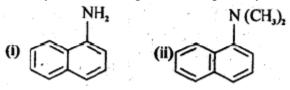


Chapter 13 — Amines

Question 1:

Classify the following amines as primary, secondary and tertiary:



(iii) $(C_2H_5)_2$ CHNH₂

 $(iv)(C_2H_5)_2NH$

Solution 1:

(i) 1° (ii) 3° (iii) 1°(iv) 2°

Question 2:

- (i) Write the structures of different isomeric amines corresponding to the molecular formula, . $C_4H_{11}N$
- (ii) Write IUPAC names of all the isomers.
- (iii) What type of isomerism is exhibited by different pairs of amines?

Solution 2:

- (i), (ii) The structures and their IUPAC names of different isomeric amines corresponding to the molecular formula, C₄H₁₁N are given below:
- (a) CH₃-CH₂-CH₂-CH₂-NH₂ Butanamine (1⁰)

(b)
$$CH_3 - CH_2 - CH - CH_3$$

Butan-2-amine (10)

2-Methylpropanamine (10)

(d)

$$\begin{array}{c} \text{CH}_{3} \\ \text{CH}_{3} - \begin{array}{c} \text{C} - \text{NH}_{2} \\ \text{C} \\ \text{CH}_{3} \end{array}$$

2-Methylpropan-2-amine (10)

(e) CH3-CH2-CH2-NH-CH3

N-Methylpropanamine (20)

(f) CH3-CH2-NH-CH2-CH3

N-Ethylethanamine (20)

(g)

N-Methylpropan-2-amine (2º)

(h)

N,N-Dimethylethanamine (3°)

(iii) Position isomers : (a) and (b); (e) and (g)

Chain isomers: (a) and (c); (a) and (d); (b)and(c); (b)and(d)

Metamers: (e) and (f). (f) and (g)

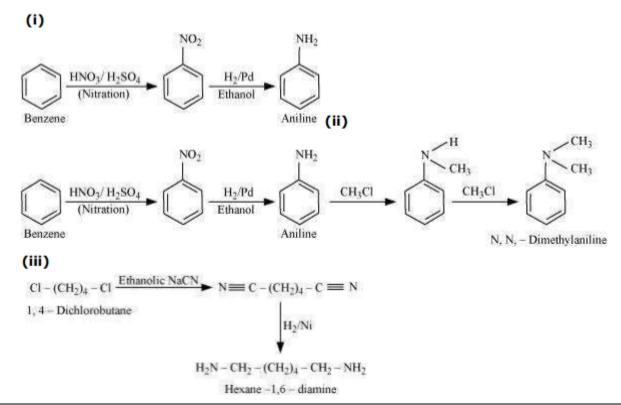
Functional isomers: All 1⁰ amines are functional isomers of 2⁰ and 3⁰ amines and vice-versa

Question 3:

How will you convert:

- (i)Benzene into aniline
- (ii)Benzene into N,N-dimethylaniline
- (iii) $Cl (CH_2)_4 Cl$ into Hexane -1, 6- diamine

Solution 3:



Ouestion 4:

Arrange the following in increasing order of their basic strength:

- (i) C₂H₅NH₂, C₆H₅NH₂, NH₃, C₆H₅CH₂NH₂ and (C₂H₅)₂NH
- (ii) C₂H₅NH₂, (C₂H₅)₂ NH, (C₂H₅)₃N, C₆H₅NH₂
- (iii) CH₃NH₂, (CH₃)₂ NH, (CH₃)₃N, C₆H₅NH₂, C₆H₅CH₂NH₂

Solution 4:

(i) Considering the inductive effect of alkyl groups, NH₃, C₂H₅NH₂, and (C₂H₅)₂NH can be arranged in the increasing order of their basic strengths as:

$$NH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$$

Again, C₆H₅NH₂ has proton acceptability less than NH₃. Thus, we have:

$$C_6H_5NH_2 < NH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$$

Due to the –I effect of C₆H₅ group, the electron density on the N-atom in C₆H₅CH₂NH₂ is lower than that on the N-atom in C₂H₅NH₂, but more than that in NH₃. Therefore, the given compounds can be arranged in the order of their basic strengths as:

$$C_6H_5NH_2 < NH_3 < C_6H_5CH_2NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$$

(ii) Considering the inductive effect and the steric hindrance of the alkyl groups, C₂H₅NH₂, (C₂ H₅)₂NH₂, and their basic strengths as follows:

$$C_1H_2NH_1 < (C_1H_2)_1N < (C_1H_2)_1NH$$

Again, due to the -R effect of C_6H_5 group, the electron density on the N atom in C_6H_5 NH₂ is lower than that on the N atom in C_2H_5 NH₂. Therefore, the basicity of C_6H_5 NH₂ is lower than that of C_2H_5 NH₂. Hence, the given compounds can be arranged in the increasing order of their basic strengths as follows:

$$C_6H_5NH_2 < C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH_3$$

(iii) Considering the inductive effect and the steric hindrance of alkyl groups, CH_3NH_2 , $(CH_3)_2NH$, and $(CH_3)_3N$ can be arranged in the increasing order of their basic strengths as: $(CH_1)_1N < CH_1NH_2 < (CH_3)_2NH$

In C₆H₅NH₂, N is directly attached to the benzene ring. Thus, the lone pair of electrons on the N-atom is delocalized over the benzene ring. In C₆H₅CH₂NH₂, N is not directly attached to the benzene ring. Thus, its lone pair is not delocalized over the benzene ring. Therefore, the electrons on the N atom are more easily available for protonation in C₆H₅CH₂NH₂ than in C₆H₅NH₂ i.e., C₆H₅CH₂NH₂ is more basic than C₆H₅NH₂. Again, due to the -I effect of C₆H₅ group, the electron density on the N-atom in C₆H₅CH₂NH₂ is lower than that on the N-atom in (CH₃)₃N. Therefore, (CH₃)₃N is more basic than C₆H₅CH₂NH₂. Thus, the given compounds can be arranged in the increasing order of their basic strengths as follows.

$$C_6H_5NH_2 < C_6H_5CH_2NH_2 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH_3$$

Question 5:

Complete the following acid-base reactions and name the products:

- (i) $CH_3CH_2CH_2NH_2 + HC1 \longrightarrow$
- (ii) $(C_2H_5)_3N+HC1 \longrightarrow$

Solution 5:

Ouestion 6:

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

Solution 6:

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.

$$\begin{array}{c} CH_3 \\ CH_3 \\ + CH_3I \end{array} \begin{array}{c} + \\ N_1CH_3)_3I^- \\ \hline N_1CH_3)_3I^- \\ \hline N_1CH_3I \\ \hline \end{array} \begin{array}{c} + \\ N_2CO_3 \\ \hline \end{array} \begin{array}{c} + \\ N_1CH_3)_3 \\ \hline \end{array} \begin{array}{c} + \\ N_1CH_3 \\ \hline \end{array} \begin{array}{c} + \\ N_1CH_$$

Question 7:

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

Solution 7:

N-Phenylbenzamide (Benzanilide)

Question 8:

Write structures of different isomers corresponding to the molecular formula, C₃H₉N. Write IUPAC names of the isomers which will liberate N₂ gas on treatment with nitrous acid.

Solution 8:

In all, four structural isomers are possible. These are:

1° amines:

$$\begin{array}{cccc} CH_3CH_2CH_2NH_2 & CH_3-CH-CH_3 \\ & & & & \\ & & NH_2 \\ & & Propan-2-amine \\ \end{array}$$

$$2^{\circ} \ amine: & CH_3-NH-C_2H_5 \\ & N-Methyl \ ethanamine \\ 3^{\circ} \ amine: & CH_3-N-CH_3 \\ & CH_3 \end{array}$$

N, N-Dimethyl methanamine

only 1° amines react with HNO₂ to liberate N₂ gas

$$C\!H_3C\!H_2C\!H_2N\!H_2 + H\!N\!O_2 \!\longrightarrow\! C\!H_3C\!H_2C\!H_2O\!H + N_2 + H_2O$$
 Propan-1-ol

$$H_3C$$

$$CH-NH_2 + HNO_2 \xrightarrow{H_3C} CH-OH + N_2 + H_2O$$

$$H_3C$$
Propan-2-ol

Question 9:

Convert:

- (i)3-Methylaniline into 3-nitrotoluene
- (ii)Aniline into 1,3,5- Tribromo benzene

Solution 9:

(i)
$$N_2$$
 N_2 N_2 N_2 N_2 N_3 N_4 N_2 N_4 N_2 N_4 N_4 N_4 N_4 N_5 N_4 N_5 N_4 N_5 N_5 N_6 N_6

(ii) CH₃CH₂OH/
$$\Delta$$
or H₃PO₂/Cu⁺
Br
Br
1, 3, 5-Tribromobenzene

NCERT EXERCISES

Question 1:

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

- (i) (CH₃)₂ CHNH₂
- (ii) CH₃ (CH₂)₂ NH₂
- (iii) CH₃ NHCH (CH₃)₂
- (iv) (CH₃)₃ CNH
- (v) C₆ H₅ NHCH
- (vi) (CH₃ CH₂)₂ NCH₃
- (vii) m-BrC₆ H₄ NH₂

Solution 1:

- (i) 1-Methylethanamine (1⁰ amine)
- (ii) Propan-1-amine (1⁰ amine)

- (iii) N-Methyl-2-methylethanamine (2⁰ amine)
- (iv) 2-Methylpropan-2-amine (1⁰ amine)
- (v) N-Methylbenzamine or N-methylaniline (2⁰ amine)
- (vi) N-Ethyl-N-methylethanamine (3⁰ amine)
- (vii) 3-Bromobenzenamine or 3-bromoaniline (1⁰ amine)

Ouestion 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 2:

(i) Methylamine and methylamine can be distinguished by carbylamine test.

$$\begin{array}{c} CH_3NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} CH_3NC + 2KCl + 3H_2O \\ \text{ Methylisocyanide (offencive smell)} \end{array}$$

$$(CH_3)_2 NH \xrightarrow{CHCl_3/KOH(alc)} No reaction$$

(ii) Secondary and tertiary amine can be distinguished by Liebermann's nitroamine test. Secondary amines gives Liebermann nitroamine test while tertiary amines do not.

$$(CH_3CH_2)_2NH + HO - N = O \xrightarrow{HCl + NaNO_2} (CH_3CH_2)_2N - N = O + H_2O$$
Diethylamine
(2° Amine)
$$(2^{\circ} Amine)$$

$$\begin{array}{ccc} (CH_3CH_2)_3 N + HNO_2 & \longrightarrow & [(CH_3CH_2)_3 NH]^+ NO_2^- \\ & & & & \text{Triethylamine} \\ & & & & \text{(Soluble)} \end{array}$$

(iii) Ethylamine and aniline can be distinguished by azo test:

$$C_2H_5NH_2 + HONO + HCl \xrightarrow{\quad 273-278K} C_2H_5OH + CH_2 = CH_2 + CH_3CH_2Cl + N_2CH_3CH_2Cl + N_2CH_2Cl +$$

$$NH_{2} + HONO + HCI \xrightarrow{273-278 \text{ K}} N_{2}^{+}CI^{-} + 2H_{2}O$$

$$OH \qquad \qquad OH \qquad \qquad OH \qquad OH \qquad OH \qquad PH = 9 - 10$$

$$(orangle red dye)$$

(iv) Aniline and benzylamine can be distinguished by nitrous acid test:

$$C_{6}H_{5}CH_{2}NH_{2} \xrightarrow{HONO} C_{6}H_{5}CH_{2}N_{2}^{+}Cl - \xrightarrow{Decomposes} C_{6}H_{5}CH_{2}OH + N_{2} \uparrow + HCl$$

$$C_{6}H_{5}CH_{2}NH_{2} \xrightarrow{HONO} C_{6}H_{5}CH_{2}OH + N_{2} \uparrow + HCl$$

$$NH_2 \xrightarrow{\text{HONO, HCl}} NH_2 \xrightarrow{\text{Stable}} N^+ \equiv NCl^-$$

(v) Aniline and N-methylaniline can be distinguished by carbylamines test:

$$C_6H_5NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} C_6H_5NC + 3KCl + 3H_2O$$
 Aniline Offensive smaell

$$C_6H_5-NH-CH_3 \xrightarrow{CHCl_3+3KOH} No \ reaction$$

Question 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 synthesizing primary amines.

Solution 3:

- (i) In aniline, the lone pair of electrons on the N-atom is delocalised over the benzene ring. As a result, electron density on the nitrogen atom decreases. Whereas in CH₃NH₂,+ I-effect of –CH₃ group increases the electron density on the N-atom. Therefore, aniline is a weaker base than methylamine and hence its pKb value is higher than that of methylamine.
- (ii) Ethylamine dissolves in water due to intermolecular H-bonding. However, in case of aniline, due to the large hydrophobic part, i.e., hydrocarbon part, the extent of H-bonding is very less therefore aniline is insoluble in water.

(iii) Methylamine being more basic than water, accepts a proton from water liberating OH ions.

$$CH_3NH_2 + H - OH \longrightarrow CH_3 - NH_3 + OH$$

These OH ions combine with Fe³⁺ ions present in H_2O to form brown precipitate of hydrated ferric oxide.

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

$$2Fe^{3+} + 6OH^{-} \longrightarrow 2Fe(OH)_{3} \text{ or } Fe_{2}O_{3}.3H_{2}O$$
(Brown ppt.)

(iv) Nitration is usually carried out with a mixture of conc HNO₃+ conc H₂SO₄. In presence of these acids, most of aniline gets protonated to form anilinium ion. Therefore, in presence of acids, the reaction mixture consist of aniline and anilinium ion. Now, -NH₂ group in aniline is activating and o, p-directing while the +NH₃ group in anilinium ion is deactivating and m-directing: Nitration of aniline (due to steric hindrance at o-position) mainly gives p-nitroaniline, the nitration of anilinium ion gives m-nitroaniline. In actual practice, approx a 1:1 mixture of p-nitroaniline and m-nitroaniline is obtained. Thus, nitration of aniline gives a substantial amount of m-nitroaniline due to protonation of the amino group.

NH₂

NH₂

NH₂

NNO₂

$$P$$

NItroaniline

(51%)

NH₃

NH₄

NNO₂
 P

NItroaniline

(51%)

NH₃

NH₄

NH₄

NH₄

NNO₂

NH₄

NNO₂

NH₄

NNO₂

NNO₃

NNO₄

NNO₄

NNO₅

NNO₆

NNO₆

NNO₇

NNO₈

NNO

(v) Aniline being a Lewis base reacts with Lewis acid AlCl₃ to form a salt.

$$C_6H_5NH_2 + AICI_3 \longrightarrow C_6H_5NH_2 + AICI_3$$

As a result, N of aniline acquires positive charge and hence it acts as a strong deactivating group for electrophilic substitution reactions. Consequently, aniline does not undergo Fridel Crafts reaction.

(vi) The diazonium salts of aromatic amines are more stable than those of aliphatic amines due to dispersal of the positive charge on benzene ring as a result of resonance.

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

Question 4:

Arrange the following:

(i) In decreasing order of pKb values:.

C₆H₅NH₂, 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:

C₆H₅NH₂, (C₂H₅)₂NH, (C₂H₅)₃N and NH₃

(v) In increasing order of boiling point:

C₅H₅OH, (CH₃)₂ NH, C₂H₅NH₂

(vi) In increasing order of solubility in water:

C₆H₅NH₂, (C₅H₅)₂NH, C₂H₅NH₂

Solution 4:

(i) In C₂H₅NH₂, only one –C₂H₅ group is present while in (C₂H₅)₂NH, two –C₂H₅ groups are present. Thus, the +I effect is more in (C₂H₅)₂NH than in C₂H₅NH₂. Therefore, the electron density over the N-atom is more in (C₂H₅)₂NH than in C₂H₅NH₂. Hence, (C₂H₅)₂NH is more basic than C₂H₅NH₂. Also, both C₆H₅NHCH₃ and C₆H₅NH₂ are less basic than (C₂H₅)₂NH and C₂H₅NH₂ due to the delocalization of the lone pair in the former two. Further, among C₆H₅NHCH₃ and C₆H₅NH₂, the former will be more basic due to the +I effect of –CH₃ 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 pKb values.

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

(ii) Among CH₃CH₂ and $(C_2H_5)_2NH$, primarily due to the greater +1-effect of the two $-C_2H_5$ groups over one $-CH_3$ group, $(C_2H_5)_2NH$ is more basic than CH₃NH₂. In both C₆H₅NH₂ and C₆H₅N(CH₃)₂ lone pair of electrons present on N-atom is delocalized over the benzene ring but C₆H₅N(CH₃)₂ is more basic due to +1 effect of two $-CH_3$ groups.

$$\therefore (C_2H_5)_2NH > CH_3NH_2 > C_6H_5N(CH_3)_2 > C_6H_5NH_2$$

- ----- Decreasing basic strength
- (iii) (a) The presence of electron donating –CH₃ group increases while the presence of electron withdrawing NO₂ group decreases the basic strength of amines.
- $\therefore p\text{-nitroaniline} < \text{niline} < p\text{-toluidine}$
- ----- Increasing basic strength
- (b) In C₆H₅NH₂ and C₆H₅NHCH₃, N is directly attached to the benzene ring. As a result, the lone pair of electrons on the N-atom is delocalised over the benzene ring. Therefore, both C₆H₅NH₂

and C₆H₅NHCH₃are weaker base in comparison to C₆H₅CH₂NH₂. Among C₆H₅NH₂ and C₆H₅NHCH₃, due to +1 effect of –CH₃ group C₆H₅NHCH₃ is more basic.

- $\therefore C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$
- ----- Increasing basic strength
- (iv) In gas phase or in non-aqueous solvents such as chlorobenzene etc, the solvation effects i. e. the stabilization of the conjugate acid due to H-bonding are absent. Therefore, basic strength depends only upon the +1-effect of the alkyl groups. The +1-effect increases with increase in number of alkyl groups. Thus correct order of decreasing basic strength in gas phase is,

$$(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$$

- → Decreasing basic strength
- (v) Since the electronegativity of O is higher than that of N, therefore, alcohols form stronger H-bonds than amines. Also, the extent of H-bonding depends upon the number of H-atoms on the N-atom, thus the extent of H-bonding is greater in primary amine than secondary amine.

:.
$$(CH_3)_2 NH < C_2 H_5 NH_2 < C_2 H_5 OH$$

- → Increasing boiling point
- (vi) Solubility decreases with increase in molecular mass of amines due to increase in the size of the hydrophobic hydrocarbon part and with decrease in the number of H-atoms on the N-atom which undergo H-bonding.

$$C_6H_5NH_2 < (C_6H_5)_2NH < C_2H_5NH_2$$

── Increasing solubility

Question 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 5:

$$(i) \ CH_{3}COOH \xrightarrow{SOCl_{2} \atop -SO_{2}, -HCl} \rightarrow CH_{3}COCl \xrightarrow{NH_{3}(excess) \atop NH_{4}Cl} \rightarrow CH_{3}CONH_{2} \xrightarrow{Br_{2}/NaOH} \rightarrow CH_{3}NH_{2}$$

$$(ii) \ CH_{3}(CH_{2})_{4} \ CN \xrightarrow{H_{3}O^{*}} CH_{3}(CH_{2})_{4} \ COOH \xrightarrow{SOCl_{2} \atop -SO_{2}, -HCl} \rightarrow CH_{3}(CH_{2})_{4} \ COCl \xrightarrow{NH_{3}(excess) \atop -NH_{4}Cl} \rightarrow CH_{3}(CH_{2})_{4} \ NH_{2} \xrightarrow{JBr_{2}/NaOH}$$

$$(iii) \ CH_3OH \xrightarrow{PCl_5} CH_3Cl \xrightarrow{KCN(alc)} CH_3CN \xrightarrow{H_3O^+} CH_3COOH$$

(iv)
$$CH_3CH_2NH_2 \xrightarrow{HONO} CH_3CH_2OH \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3CHO$$

$$CH_3CONH_2 \xleftarrow{-H_2O} CH_3COONH_4 \xleftarrow{NH_3} CH_3COOH \xleftarrow{K_2Cr_2O_7/H_2SO_4} CH_3NH_2$$

(v)
$$CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH \xrightarrow{P+I_2} CH_3CH_2I \xrightarrow{KCN} CH_3CH_2CN$$

$$CH_3CH_2COOH \longleftarrow H^{+}/H_2O$$

(vi)
$$CH_3NH_2 \xrightarrow{HONO} CH_3OH \xrightarrow{P+I_2} CH_3I \xrightarrow{KCN} CH_3CN$$

$$CH_3CH_2NH_2 \longleftarrow Na/C_2H_5OH$$

$$(vii) CH_3NO_2 \xrightarrow{Sn/HCl} CH_3NH_2 \xrightarrow{CHCl_3.KOH\Delta} CH_3NC \xrightarrow{LiAlH_4} CH_3NHCH_3$$

$$(viii) CH_3CH_2COOH \xrightarrow{NH_3} CH_3CH_2CONH_2 \xrightarrow{Br_2/NaOH} CH_3CH_2NH_2$$

$$\downarrow HNO_2$$

$$CH_3COOH \xleftarrow{Alk. KMnO_4} CH_3CH_2OH$$

Question 6:

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

Solution 6:

The three type of amines can be distinguished by Hinsberg test. In this test, the amine is shaken with benzenesulphonyl chloride (C₆H₅SO₂Cl) in the presence of excess of aqueous NaOH or KOH. A primary amine reacts to give a clear solution, which on acidification yields an insoluble compound.

$$RNH_2 + C_6H_5SO_2CI \xrightarrow{OH^-} C_6H_5SO_2NHR \xrightarrow{KOH} C_6H_5SO_2N^-RK^+ \xrightarrow{H^+} C_6H_5SO_2NHR$$
(Clear solution) (Insoluble)

A secondary amine forms an insoluble compound, which remains insoluble even on acidification.

$$R_2NH + C_6H_5SO_2CI \xrightarrow{OH^-} C_6H_5SO_2NR_2 \xrightarrow{H^+} No reaction$$

A tertiary amine does not react with the reagent, but dissolves is acid.

$$C_6H_5SO_2Cl + R_3N \xrightarrow{OH^+} No \ reaction$$

$$R_3N + H^+ \longrightarrow [R_3NH]^+$$
(Clear solution)

Question 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 7:

(i) **Carbylamine reaction:** Both aliphatic and aromatic primary amines when warmed with chloroform and an alcoholic solution of KOH, produces isocyanides or carbylamines which have very unpleasant odours. This reaction is called carbylamine reaction.

$$R - NH_2 + CHCl_3 + 3KOH(alc) \longrightarrow R - N = C + 3KCl + 3H_2O$$

(ii) **Diazotisation:** The process of conversion of a primary aromatic amino compound into a diazonium salt, is known as diazotisation. This process is carried out by adding an aqueous solution of sodium nitrite to a solution of primary aromatic amine (e.g., aniline) in excess of at a temperature below 5°C. HCl

$$ArNH_2 + NaOH_2 + 2HX \xrightarrow{273-278K} Ar \stackrel{+}{N_2} X^- + NaX + 2H_2O$$
1° amine Arene Diazonium solt

(iii) **Hoffmann's bromamide reaction:** When an amide is treated with bromine in alkali solution, it is converted to a primary amine that has one carbon atom less than the starting amide. This reaction is known as Hoffmann's bromamide degradation reaction.

$$C_6H_5CONH_2 \xrightarrow{Br_2+NaOH} C_6H_5NH_2$$

(iv) **Coupling reaction:** In this reaction, arenediazonium salt reacts with aromatic amino compound (in acidic medium) or a phenol (in alkaline medium) to form brightly coloured azo compounds. The reaction generally takes place at para position to the hydroxy or amino group. If para position is blocked, it occurs at ortho position and if both ortho and para positions are occupied, than no coupling takes place.

(v) **Ammonolysis:** It is a process of replacement of either halogen atom in alkyl halides (or aryl halides) or hydroxyl group in alcohols (or phenols) by amino group. The reagent used for ammonolysis is alcoholic ammonia. Generally, a mixture of primary, secondary and tertiary amine is formed.

$$\begin{split} ROH + NH_3 &\xrightarrow{\frac{Al_2O_3.\Delta}{\text{Hightemp. Prerssure}}} RNH_2 + H_2O \\ R - NH_2 &\xrightarrow{\frac{+R - OH}{-H_2O}} R_2NH \xrightarrow{\frac{+R - OH}{-H_2O}} R_3N \xrightarrow{\frac{+R - OH}{-H_2O}} R_4N^+OH^- \end{split}$$

(vi) **Acetylation:** The process of introducing an acetyl (CH₃CO-) group into molecule using acetyl chloride or acetic anhydride is called acetylation.

$$CH_{3}CH_{2}NH_{2} + CH_{3}COCl \longrightarrow CH_{3}CH_{2} \stackrel{+}{N}H \stackrel{-}{C} - Cl \xrightarrow{-HCl} CH_{3}CH_{2} - \stackrel{-}{N} - \stackrel{-}{C} - CH_{3}$$

(vii) **Gabriel phthalimide synthesis:** It is a method of preparation of pure aliphatic and aralkyl primary amines. Phthalimide on treatment with ethanolic KOH gives potassium phathalimide which on heating with a suitable alkyl or aralkyl halides gives N-substituted phthalimides, which on hydrolysis with dil HCl or with alkali give primary amines.

Question 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.

(iii)
$$SOCI_2$$
SOCI₂
SOCI₂
SOCI₂
SOCI₂
NH₄CI

Benzoic acid

CONH₂
NH₂

Br₂-NaOH
Aniline

(iv)
$$\xrightarrow{\text{NH}_2} \xrightarrow{\text{Br}_2/\text{H}_2\text{O}} \xrightarrow{\text{Br}} \xrightarrow{\text{NH}_2} \xrightarrow{\text{Br}} \xrightarrow{\text{N}_2^+\text{Cl}^-} \xrightarrow{\text{Br}} \xrightarrow{\text{HBF}_4,\Delta} \xrightarrow{\text{Br}} \xrightarrow{\text{Br}}$$

$$(vii) \begin{picture}(10,0) \put(0.5,0){\line(1,0){100}} \put(0.5,0){\line(1,$$

$$(viii) \longrightarrow \xrightarrow{Br_2/NaOH} \xrightarrow{NH_2} \xrightarrow{N_2/Cl} \xrightarrow{H_3PO_2-H_2O, Cu} \xrightarrow{H_3PO_2-H_2O, Cu}$$

$$\longrightarrow \xrightarrow{CH_3Cl/Anhyd. AlCl_3}$$

$$\longrightarrow \xrightarrow{Toluene}$$

Question 9:

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

(i)
$$CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow{OH^-} B \xrightarrow{NaOH+Br_2} C$$

(ii) $C_6H_5Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow{NH_3} C$
(iii) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow{HNO_2} C$

(iv)
$$C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow{NaNO_2+HCl} B \xrightarrow{H_2O/H^+} C$$

$$(v) CH_3COOH \xrightarrow{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$$

$$(vi) C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow{HNO_2} B \xrightarrow{C_6H_5OH} C$$

Solution 9:

(i)
$$A = CH_3CH_2CN$$
, $B = CH_3CH_2 - C - NH_2$ and $C = CH_3CH_2 - NH_2$.

(ii)
$$A = C_6 H_5 CN$$
, $B = C_6 H_5 COOH$ and $C = C_6 H_5 CONH_2$

(iii)
$$A = CH_3CH_2CN$$
, $B = CH_3CH_2CH_2NH_2$ and $C = CH_3CH_2CH_2OH_2$

(iv)
$$A = C_6 H_5 N H_2$$
, $B = C_6 H_5 N^+ \equiv NCl^- = C_6 H_5 O H$

(v)
$$A = CH_3CONH_2$$
, $B = CH_3NH_2$ and $C = CH_3OH$

$$(vi) A = C_6H_5NH_2$$
, $B = C_6H_5N^+ \equiv NCl^-$ and $C = OH_5N^+$

Question 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 10:

Since the compound C with molecular formula C₆H₇N is formed from compound B on treatment with *Br*₂ and *KOH*, therefore, compound 'B' must be an amide and 'C' must be an amine. The only amine having the molecular formula C₆H₇N, i.e., C₆H₅NH₂ is aniline. Since 'C is aniline, therefore, the amide from which it is formed must be benzamide (C₆H₅CONH₂). Thus, compound 'B' is benzamide. Since compound 'B is formed from compound with aqueous ammonia and heating, therefore, compound 'A' must be benzoic acid.

Question 11:

Complete the following reactions:

(i)
$$C_6H_5NH_2 + CHCl_3 + alc KOH$$

$$(ii) C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$$

(iii)
$$C_6H_5NH_2 + H_2SO_4$$
 (conc) \longrightarrow

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

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

$$(vi)$$
 $C_6H_5NH_2+(CH_3CO)_5O\longrightarrow$

$$(vii) \ C_6 H_5 N_2 Cl \xrightarrow{(i) \ HBF_4} \longrightarrow$$

Solution 11:

(i)
$$C_6H_5NH_2 + CHCl_3 + 3KOH(alc) \xrightarrow{\Delta} C_6H_5N \equiv C + 3KCl + 3H_2O$$

(ii)
$$C_6H_5N_2Cl + H_3PO_2 + H_2O \xrightarrow{-Cu^+} C_6H_6 + N_2 + H_3PO_3 + HCl$$

(iii)
$$\stackrel{\text{NH}_2}{\longrightarrow}$$
 $\stackrel{\text{NH}_3}{\longrightarrow}$ $\stackrel{\text{NH}_2}{\longrightarrow}$ $\stackrel{\text{NH}_2}{\longrightarrow}$ $\stackrel{\text{NH}_3}{\longrightarrow}$ $\stackrel{\text{NH$

(iv)
$$C_6H_5N_2Cl + C_2H_5OH \xrightarrow{Reduction} C_6H_6 + CH_3CHO + N_2 + HCl$$

(v)
$$+Br_2(aq) \longrightarrow Br + 3HBr$$

$$(vi) C_6H_5NH_2 + CH_3CO - O - COCH_3 \xrightarrow{CH_3COOH} C_6H_5NHCOCH_3 + CH_3COOH$$

$$(vii) C_6H_5N_2CI \xrightarrow{HBF_4} C_6H_5N_2^+BF_4^- \xrightarrow{NaNO_2/Cu} C_6H_5NO_2 + N_2 + NaBF_4$$

Question 12:

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

Solution 12:

The success of Gabriel phthalimide reaction depends upon the nucleophilic attack by the phthalimide anion on the organic halogen compound. Since aryl halides do not undergo nucleophilic substitution reactions easily, therefore, arylamines, i.e. aromatic, primary amines cannot be prepared by Gabriel phthalimide reaction.

$$\begin{array}{c}
0 \\
C \\
N+R-X
\end{array}$$

$$\begin{array}{c}
0 \\
C \\
N-R
\end{array}$$

$$\begin{array}{c}
0 \\
N-R
\end{array}$$

$$\begin{array}{c}
0 \\
0 \\
0
\end{array}$$
No reaction

Question 13:

Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid.

Solution 13:

Both aromatic and aliphatic primary amines react with HNO₂ at 273-278 K to form aromatic and aliphatic diazonium salts respectively. But aliphatic diazonium salts are unstable even at this low temperature and thus decompose readily to form a mixture of compounds. Aromatic and aliphatic primary amines react with HNO₂as follows

$$NH_{2}$$
+ HONO + HCI $\xrightarrow{273-278 \text{ K}}$

$$(Stable)$$

$$(Stable)$$

$$CH_{3}CH_{2}NH_{2} + HONO + HCl \xrightarrow{273-278K} CH_{3}CH_{2} - N^{+} \equiv NCl^{-} \underbrace{ \begin{bmatrix} Decomposes \\ 273-278K \end{bmatrix} } CH_{3}CH_{2}OH + CH_{2} = CH_{2} + CH_{3}CH_{2}Cl + N_{2}Cl + N_{2}Cl + N_{3}CH_{2}OH + CH_{3}CH_{2}Cl + N_{3}CH_{3}CH_{2}OH + CH_{3}CH_{3$$

Ouestion 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?

Solution 14:

i) Loss of proton from an amine gives an amide ion while loss of a proton from alcohol give an alkoxide ion.

$$R - NH_2 \rightarrow R - NH^- + H^+$$

$$R-O-H \rightarrow R-O^-+H^+$$

Since O is more electronegative than N, so it will attract positive species more strongly in comparison to N. Thus, RO is more stable than RNH⁻. Thus, alcohols are more acidic than amines. Conversely, amines are less acidic than alcohols.

- (ii) Due to the presence of two H-atoms on N-atom of primary amines, they undergo extensive intermolecular H-bonding while tertiary amines due to the absence of H-atom on the N-atom do not undergo H-bonding. As a result, primary amines have higher boiling points than tertiary amines of comparable molecular mass.
- (iii) Aromatic amines are far less basic than ammonia and aliphatic amines because of following reasons:
- (a)Due to resonance in aniline and other aromatic amines, the lone pair of electrons on the nitrogen atom gets delocalized over the benzene ring and thus it is less easily available for protonation. Therefore, aromatic amines are weaker bases than ammonia and aliphatic amines.
- (b)Aromatic amines are more stable than corresponding protonated ion; Hence, they have very less tendency to combine with a proton to form corresponding protonated ion, and thus they are less basic.

