' with Br_2 & KOH. This is a Hoffmann bromamide degradation reaction. Therefore, compound 'B' is an amide & compound 'C' is an amine. The only amine having the molecular formula, C_6H_7N is aniline, ($C_6H_5NH_2$).

Therefore, compound 'B' (from which 'C' is formed) must be benzamide, (C₆ H₅ CO NH₂).

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

Therefore, compound 'A' must be benzoic acid.

COOH

Benzoic acid

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

COOH

CONH₂

$$(i)$$
 Aq aOH

 (ii) Δ

Benzamude

 (A)

Benzamude

 (B)

Benzamude

 (C)

Question 13.11:

Complete the following reactions:

(i)
$$C_6H_5NH_2 + CHCl_3 + alc.KOH \rightarrow$$

(ii)
$$C_6H_5N_2CI + H_3PO_2 + H_2O \rightarrow$$

(iii)
$$C_6H_5NH_2 + H_2SO_4(conc.) \rightarrow$$

(iv)
$$C_6H_5N_2Cl+C_2H_5OH \rightarrow$$

(v)
$$C_6H_5NH_2 + Br_2(aq) \rightarrow$$



(vi)
$$C_6H_5NH_2 + (CH_3CO)_2O \rightarrow (Vii)$$
 $C_6H_5N_2CI \xrightarrow{(i)HBF_4} (ii)NaNO_2/Cu_A \rightarrow (Vii)$

Solution:

Question 13.12:

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

Gabriel phthalimide synthesis is usually used for the formation of aliphatic primary amines. This includes nucleophilic substitution (SN_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 .

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



(vi)
$$C_6H_5NH_2 + (CH_3CO)_2O \rightarrow (Vii)$$
 $C_6H_5N_2CI \xrightarrow{(i)HBF_4} (ii)NaNO_2/Cu_A \rightarrow (Vii)$

Solution:

Question 13.12:

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

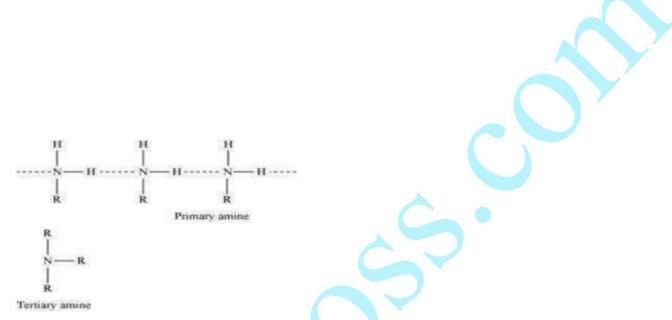
Gabriel phthalimide synthesis is usually used for the formation of aliphatic primary amines. This includes nucleophilic substitution (SN_2) of alkyl halides by the anion produced by the phthalimide.

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

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





Consequently, additional energy would be required to detach the molecules of primary amines. Therefore, tertiary amines have a 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.