

NCERT EXRECISES

- 13.1. Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines.
- (i) (CH₃)₂ CHNH₂
- (ii) CH₃(CH₂)₂NH₂
- (iii) CH₃NHCH(CH₃)₂
- (iv) (CH₃)₃ CNH₂
- (v) C₆H₅NHCH₃
- (vi) (CH₃CH₂)₂NCH₃
- (vii) m-BrC₆H₄NH₂

Ans:

- (i) Propan-2-amine(1°)
- (ii) Propan-1-amine (1°),
- (iii) N-Methylpropan-2-amine (2°).
- (iv) 2-Methylpropan-2-amine(I°)
- (v) N-MethylbenzenamineorN-methylaniline(2°)
- (vi) N-Ethyl-N-methylethanamine (3°)
- (vii) 3-Bromobenzenamine or 3-bromoaniline (1°)
- 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.

Ans:

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

CH₃NH₂+CHCl₃+3KOH
$$\stackrel{\Delta}{\longrightarrow}$$
 CH₃NC +3KCl+3H₂O

Methylisocyanide (offensive smell)

$$(CH_3)_2NH \xrightarrow{CHCl_3/KOH(alc)} No reaction$$
^{2°}Amine

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

$$(CH_3CH_2)_2NH + HO - N = O \xrightarrow{HCI+NaNO_2} (CH_3CH_2)_2N - N = O + H_2O$$
Diethylamine

(28 Amine)

Yellow colour

$$\begin{array}{c} (CH_3CH_2)_3 \, \text{N+} \, \text{HNO}_2 \longrightarrow & [(CH_3CH_2)_3 \, \text{NH}]^+ \, \text{NO}_2 \\ \text{Tricthylamine} \\ \text{(3°Amine)} & \text{Tricthylammonium nitrite} \\ \text{(Soluble)} \end{array}$$

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

$$\textbf{C}_2\textbf{H}_5\textbf{N}\textbf{H}_2 + \textbf{HONO} + \textbf{HCI} \xrightarrow{273-278K} \textbf{C}_2\textbf{H}_5\textbf{OH} + \textbf{CH}_2 = \textbf{CH}_2 + \textbf{CH}_3\textbf{CH}_2\textbf{CI} + \textbf{N}_2$$

$$NH_{2} + HONO + HC1 \xrightarrow{273-278 \text{ K}} N_{2}^{+}C1^{-} + 2H_{2}C1^{-} + 2H_{2}C1^$$

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

$$C_{6}H_{5}CH_{2}NH_{2} \xrightarrow{HONO} C_{6}H_{5}CH_{2}N_{2}^{+}C1 \xrightarrow{Decomposes} C_{6}H_{5}CH_{2}OH + N_{2} \uparrow + HCI$$

$$NH_{2} \xrightarrow{HONO, HCI} NH_{2} \xrightarrow{HONO, HCI} NH_{2} \xrightarrow{N^{+}} N^{+} = NC1$$
Stable

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

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

$$C_6H_5$$
 - NH - CH₃ - CHCl₃+3KOH \rightarrow No reaction

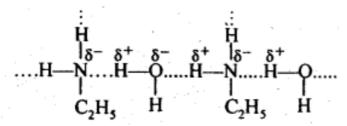
- 13.3. Account for the following
- (i) pKb of aniline is more than that of methylamine
- (ii) Ethylamine is soluble in water whereas aniline is not.
- (iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.
- (iv) Although amino group is o and p directing in aromatic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

Ans:

(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 $\text{CH}_3\text{NH}_2\text{,+}$ I-effect of -CH $_3$ 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,

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

These OH⁻ ions combine with Fe³⁺ ions present in H₂O to form brown precipitate of hydrated ferric oxide.

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

 $2Fe^{3+} + 6OH^- \longrightarrow$

(iv) Nitration is usually carried out with a mixture of cone $HNO_3 +$

cone H₂SO₄. In presence of these acids, most of aniline gets protonated to form ahilinium 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 rw-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.

$$\begin{array}{c|c} NH_2 & NH_2 \\ \hline & NN_2 \\ \hline & H^* & NO_2 \\ \hline & NN_3 \\ \hline & NN_3 \\ \hline & NN_4 \\ \hline & NN_5 \\ \hline &$$

(v) Aniline being a Lewis base reacts with Lewis acid $AlCl_3$ to form a salt. $C_6H_5NH_2+AlCl_3 \longrightarrow C_6H_5NH_2^+AlCl_3^-$

As a result, N of aniline acquires positive charge and hence it act 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.

13.4. Arrange the following:

(i) In decreasing order of pKb values:

 $C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

(ii) In increasing order of basic strength:

 $C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2$ NH and CH_3NH_2 .

- (iii) In increasing order of basic strength:
- (a) Aniline,p-nitroaniline andp-toluidine
- (b) C₆H₅NH₂, C₆H₅NHCH₃, C₆H₅CH₂NH₂
- (iv) In decreasing order of basic strength in gas phase:

 $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3

(v) In increasing order of boiling point:

C₂H₅OH, (CH₃)₂NH, C₂H₅NH₂

(vi) In increasing order of solubility in water:

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

Ans:

(i) Due to delocalisation of lone pair of electrons of the N-atom over the benzene ring, $C_6H_5NH_2$ and $C_6H_5NHCH_3$ are far less basic than $C_2H_5NH_2$ and $(C_2H_1)_2NH$. Due to +1-effect of the -CH $_3$ group, $C_6H_5NHCH_3$ is little more basic that $C_6H_5NH_2$. Among $C_2H_5NH_2$ and $(C_2H_5)_2NH$, $(C_2H_5)_2NH$ is more basic than $C_2H_5NH_2$ due to greater+1-effect of two - C_2H_5 groups. Therefore correct order of decreasing pKb values is:

(ii) Among CH_3NH_2 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 CH_3NH_2 .In both $C_6H_5NH_2$ and $C_6H_5N(CH_3)_2$ lone

pair of electrons present on N-atom is delocalized over the benzene ring but $C_6H_5N(CH_3)_2$ is more basic due to +1 effect of two- CH_3 groups.

$(C_2H_5)_2NH > CH_3NH_2 > C_6H_5N(CH_3)_2 > C_6H_5NH_2$ $\xrightarrow{\text{Decreasing basic strength}}$

(iii) (a) The presence of electron donating - ${\rm CH_3}$ group increases while the presence of electron withdrawing - ${\rm NO_2}$ group decreases the basic strength of amines.

.. p-nitroaniline < aniline < p-toluidine

(b) In $C_6H_5NH_2$ and $C_6H_5NHCH_3$, 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 $C_6H_5NH_2$ and $C_6H_5NHCH_3$ are weaker base in comparison to $C_6H_5CH_2NH_2$. Among $C_6H_5NH_2$ and $C_6H_5NHCH_3$, due to +1 effect of-CH $_3$ group $C_6H_5NHCH_3$ is more basic.

$C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$ $\longrightarrow \text{Increasing basic strength}$

(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,

$(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$ $\longrightarrow Decreasing basic strength$

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

∴ (CH₃)₂NH < C₂H₅NH₂ < C₂H₅OH 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 iirthe number of H-atoms on the N-atom which undergo H-bonding.

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

Increasing solubility

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?
- (i) $CH_3COOH \xrightarrow{SOCl_3} CH_3COCI \xrightarrow{NH_3(excess)} CH_3CONH_2 \xrightarrow{Br_2/NaOH} CH_3NH_2$
- $(ii) \quad \text{CH}_3(\text{CH}_2)_4\text{CN} \xrightarrow{\text{H}_3\text{O}^+} \text{CH}_3(\text{CH}_2)_4\text{COOH} \xrightarrow{\text{SOCI}_2 \atop -\text{SO}_2 \text{HCI}} \text{CH}_3(\text{CH}_2)_4\text{COCI} \xrightarrow{\text{NH}_3(\text{excess}) \atop -\text{NH}_4\text{CI}} \text{CH}_3(\text{CH}_2)_4\text{CONH}_2 \xrightarrow{\text{CH}_3(\text{CH}_2)_4\text{NH}_2} \text{CH}_3(\text{CH}_2)_4\text{NH}_2 \xrightarrow{\text{CH}_3(\text{CH}_2)_4\text{NH}_2} \text{CH}_3(\text{CH}_2)_4 \text{COOH}_2 \xrightarrow{\text{CH}_3(\text{CH}_2)_4 \text{COOH}_2} \text{CH}_3(\text{CH}_2)_4 \text{COOH}_2 \xrightarrow{\text{COOH}_2} \text{CH}_3(\text{CH}_2)_4 \text{COOH}_2 \xrightarrow{\text{COOH}_2} \text{CH}_3(\text{CH}_2)_4 \text{COOH}_2 \xrightarrow{\text{COOH}_2} \xrightarrow{\text{COOH}_2} \text{COOH}_2 \xrightarrow{\text{COOH}_2} \xrightarrow{\text{COOH}_2} \text{COOH}_2 \xrightarrow{\text{COOH}_2} \xrightarrow{\text{COOH}_2}$

(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)
$$CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH \xrightarrow{P+l_2} CH_3CH_2 \vdash \xrightarrow{KCN} CH_3CH_2CN$$

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

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

$$CH_3CH_3NH_4 \xrightarrow{KCN} CH_3CN$$

$$CH_3CH_3NH_4 \xrightarrow{NA/C_2H_3OH} CH_3CN$$

$$(vii) \ \text{CH}_3 \text{NO}_2 \xrightarrow{\text{Sn/HCl}} \text{CH}_3 \text{NH}_2 \xrightarrow{\text{CHCl}_3, \text{KOH}, \Delta} \text{CH}_3 \text{NC} \xrightarrow{\text{LiAlH}_4} \text{CH}_3 \text{NHCH}_3$$

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

$$\downarrow HNO_2$$

$$CH_2COOH \xleftarrow{Alk. KMnO_4} CH_2CH_2OH$$

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

Ans: The three type of amines can be distinguished by Hinsberg test. In this test, the amine is shaken with benzenesulphonyt chloride ($C_6H_5SO_2CI$) 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)

- 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

Ans:

(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 HCl at a temperature below 5°C.

ArNH₂+ NaNO₂ + 2HX
$$\xrightarrow{273-278K}$$
 ArN₂X + NaX + 2H₂O

1° amine 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 Hoffinann's bromamide degradation reaction.

$C_6H_5CONH_2 \xrightarrow{Br_2 + NaOH} C_6H_5NH_2$

(iv) Coupling reaction: In this reaction, arene diazonium 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.

$$ROH + NH_3 \xrightarrow{\text{Al}_2O_3, \Delta} RNH_2 + H_2O$$

$$R \xrightarrow{-NH_2} \xrightarrow{+R-OH} R_2NH \xrightarrow{+R-OH} R_3N \xrightarrow{+R-OH} R_4N^+OH^-$$

(vi) Acetylation: The process of introducing an acetyl (CH_3CO -) 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 HCI or with alkali give primary amines.

CO NH + KOH (alc)
$$CO = \frac{CO}{-H_2O}$$

$$CO = \frac{CO}{N} + \frac{C_2H_3I_1\Delta}{-KI}$$

$$COOH$$

$$C_2H_3NH_2 + \frac{COOH}{COOH}$$

$$COOH$$

$$COOH$$

$$COOH$$

- 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.

Ans:

(i)
$$NO_2$$
 NH_2 $N_2^+C\Gamma$ $COOH$ $N_3NO_2 + HCI$ $N_3NO_2 +$

(iv)
$$\underbrace{ \begin{array}{c} NH_2 \\ Br_2/H_2O \end{array}}_{Aniline} \underbrace{ \begin{array}{c} NH_2 \\ Br \end{array}}_{DR} \underbrace{ \begin{array}{c} NH_2 \\ Pr \end{array}}_{DR} \underbrace{ \begin{array}{c} N_2C\Gamma \\ Pr \end{array}}_{Br} \underbrace{ \begin{array}{c} Br \\ HBF_4\Delta \end{array}}_{Br} \underbrace{ \begin{array}{c} F \\ Br \end{array}}_{Br}$$

$$(vi) \qquad \begin{array}{c} Cl \\ \\ \text{Chlorobenzene} \end{array} \qquad \begin{array}{c} Cl \\ \\ \text{NO}_2 \end{array} \qquad \begin{array}{c} Cl \\ \\ \text{Sn/HCl} \end{array}$$

$$(vii) \underbrace{ \begin{array}{c} \text{NH}_2 \\ \text{(CH}_3\text{CO})_2\text{O} \\ \text{-CH}_3\text{COOH} \end{array}}_{\text{Aniline}} \underbrace{ \begin{array}{c} \text{NHCOCH}_3 \\ \text{-CH}_3\text{COOH} \end{array}}_{\text{Br}} \underbrace{ \begin{array}{c} \text{NH}_2\text{O} \\ \text{-CH}_3\text{COOH} \end{array}}_{\text{Br}} \underbrace{ \begin{array}{$$

$$(viii) \longrightarrow \begin{array}{c} \text{CONH}_2 \\ \text{Br}_2/\text{NaOH} \end{array} \longrightarrow \begin{array}{c} \text{NH}_2 \\ \text{NaNO}_2 + \text{HCl} \\ \text{273-278 K} \end{array} \longrightarrow \begin{array}{c} \text{N}_2^*\text{CCI} \\ \text{H}_3\text{PO}_2 - \text{H}_2\text{O}, \text{Cu} \\ \text{Anhyd. AlCl}_3 \end{array}$$

13.9. Give the structures of A,B and C in the following reaction: $\frac{1}{2}$

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

(ii)
$$C_6H_5N_2CI \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow{NH_3} C$$

(iii)
$$CH_3CH_2Br \xrightarrow{KCN} A_8 \xrightarrow{LIAIH_4} B \xrightarrow{HNO_2} C$$

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

(
$$\nu$$
) CH₃COOH $\xrightarrow{NH_3}$ A \xrightarrow{NaOBr} B $\xrightarrow{NaNO_2/HCl}$ C

(vii)
$$C_6H_5NO_2 \xrightarrow{Fe/HCI} A \xrightarrow{HNO_2} B \xrightarrow{C_6H_5OH} C$$

Ans:

(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) $A = C_6H_5NH_2$, $B = C_6H_5N^+ = NCl^-$ and $C = C_6H_5OH$.
- (v) $A = CH_3CONH_2$, $B = CH_3NH_2$ and $C = CH_3OH$.