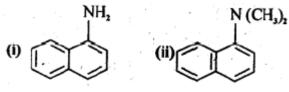
Amines



INTEX QUESTIONS

1:

Classify the following amines as primary, secondary and tertiary:



(iii) $(C_2H_5)_2$ CHNH₂

 $(iv)(C_2H_5)_2NH$

Solution:

(i) 1° (ii) 3° (iii) 1°(iv) 2°

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?

- (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)

$$\begin{array}{c} \text{CH}_3 \\ \text{I} \\ \text{CH}_3 - \text{C} - \text{NH}_2 \\ \text{I} \\ \text{CH}_3 \end{array}$$

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 (20)

(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

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

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:

(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:

$$C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$$

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 $C_2H_5NH_2$. Therefore, the basicity of $C_6H_5NH_2$ is lower than that of $C_2H_5NH_2$. Hence, the given compounds can be arranged in the increasing order of their basic strengths as follows:

$$C_6H_5NH_7 < C_7H_5NH_7 < (C_7H_5)_7N < (C_7H_5)_7NH$$

(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: $(CH_1)_3N < CH_3NH_2 < (CH_3)_2NH$

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.

$$C_6H_5NH_7 < C_6H_5CH_7NH_7 < (CH_3)_3N < CH_3NH_7 < (CH_1)_7NH_7$$

5:

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

- (i) $CH_3CH_2CH_2NH_2 + HC1$
- (ii) (C₂H₅)₃N+HCl

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

Solution:

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.

$$CH_3$$
 CH_3
 $+ CH_3I$
 Na_2CO_3
 $CO_3^{2-} + 2 Na I$

N, N - Dimethylaniline N, N, N - Trimethylanilinium iodide

N, N, N - Trimethylanilinium Carbonate

7:

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

Solution:

H

N:
$$+C_6H_5$$
— $C = O$

Aniline

Benzoyl chloride

H

O

Na⁺

Na⁺

Na⁺

Na^{-NaCl}

H

Cl

H

O

H

Cl

H

Cl

H

Cl

H

Cl

H

Cl

H

Cl

N-Phenylbenzamide (Benzanilide)

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:

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

1° amines:

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

N, N-Dimethyl methanamine

only 1° amines react with HNO2 to liberate N2 gas

$$CH_{3}CH_{2}CH_{2}NH_{2} + HNO_{2} \longrightarrow CH_{3}CH_{2}CH_{2}OH + N_{2} + H_{2}O$$

$$H_{3}C$$

$$CH \longrightarrow NH_{2} + HNO_{2} \longrightarrow CH \longrightarrow CH + N_{2} + H_{2}O$$

$$H_{3}C$$

$$Propan-2-ol$$

9:

Convert:

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

(i)
$$NH_2$$
 N_2 N_2 N_2 N_3 NO_2 N_4 NO_2 /Cu $N_$

(ii)
$$CH_3CH_2OH/\Delta$$
Or H_3PO_2/Cu^+
Br
Br
Br

1, 3, 5-Tribromobenzene

NCERT EXERCISES

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:

- (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)

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) Methylamine and methylamine can be distinguished by carbylamine test.

$$\begin{array}{c} CH_{3}NH_{2} + CHCl_{3} + 3KOH \xrightarrow{\Delta} CH_{3}NC + 2KCl + 3H_{2}O \\ \\ ^{1^{\circ}\text{ Amine}} \end{array}$$
 Methylisocyanide (offencive smell)

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

(ii) Secondary and tertiary amine can be distinguished by Liebermann's nitroamine test.

Secondary amines gives Liebermann nitroamine test while tertiary amines do not.

$$(CH_{3}CH_{2})_{2}NH + HO - N = O \xrightarrow{HCl + NaNO_{2}} (CH_{3}CH_{2})_{2}N - N = O + H_{2}O$$
Diethylamine
(2° Amine)

Yellow colour

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

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

$$C_2H_5NH_2 + HONO + HCl \xrightarrow{273-278K} C_2H_5OH + CH_2 = CH_2 + CH_3CH_2Cl + N_2$$

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

$$OH \qquad \qquad OH$$

$$HCI + N = N$$

$$OH \qquad \qquad OH$$

$$pH = 9 - 10$$

$$OH \qquad \qquad OH$$

$$pH = 9 - 10$$

$$OH \qquad \qquad OH$$

$$pH = 9 - 10$$

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

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

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

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

$$NH_2 \xrightarrow{\text{HONO, HCl}} N^{\dagger} \equiv NCl^{-1}$$
Aniline Stable

(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

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

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.

- (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.

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

$$2Fe^+ + 6OH^- \longrightarrow 2Fe(OH)_3 \text{ or } Fe_2O_3.3H_2O$$
(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

$$\begin{array}{c}
 & \text{NH}_2 \\
 & \text{NH}_2
\end{array}$$

$$\begin{array}{c}
 & \text{NH}_2 \\
 & \text{NH}_2
\end{array}$$

$$\begin{array}{c}
 & \text{NH}_2 \\
 & \text{NO}_2
\end{array}$$

$$\begin{array}{c}
 & \text{NO}_2 \\
 & \text{NO}_2
\end{array}$$

$$\begin{array}{c}
 & \text{NItroaniline} \\
 & \text{(2\%)}
\end{array}$$

$$\begin{array}{c}
 & \text{NH}_3 \\
 & \text{NH}_3 \\
\end{array}$$

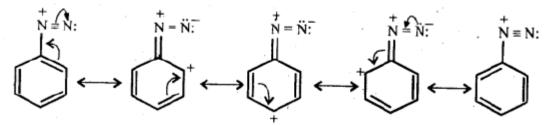
$$\begin{array}{c}
 & \text{NH}_4 \\
 & \text{NO}_2
\end{array}$$

(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.

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:

(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.

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

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.
- ∴ p-nitroaniline < p-toluidine

Increasing basic strength

(b) In C₆H₅NH₂ andC₆H₅NHCH₃, 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 C₆H₅NHCH₃ are 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.

$$\therefore (CH_3), NH < C_2H_5NH_2 < C_2H_5OH$$

- ----- 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.

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

→ Increasing solubility

How will you convert:

(i) Ethanoic acid into methanamine

5:

- (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

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

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

(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)
$$CH_3COOH \xrightarrow{LiAiH_4} CH_3CH_2OH \xrightarrow{P+l_2} CH_3CH_2I \xrightarrow{KCN} CH_3CH_2CN$$

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

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

$$CH_3CH_2NH_2 \longleftarrow Na/C_2H_5OH$$

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

$$(viii) CH_3CH_2COOH \xrightarrow{NH_3} CH_3CH_2CONH_2 \xrightarrow{Br_2/N_2OH} CH_3CH_2NH_2$$

$$\downarrow HNO_2$$

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

6:

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

Solution:

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.

$$RNH_2 + C_6H_5SO_2Cl \xrightarrow{OH^-} C_6H_5SO_2NHR \xrightarrow{KOH} C_6H_5SO_2N^-RK^+ \xrightarrow{H^+} C_6H_5SO_2NHR \xrightarrow{(Clear solution)} C_6H_5SO_2NHR$$

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

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

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)

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:** 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
$$Arene Diazonium$$
salt

(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 para position is blocked, it occurs at ortho position and if both ortho and para positions are compounds. The reaction generally takes place at para position to the hydroxy or amino group. If occupied, than no coupling takes place.

$$OH \xrightarrow{OH \cdot (pH9-10)} OH + HC$$

$$OH \xrightarrow{OH \cdot (pH9-10)} OH + HC$$

$$OH +$$

(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.

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

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

(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.

CO NH + KOH (alc)
$$\xrightarrow{-H_2O}$$
 CO N $\stackrel{+}{\sim}$ CO OH CO N $\stackrel{+}{\sim}$ CO OH CO N $\stackrel{+}{\sim}$ CO OH $\stackrel{+}{\sim}$ C

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.

(v)

Benzyl chloride

LiAlH₄

2-Phenylethanamine

(vi) Chlorobenzene
$$Cl$$

cone HNO_3 +

cone H_2SO_4 A
 NO_2
 Cl
 Sn/HCl
 NH_2
 p -Chloroaniline

$$(vii) \xrightarrow[Aniline]{NH_2} \xrightarrow{(CH_3CO)_2O} \xrightarrow[Br_2/CH_3COOH]{NHCOCH_3} \xrightarrow[Br_4/CH_3COOH]{NHCOCH_3} \xrightarrow[Br_4/C$$

$$(viii) \longrightarrow \xrightarrow{Br_2/N_0OH} \xrightarrow{NH_2} \xrightarrow{N_2^4Cl} \xrightarrow{H_3PO_2-H_2O, Cu} \xrightarrow{H_3PO_2-H_2O, Cu} \xrightarrow{CH_3Cl/Anhyd. AlCl_3}$$

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:

(i)
$$A = CH_3CH_2CN$$
, $B = CH_3CH_2 - C - NH_2$ and $C = CH_3CH_2 - NH_2$.
(ii) $A = C_6H_5CN$, $B = C_6H_5COOH$ and $C = C_6H_5CONH_2$
(iii) $A = CH_3CH_2CN$, $B = CH_3CH_2CH_2NH_2$ and $C = CH_3CH_2CH_2OH$
(iv) $A = C_6H_5NH_2$, $B = C_6H_5N^+ \equiv NCl^- = C_6H_5OH$
(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 $C = CH_3OH$

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:

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.

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)
$$C_6H_5NH_2+(CH_3CO)_2O \longrightarrow$$

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

Solution:

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

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

(iii)
$$\stackrel{\text{NH}_2}{\longrightarrow}$$
 $\stackrel{\text{H}_2\text{SO}_4}{\longrightarrow}$ $\stackrel{\text{NH}_3}{\longrightarrow}$ $\stackrel{\text{NH}_2}{\longrightarrow}$ $\stackrel{\text{NH}_2}{\longrightarrow}$ $\stackrel{\text{NH}_2}{\longrightarrow}$ $\stackrel{\text{NH}_3}{\longrightarrow}$ $\stackrel{\text{NH}_3}{\longrightarrow}$

(iv)
$$C_cH_cN_2Cl+C_2H_5OH \xrightarrow{Reduction} C_6H_6+CH_3CHO+N_2+HCl$$

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

12:

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

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.

13:

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

Solution:

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

$$NH_{2}$$

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

$$CH_{3}CH_{2}NH_{2} + HONO + HCI \xrightarrow{273-278K} CH_{3}CH_{2} - N^{+} \equiv NCI^{-}$$

$$CH_{3}CH_{2}NH_{2} + HONO + HCI \xrightarrow{273-278K} CH_{3}CH_{2}OH + CH_{2} = CH_{2} + CH_{3}CH_{2}CI + N_{2}CI +$$

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?

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
- (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.