(Chapter 13)(Amines) XII

Intext Questions

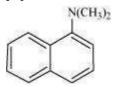
Question 13.1:

Classify the following amines as primary, secondary or tertiary:

(i)



(ii)



(iii) (C₂H₅)₂CHNH₂

(iv) $(C_2H_5)_2NH$

Answer

Primary: (i) and (iii)

Secondary: (iv)
Tertiary: (ii)

Question 13.2:

- (i) Write 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?

Answer

- (i), (ii) The structures and their IUPAC names of different isomeric amines corresponding to the molecular formula, $C_4H_{11}N$ are given below:
- (a) CH₃-CH₂-CH₂-CH₂-NH₂

Butanamine (10)

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

Butan-2-amine (1⁰)

(c)
$$CH_3 - CH_2 - CH_2 - NH_2$$

2-Methylpropanamine (10)

(d)

2-Methylpropan-2-amine (10)

(e) CH₃-CH₂-CH₂-NH-CH₃

N-Methylpropanamine (20)

(f) CH₃-CH₂-NH-CH₂-CH₃

N-Ethylethanamine (2°)

(g)

N-Methylpropan-2-amine (2⁰)

(h)

$$CH_3 - CH_2 - N - CH_3$$

N,N-Dimethylethanamine (3°)

(iii) The pairs (a) and (b) and (e) and (g) exhibit position isomerism.

The pairs (a) and (c); (a) and (d); (b) and (c); (b) and (d) exhibit chain isomerism.

The pairs (e) and (f) and (g) exhibit metamerism.

All primary amines exhibit functional isomerism with secondary and tertiary amines and vice-versa.

Question 13.3:

How will you convert?

- (i) Benzene into aniline
- (ii) Benzene into N, N-dimethylaniline
- (iii) Cl-(CH₂)₄-Cl into hexan-1, 6-diamine?

Answer

(i) NO_2 NH_2 HNO3/H2SO3 H2/Pd (Nitration) Ethanol Aniline (ii) Benzene NO_2 NH₂ CH₃ CH₃Cl HNO₃/H₂SO₄ H2/Pd CH₃Cl Ethanol Aniline Benzene N, N, - Dimethylaniline (iii)

$$C1-(CH_2)_4-C1 \xrightarrow{\text{Ethanolic NaCN}} N \Longrightarrow C-(CH_2)_4-C \Longrightarrow N$$

$$1,4-\text{Dichlorobutane}$$

$$H_2N-CH_2-(CH_2)_4-CH_2-NH_2$$

$$Hexane -1,6-\text{diamine}$$

Question 13.4:

Arrange the following in increasing order of their basic strength:

- (i) $C_2H_5NH_2$, $C_6H_5NH_2$, NH_3 , $C_6H_5CH_2NH_2$ and $(C_2H_5)_2NH$
- (ii) $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$, $C_6H_5NH_2$
- (iii) CH₃NH₂, (CH₃)₂NH, (CH₃)₃N, C₆H₅NH₂, C₆H₅CH₂NH₂.

Answer

(i) Considering the inductive effect of alkyl groups, NH_3 , $C_2H_5NH_2$, and $(C_2H_5)_2NH$ can be arranged in the increasing order of their basic strengths as:

$$NH_1 < C_2H_5NH_3 < (C_3H_5), NH_3$$

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 C_6H_5 group, the electron density on the N-atom in $C_6H_5CH_2NH_2$ is lower than that on the N-atom in $C_2H_5NH_2$, but more than that in NH_3 . Therefore, the given compounds can be arranged in the order of their basic strengths as:

$$C_6H_5NH_7 < NH_3 < C_6H_5CH_7NH_7 < C_7H_5NH_7 < (C_7H_5), NH_7$$

(ii) Considering the inductive effect and the steric hindrance of the alkyl groups, $C_2H_5NH_2$, $(C_2H_5)_2NH_2$, 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:

$$C_6H_5NH_2 < C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$$

(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:

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

In $C_6H_5NH_2$, 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 $C_6H_5CH_2NH_2$, 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 C_6H_5 group, the electron density on the N-atom in $C_6H_5CH_2NH_2$ is lower than that on the N-atom in $(CH_3)_3N$. Therefore, $(CH_3)_3N$ is more basic

than $C_6H_5CH_2NH_2$. 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 13.5:

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

- (i) CH₃CH₂CH₂NH₂ + HCl →
- (ii) $(C_2H_5)_3N + HCI \rightarrow$

Answer

(ii)
$$(C_2H_5)_3N + HC1 \longrightarrow (C_2H_5)_3NH_3CI$$

Triethylamine Triemethylammoniumchloride

Question 13.6:

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

Answer

Aniline reacts with methyl iodide to produce N, N-dimethylaniline.

$$\begin{array}{c|c} NH_2 & & & \\ \hline \\ NH_2 & & \\ \hline \\ CH_3I & & \\ \hline \\ Aniline & & \\ N, N-Dimethylaniline \\ \end{array}$$

With excess methyl iodide, in the presence of Na2CO3 solution, N, N-dimethylaniline produces N, N, N-trimethylanilinium carbonate.

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

N, N, N - Trimethylanilinium Carbonate

Question 13.7:

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

Answer

N - Phenylbenzamide

Question 13.8:

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

Answer

The structures of different isomers corresponding to the molecular formula, C₃H₉N are given below:

(a)
$$CH_3 - CH_2 - CH_2 - NH_2$$

Propan-1-amine (1⁰)

(b)

Propan-2-amine (1⁰)

(c)

N-Methylethanamine (2°)

(d)

N,N-Dimethylmethanamine (30)

1ºamines, (a) propan-1-amine, and (b) Propan-2-amine will liberate nitrogen gas on treatment with nitrous acid.

$$CH_3CH_2CH_2NH_2 + HNO_2 \longrightarrow CH_3CH_2CH_2OH + N_2 + HCI$$

Propan-1-amine

Propan-1-ol

Propan - 2 - amine

Propan - 2 - ol

Question 13.9:

Convert

- (i) 3-Methylaniline into 3-nitrotoluene.
- (ii) Aniline into 1,3,5-tribromobenzene.

Answer

(i)

$$\begin{array}{c} NH_2 \\ + NaNO_2 + 2HCI \\ \hline \\ CH_3 \\ 3 - Methylaniline \\ \end{array} \\ \begin{array}{c} + NaCI + 2H_2O \\ CH_3 \\ \hline \\ NO_2 \\ \hline \\ NaBF_4 \\ \hline \\ N_2B\overline{F}_4 \\ \hline \\ N_2B\overline{F}_4 \\ \hline \\ CH_3 \\ \end{array}$$

3 - Nitrotoluene

(ii)
$$\begin{array}{c} NH_2 \\ Br_2/H_2O \\ \hline -3 \text{ HBr} \end{array}$$

$$\begin{array}{c} Br \\ NaNO_2/HCl \\ \hline \end{array}$$

$$\begin{array}{c} Br \\ NaNO_2/HCl \\ \hline \end{array}$$

$$\begin{array}{c} Br \\ Br \\ \hline \end{array}$$

1, 3, 5 - Tribromobenzene