(Chapter 13)(Amines)

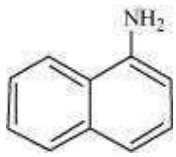
XII

Intext Questions

Question 13.1:

Classify the following amines as primary, secondary or tertiary:

(i)



(ii)

(iii) $(C_2H_5)_2CHNH_2$

(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.

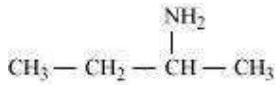
(iii) What type of isomerism is exhibited by different pairs of amines?

Answer

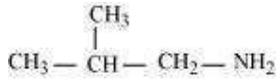
(i), (ii) The structures and their IUPAC names of different isomeric amines corresponding to the molecular formula, $C_4H_{11}N$ are given below:

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

Butanamine (1^0)

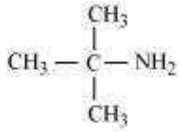
(b) 

Butan-2-amine (1^0)

(c) 

2-Methylpropanamine (1^0)

(d)



2-Methylpropan-2-amine (1^0)

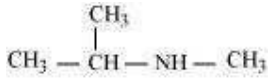
(e) CH_3-CH_2-CH_2-NH-CH_3

N-Methylpropanamine (2^0)

(f) CH_3-CH_2-NH-CH_2-CH_3

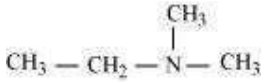
N-Ethylethanamine (2^0)

(g)



N-Methylpropan-2-amine (2^0)

(h)



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 (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?

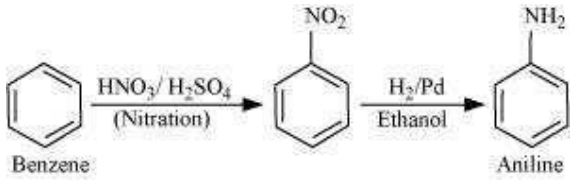
(i) Benzene into aniline

(ii) Benzene into N, N-dimethylaniline

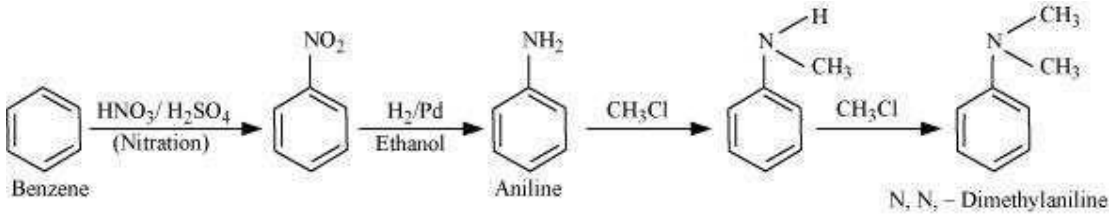
(iii) $Cl-(CH_2)_4-Cl$ into hexan-1, 6-diamine?

Answer

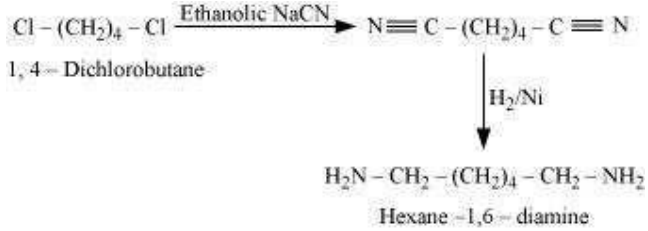
(i)



(ii)



(iii)



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) CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5NH_2$, $C_6H_5CH_2NH_2$.

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:

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

Again, $C_6H_5NH_2$ has proton acceptability less than NH_3. 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:

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

(ii) Considering the inductive effect and the steric hindrance of the alkyl groups, $C_2H_5NH_2$, $(C_2H_5)_2NH_2$, 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 $C_6H_5NH_2$ 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 $C_6H_5CH_2NH_2$ than in $C_6H_5NH_2$ i.e., $C_6H_5CH_2NH_2$ is more basic than $C_6H_5NH_2$.

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.

$$C_6H_5NH_2 < C_6H_5CH_2NH_2 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$$

Question 13.5:

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

(i) $CH_3CH_2CH_2NH_2 + HCl \rightarrow$

(ii) $(C_2H_5)_3N + HCl \rightarrow$

Answer

(i) $CH_3CH_2CH_2NH_2 + HCl \longrightarrow CH_3CH_2CH_2\overset{+}{N}H_3\,\overset{-}{Cl}$

n-Propylamine — n-Propylammoniumchloride

(ii) $(C_2H_5)_3N + HCl \longrightarrow (C_2H_5)_3\overset{+}{N}H\,\overset{-}{Cl}$

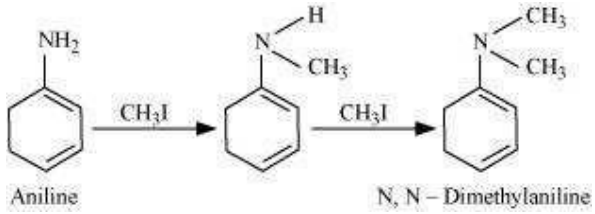
Triethylamine — Triemethylammoniumchloride

Question 13.6:

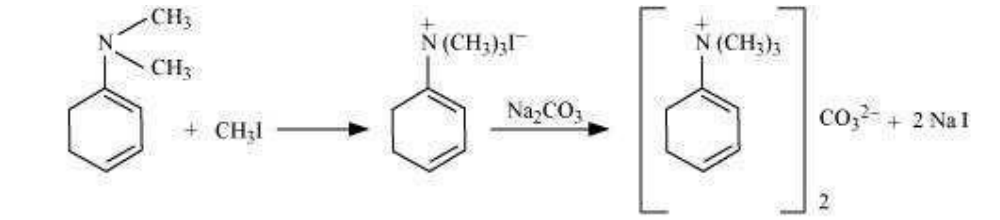
Write reactions of the final alkylation product of aniline with excess of methyl iodide in the presence of sodium carbonate solution.

Answer

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



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

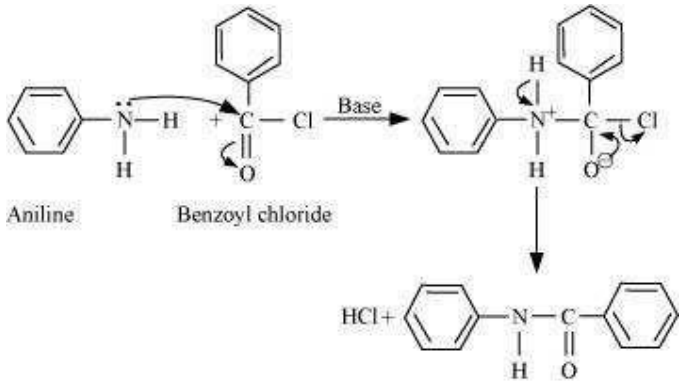


N, N – Dimethylaniline N, N, N – Trimethylanilinium iodide N, N, N – Trimethylanilinium Carbonate

Question 13.7:

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

Answer



Aniline Benzoyl chloride N – Phenylbenzamide

Question 13.8:

Write structures of different isomers corresponding to the molecular formula, C_3H_9N. Write IUPAC names of the isomers which will liberate nitrogen gas on treatment with nitrous acid.

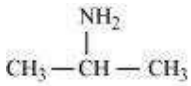
Answer

The structures of different isomers corresponding to the molecular formula, C_3H_9N are given below:

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

Propan-1-amine (1^0)

(b)



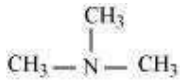
Propan-2-amine (1^0)

(c)

CH_3-NH-C_2H_5

N-Methylethanamine (2^0)

(d)



N,N-Dimethylmethanamine (3^0)

1^0amines, (a) propan-1-amine, and (b) Propan-2-amine will liberate nitrogen gas on treatment with nitrous acid.

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

Propan-1-amine Propan-1-ol

Propan – 2 – amine Propan – 2 – ol

Question 13.9:

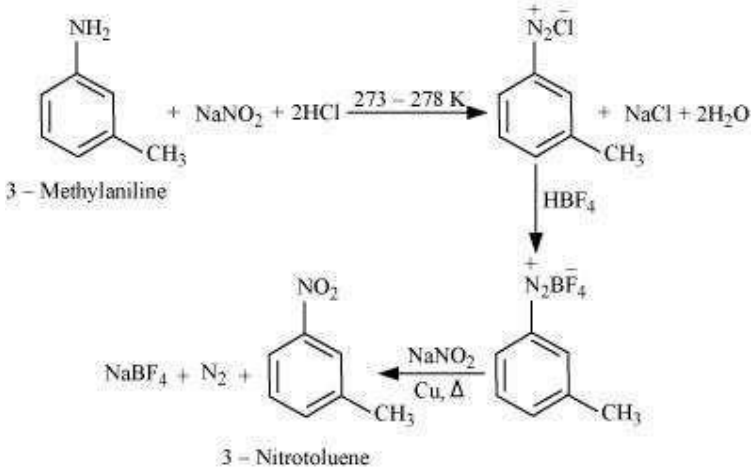
Convert

(i) 3-Methylaniline into 3-nitrotoluene.

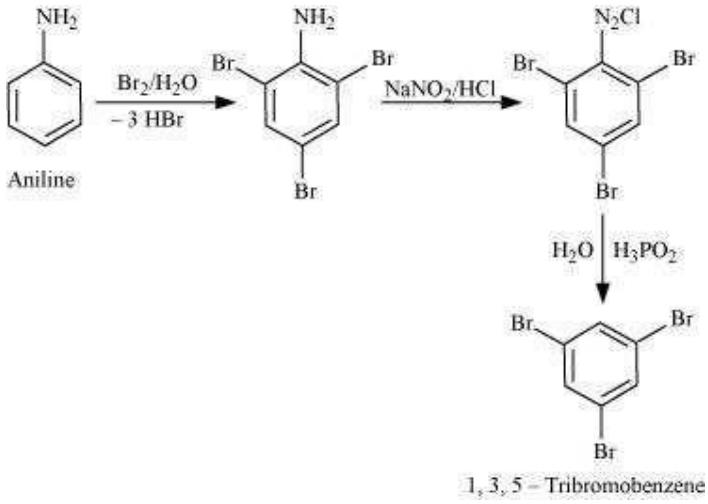
(ii) Aniline into 1,3,5-tribromobenzene.

Answer

(i)


NH2
+ NaNO2 + 2HCl
273 – 278 K
+ NaCl + 2H2O
CH3
3 – Methylaniline
HBF4
NaBF4 + N2 +
NaNO2
Cu, Δ
NO2
3 – Nitrotoluene

(ii)


NH2
Aniline
Br2/H2O
– 3 HBr
Br
NaNO2/HCl
N2Cl
H2O
H3PO2
1, 3, 5 – Tribromobenzene