- Digvijay

Maharashtra State Board Class 12 Chemistry Solutions Chapter 13 Amines

1. Choose the most correct option.

Question i.
The hybridization of nitrogen in primary amine is
a. sp
b. sp2
c. sp ₃
d. sp3d
Answer:
c. sp ₃
Question ii.

Isobutylamine is an example of

- a. 2° amine
- b. 3° amine
- c. 1° amine
- d. quaternary ammonium salt.

Answer:

a. 2° amine

Question iii.

Which one of the following compounds has the highest boiling point?

- a. n-Butylamine
- b. sec-Butylamine
- c. isobutylamine
- d. tert-Butylamine

Answer:

a. n-Butylamine

Question iv.

Which of the following has the highest basic strength?

- a. Trimethylamine
- b. Methylamine
- c. Ammonia
- d. Dimethylamine

Answer:

d. Dimethylamine

Question v.

Which type of amine does produce N2 when treated with HNO2?

- a. Primary amine
- b. Secondary amine
- c. Tertiary amine
- d. Both primary and secondary amines

Answer:

a. Primary amine

Question vi.

Carbylamine test is given by

- a. Primary amine
- b. Secondary amine
- c. Tertiary amine
- d. Both secondary and tertiary amines

Answer:

a. Primary amine

Question vii.

Which one of the following compounds does not react with acetyl chloride?

- a. CH₃-CH₂-NH₂
- b. (CH₃-CH₂)₂NH
- c. (CH₃-CH₂)₃N
- $d.\ C_6H_5\text{-}NH_2$

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Answer:

c. (CH3 - CH2)3N

Question viii.

Which of the following compounds will dissolve in aqueous NaOH after undergoing reaction with Hinsberg reagent?

- a. Ethylamine
- b. Triethylamine
- c. Trimethylamine
- d. Diethylamine

Answer:

a. Ethyl amine

Question ix.

Identify 'B' in the following reactions

 CH_3 - $C=N \xrightarrow{Na/C_2H_3OH} A \xrightarrow{NaNO_2/dilHCl} B$

a. CH₃-CH₂-NH₂ b. CH₃-CH₂-NO₂

c. CH₃-CH₂N₂⊕Cl[⊕] d. CH₃-CH₂-OH

Answer:

d. CH3-CH2-OH

Question x.

Which one of the following compounds contains azo linkage?

- a. Hydrazine
- b. p-Hydroxyazobenzene
- c. N-Nitrosodiethylamine
- d. Ethylenediamine

Answer:

b. p-Hydroxyazobenzene

2. Answer in one sentence.

Question i.

Write reaction of p-toluenesulfonyl chloride with diethylamine.

Answer:

$$H_3C$$
 — $SOCl_2 + HN$ C_2H_5 — H_3C — C_2H_5 —

Question ii.

chloride

How many moles of methylbromide are required to convert ethanamine to N, N-dimethyl ethanamine?

2 moles of methylbromide are required to convert ethanamine to N, N-dimethyl ethanamine.

Question iii.

Which amide does produce ethanamine by Hofmann bromamide degradation reaction?

Propanamide (CH₃ – CH₂ – CONH₂) produces ethanamine by Hofmann bromamide degradation reaction.

Question iv.

Write the order of basicity of aliphatic alkylamine in gaseous phase.

The order of basicity of aliphatic alkyl amines in the gaseous follows the order: tertiary amine > secondary amine > primary amine > NH₃.

sulphon amide

Question v.

Why are primary aliphatic amines stronger bases than ammonia?

Answer:

The alkyl group tends to increase the electron density on the nitrogen atom. As a result, amines can donate the lone f pair of electrons on nitrogen more easily than ammonia. Hence, aliphatic amines are stronger bases than ammonia.

Question vi.

Predict the product of the following reaction. Nitrobenzene Sn/Conc. HCI?

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Answer:

The product is aniline/
$$NH_2$$
 .

Question vii.

Write the IUPAC name of benzylamine.

Answer

The IUPAC name is Phenylmethanamine.

Question viii.

Arrange the following amines in an increasing order of boiling points. n-propylamine, ethylmethyl amine, trimethylamine.

Answer:

Amines in an increasing order of boiling points: trimethyl amine, ethyl methyl amine, n-propyl amine

Question ix.

Write the balanced chemical equations for the action of dil H2SO4 on diethylamine.

Answer

$$2(C_2H_5)_2 \text{ NH} + H_2SO_4 \rightarrow [(C_2H_5)_2 \text{ NH}_2]_2 \text{ SO}_4^{2-}$$

Diethyl amine diethylammonium sulphate

Question x.

Arrange the following amines in the increasing order of their pKb values. Aniline, Cyclohexylamine, 4-Nitroaniline

Answer:

Cyclohexyl amine (pKA 3.34), aniline (pKA 9.13) 4-nitroaniline (pKA 12.99)

3. Answer the following

Question i.

Identify A and B in the following reactions.

$$C_6H_5CH_2Br \xrightarrow{\text{alco.}} A \xrightarrow{\text{Na/ethanol}} B.$$

Answer

$$\begin{array}{c} C_6H_5CH_2 \text{ Br} \xrightarrow{\text{alc.KCN}} C_6H_5CH_2CN + 4(H) \xrightarrow{\text{Na/C}_2H_5OH} C_6H_5CH_2 - CH_2 - NH_2 \\ \text{phenyl acetonitrile} & \beta\text{-phenyl ethyl amine} \\ \text{(A)} & \text{(B)} \end{array}$$

 $A = C_6H_5CH_2CN$ phenyl acetonitrile

$$\mathbf{B} = C_6 H_5 C H_2 - C H_2 - N H_2 \beta$$
-phenyl ethyl amine

Question ii.

Explain the basic nature of amines with suitable example.

Answer

The basic strength of amines is expressed in terms of Kb or pKb value. According to Lowry-Bron-sted theory the basic nature of amines is explained by the following equilibrium equation.

$$N: + H_2O \implies N - H + OH$$
Amine conjugate acid

In this equilibrium amine accepts H+, hence an amine is a Lowry-Bronsted base.

According to Lewis theory, the species which donates a pair of electrons is called a base

The nitrogen atom in amiqes has a lone pair of electrons, which can be donated to suitable acceptor like proton H+.

The aqueous solutions of amines are basic in nature due to release of free OH- ions in solutions. Hence amines are Lewis bases. There exists an equilibrium in their aqueous solutions as follows:

3

$$R - NH_2 + H_2O \Rightarrow RNH_3 + OH_-$$

Since OH- is a stronger base, equilibrium shifts towards left-hand side giving less concentration of OH-.

Here, Kb value is smaller and pKb value is larger.

Hence amines are weak bases.

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Question iii.

What is diazotisation? Write diazotisation reaction of aniline.

Answer

Aryl amines react with nitrous acid in cold condition (273 – 278 K) forms arene diazonium salts. The conversion of primary aromatic amine into diazonium salts is called diazotisation.

Diazotisation of aniline:

$$NH_2$$
 + NaNO₂ + 2HCl $\xrightarrow{273-278 \text{ K}}$ + NaCl + 2H₂Cl
Aniline Benzene diazonium chloride

Question iv.

Write reaction to convert acetic acid into methylamine.

Answer:

$$C_2H_5NH_2 \xrightarrow{HONO} C_2H_5OH \xrightarrow{2(O)} C_2H_5OH \xrightarrow{2(O)} CH_3COOH \xrightarrow{NH_3} CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2 \xrightarrow{Br_2/4KOH} CH_3NH_2$$
 ethyl amine Ethyl alcohol Acetic acid Ammonium acetate
$$C_2H_5NH_2 \xrightarrow{HONO} C_2H_5OH \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3COOH \xrightarrow{NH_3} CH_3COONH_4 \xrightarrow{\Delta} CH_3COONH_2 \xrightarrow{Br_2/4KOH} CH_3NH_2$$
 methyl amine

Question v.

Write a short note on coupling reactions.

Answer

(1) Ar - NH₂
$$\xrightarrow{?}$$
 Ar - $\overset{+}{N_2}$ Cl - $\xrightarrow{\text{HCl}}$ Cuprous chloride $\xrightarrow{}$ (ii) ?

(i)
$$\xrightarrow{\text{NaNO}_2/2\text{HCl}}$$
 (Reagent)

(ii) ArCl +
$$N_2 \uparrow$$
 (Product)

(2) Ar
$$-N_2Cl^- \xrightarrow{H_3PO_2} ?$$

$$ArH + N_2 + H_3PO_3 + HCI$$

Arene

Reactions involving retention of diazo group: (Coupling reactions):

Question vi.

Explain Gabriel phthalimide synthesis.

Answer

Phthalimide is reacted with alcoholic KOH to form potassium phthalimide. Further potassium phthalimide is treated with an ethyl iodide. The product N-ethylphthalimide is hydrolysed with aq NaOH to form ethyl amine. This reaction is known Gabriel phthalimide synthesis.

Phthalimide

Potassium phthalimide

$$CO$$
 $N - C_2H_5$
 $N - C_2H_5$

Question vii.

Explain carbylamine reaction with suitable examples.

Answer

Aliphatic or aromatic primary amines on heating with chloroform and alcoholic potassium hydroxide solution form carbyl amines or isocyanides with extremely unpleasant smell. This reaction is a test for primary amines.

Secondary and tertiary amines do not give this test.

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$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} RNC + 3KCl + 3H_2O$$

Primary amine

(alc.) Alkyl

isocyanide

$$C_2H_5-NH_2+CHCl_3+3KOH \xrightarrow{\Delta} C_2H_5NC+3KCl+3H_2O$$

Ethylamine

(alc.)

Ethyl isocyanide

chloride

Question viii.

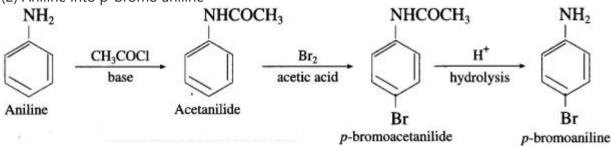
Write reaction to convert

- (i) methanamine into ethanamine
- (ii) Aniline into p-bromoaniline.

Answer:

(1) Methanamine into ethanamine

(2) Aniline into p-bromo aniline



Question ix.

Complete the following reactions:

- a. C6H5N2 CI + C2H5OH \rightarrow
- b. $C6H_5NH_2 + Br_2(aq) \rightarrow ?$

Answer:

$$C_6H_5N_2Cl^- + C_2H_5OH \longrightarrow C_6H_5 - N = N - CH_2 - CH_2 - OH + HCl$$

2,4,6-Tribromoaniline

(b)
$$RH_{2} + 3Br_{2}(aq) \longrightarrow RH_{2}$$
 Br
$$RH_{2} + 3HBr$$
 Br
$$RH_{2} + 3HBr$$

Question x.

Explain Ammonolysis of alkyl halides.

Answer:

When an alkyl halide is heated with alcoholic ammonia in a sealed tube under pressure at 373 K, a mixture of primary, secondary, tertiary amines and a quaternary ammonium salt is obtained. In this reaction, breaking of C – X bond by ammonia is called ammonolysis of alkyl halides. The reaction is also known as alkylation. For example, when methyl bromide is heated with alcoholic ammonia at 373 K, it gives a mixture of methylamine (a primary amine), dimethylamine (a secondary amine), trimethyl amine (a tertiary amine) and tetramethylam-

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monium bromide (a quaternary ammonium salt).

$$CH_3 - Br + NH_3 \xrightarrow{\Delta} CH_3 - NH_2 + HBr$$

methylbromide alc.

. methylamine

$$CH_3 - NH_2 + CH_3 - Br \xrightarrow{\Delta} (CH_3)_2NH + HBr$$

methyl amine

dimethyl amine

$$(CH_3)_2 NH + CH_3 - Br \xrightarrow{\Delta} (CH_3)_3 N + HBr$$

dimethyl amine

trimethyl amine

$$(CH_3)_3 N + CH_3 - Br \xrightarrow{\Delta} (CH_3)_4 N^+ Br^-$$

trimethyl amine

tetramethyl ammonium bromide

(quaternary ammonium salt)

The order of reactivity of alkyl halides with ammonia is R - I > R - Br > R - CI.

Question xi.

Write reaction to convert ethylamine into methylamine.

Answer

4. Answer the following.

Question i.

Write the IUPAC names of the following amines:

b.
$$CH_3$$
- C - CH_2 - CH_2 - CH_2 - CH_3

Answer:

Compound	IUPAC name	
(1) CH ₃ - CH ₂ - N - CH ₂ - CH ₂ - CH ₃ CH ₃	N-Ethyl, N-methyl propan-1-amine	
CH ₃		
(2) $CH_3 - C - CH_2 - CH_2 - NH_2$	3, 3-Dimethylbutan-1-amine	
CH ₃		
(3) CH ₃ - CH - NH - CH ₂ - CH ₃	N-Ethyl propan-2-amine	
CH ₃		

Question ii.

What are amines? How are they classified?

Answer:

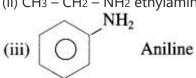
Amines are classified on the basis of the number of hydrogen atoms of ammonia that are replaced by alkyl group. Amines are classified as primary (1°), secondary (2°) and tertiary (3°).

(1) Primary amines (1° amines): The amines in which only one hydrogen atom of ammonia is replaced by an alkyl group or aryl group are called primary (1°) amines.

Examples:

(i) CH₃ – NH₂ methylamine

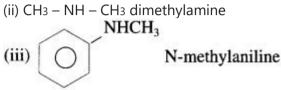
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- (ii) CH₃ CH₂ NH₂ ethylamine



(2) Secondary amines (2° amines): The amines in which two hydrogen atoms of ammonia are replaced by two, same or different alkyl or aryl groups are called secondary (2°) amines.

Examples:

- (i) C₂H₅ NH CH₃ ethylmethylamine



(3) Tertiary amines (3° amines): The amines in which all the three hydrogen atoms of ammonia are replaced by three same or different alkyl or aryl groups are called tertiary (3°) amines.

Examples:

CH₃

$$(i) CH_3 - N - CH_3 \text{ trimethylamine}$$

$$C_2H_5$$

$$(ii) C_2H_5 - N - C_2H_5 \text{ triethylamine}$$

$$(iii) C_2H_5 - N - C_2H_5 \text{ triethylamine}$$

Secondary and tertiary amines are further classified as (1) Simple or symmetrical amines (2) Mixed or unsymmetrical amines.

(i) Simple or symmetrical amines: In simple amines same alkyl groups are attached to the nitrogen e.g.

 C_2H_5 -NH- C_2H_5 Diethylamine

(ii) Mixed or unsymmetrical amines: In mixed amines different alkyl groups are attached to the nitrogen.

$$CH_3$$
 $C_2H_5-N-C_2H_5$ Diethyl methylamine

Question iii.

Write IUPAC names of the following amines.

a. H,N-(CH,),-NH,

b.
$$OCH_3$$
 CH₃ CH₃ OCH_3 C. OCH_3

Answer:

Compound	IUPAC name	
(1) $H_2N - (CH_2)_6 - NH_2$	Hexan-1, 6-diamine	
(2) CH ₃	2, 4-Dimethylaniline	
CH ₃		
(3) NH ₂	Benzene-1, 4-diamine	
NH ₂		

Question iv.

Write reactions to prepare ethanamine from

- a. Acetonitrile
- b. Nitroethane
- c. Propionamide

Answer:

a. Ethanamine from acetonitrile:

$$CH_3 - C \equiv N + 4 [H] \xrightarrow{Na/C_2H_5OH} CH_3 - CH_2 - NH_2$$

Acetonitrile

b. Ethanamine from nitroethane :
$$CH_3 - CH_2 - NO_2 + 6[H] \xrightarrow{Sn/conc. \ HCl} CH_3 - CH_2 - NH_2 + 2H_2O$$
Nitroethane

Ethanamine

Nitroethane

c. Ethanamine from Propionamide:

$$CH_3 - CH_2 - C - NH_2 + Br_2 + 4KOH \longrightarrow CH_3 - CH_2 - NH_2 + K_2CO_3 + 2KBr + 2H_2O.$$

Propionamide

What is the action of acetic anhydride on ethylamine, diethylamine and triethylamine?

Answer:

Acetylation of amines : The reaction in which the H atom attached to nitrogen in amine is replaced by acetyl group $(CH_3 - \ddot{C} -)$ is called acetylation of amines.

(1) Ethylamine on reaction with acetic anhydride forms monoacetyl derivative, N-acetylethylamine.

CH₃ - C - O - C - CH₃ + C₂H₅ -
$$\stackrel{..}{N}$$
H₂ $\xrightarrow{Pyridine}$ CH₃ - C - $\stackrel{..}{N}$ $\stackrel{..}{<}$ CH₃ - C - $\stackrel{..}{N}$ $\stackrel{..}{<}$ CH₃ - C - $\stackrel{..}{N}$ $\stackrel{..}{<}$ CH₃ - C $\stackrel{..}{>}$ OH

Acetic anhydride

Ethyl amine

N-Acetylethylamine

(2) Diethylamine (a secondary amine) on reaction with acetic anhydride forms a monoacetyl derivative, N-acetyldiethyl amine (or N,Ndiethyl acetamide).

$$CH_{3} - C - O - C - CH_{3} + \frac{C_{2}H_{5}}{C_{2}H_{5}} \stackrel{\text{"`}}{\stackrel{\text{N}}{=}} H \xrightarrow{\text{Pyridine}} CH_{3} - C - \stackrel{\text{"}}{\stackrel{\text{N}}{=}} \frac{C_{2}H_{5}}{C_{2}H_{5}} + CH_{3} - C \stackrel{\text{O}}{\stackrel{\text{O}}{=}} O$$

Acetic anhydride

Diethyl amine

N-Acetyldiethylamine

Acetic acid

(N, N-diethyl acetamide)

(3) Triethylamine does not react with acetic anhydride as it does not have any H atom attached nitrogen atom of amin e

 $(C_2H_5)_3 \stackrel{..}{N} + (CH_3CO)_2 \stackrel{Pyridine}{\longrightarrow} No reaction$

Question vii.

Distinguish between ethylamine, diethylamine and triethylamine by using Hinsberg's reagent?

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Answer:

This reaction is useful for the distinction of primary, secondary and tertiary amines.

(i) Primary amine (like ethyl amine) is treated with Hinsberg's reagent (benzene sulphonyl chloride) forms N-alkyl benzene sulphonamide which dissolve in aqueous KOH solution to form a clear solution of potassium salt and upon acidification gives insoluble N-alkyl benzene sulphonamide.

$$-KC1$$
 $+KC1$
 $-SO_2NHC_2H_5$

N-ethyl benzene sulphonamide

(ii) Secondary amine like diethyl amine is treated with benzene sulphonyl chloride forms N,N-diethyl benzene which sulphonyl amide remains insoluble in aqueous KOH and does not dissolve in acid.

(iii) Tertiary amine like triethyl amine does not react with benzene sulphonyl chloride and remains insoluble in KOH, however it dissolves in dil. HCl to give a clear solution due to formation of ammonium salt.

$$-SO_2C1 + (C_2H_5)_3N \longrightarrow No reaction (insoluble in KOH)$$

$$+C1$$

$$+C2$$

$$+C3$$

$$+C1$$

$$+C1$$

Triethyl ammonium chloride

Question viii.

Write reactions to bring about the following conversions:

- a. Aniline into p-nitroaniline
- b. Aniline into sulphanilic acid?

Answer:

(1) Aniline into p-nitroaniline

(2) Aniline into sulphanilic acid.

Activity:

- Prepare a chart of azodyes, colours and its application.
- Prepare a list of names and structures of N-containing ingredients of diet.

12th Chemistry Digest Chapter 13 Amines Intext Questions and Answers

Use your brain power! (Textbook Page No 282)

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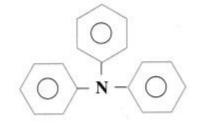
Question 1.

Classify the following amines as simple/mixed; 1°, 2°, 3° and aliphatic or aromatic. (C2H5)2NH, (CH3)3N, C2H5 – NH – CH3,

$$(C_2H_5)_2NH$$
, $(CH_3)_3N$, $C_2H_5 - NH - CH_3$,
 $NH - C_6H_5$

$$CH_3$$
 $C_6H_5 - NH_2$, $CH_3 - CH - NH_2$,

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Answer:

Compound	Simple/mixed	Туре	Aliphatic/Aromatic amine
(1) (C ₂ H ₅) ₂ NH	Simple	Secondary (2°) amine	Aliphatic
(2) (CH ₃) ₃ N	Mixed	Tertiary (3°) amine	Aliphatic
(3) $C_2H_5 - NH - CH_3$	Mixed	Secondary (2°) amine	Aliphatic
(4) $C_6H_5 - NH_2$	Simple	Primary (1°) amine	Aromatic
(5) CH ₃ - CH - CH ₃	Simple	Primary (1°) amine	Aliphatic
$(6) \bigcirc NH - C_6H_5$	Simple	Secondary (2°) amine	Aromatic
CH ₃ (7) CH ₃ - C - NH ₂ CH ₃	Mixed	Primary (1°) amine	Aliphatic
(8) N (CH ₃) ₂	Mixed	Tertiary (3°) amine	Aromatic
(9) O N O	Mixed	Tertiary (3°) amine	Aromatic

(A) Common Names: Rules

- 1. According to common naming system, the amines are named as alkylamines.
- 2. The common name of a primary amine is obtained by writing the name of the alkyl group followed by the word 'amine'. Example: CH₃ NH₂: methyl-amine
- 3. The simple (symmetrical) secondary and tertiary amines are written by adding prefix 'di- (forpresence of two alkyl groups) and 'tri'- (for presence of three alkyl groups) respectively to the name of alkyl groups.

 Examples: (i) CH₃ NH CH₃ dimethylamine, (ii) (C₂H₅)₃ N triethylamine
- 4. The mixed (or unsymmetrical) secondary and tertiary amines are given names by writing the names of alkyl groups in alphabetical order, followed by the word 'amine'.

 Example: CH₃ CH₂ NH CH₃ ethyhnethylamine

(B) IUPAC names: Rules

- 1. According to IUPAC system of nomenclature of amines, aliphatic amines are named as alkanarnines.
- 2. The name of the amine is obtained by replacing the suffix 'e' from parent alkane's name by 'amine'.
- 3. The position of the amino group is indicated by the lowest possible locant. Example:

$$\overset{4}{C}H_3 - \overset{3}{C}H_2 - \overset{2}{C}H - NH_2$$
 Butan-2-amine $\overset{1}{C}H_3$

- 4. In case of secondary and tertiary amines, the largest alkyl group is considered to be the parent alkane and other alkyl groups are written as N-substituents.
 - Example : CIH5NH CH3 N Methylethanamine
- 5. A complete name of amine is written as one word.

Try this.... (Textbook Page No 283)

Question 1.

Draw possible structures of all the isomers of C4H11N. Write their common as well as IUPAC names.

Answer:

Compound	Common name	IUPAC name	Primary/Secondary/ Tertiary amines
(1) CH ₃ -CH ₂ -CH ₂ -CH ₂ -NH ₂	1-Aminobutane	Butan-1-amine	Primary
(2) CH ₃ -CH ₂ -CH-CH ₃	2-Aminobutane	Butan-2-amine	Primary
(3) CH ₃ -CH-CH ₂ -NH ₂ CH ₃	1-Amino-2-methyl propane	2-Methyl propan-1-amine	Primary
CH ₃ (4) CH ₃ -C-NH ₂ CH ₃	2-Amino-2-methyl propane	2-Methylpropan-2-amine	Primary
(5) CH ₃ -CH ₂ -CH ₂ -NH-CH ₃	N-Methylaminopropane	N-Methylpropan-1-amine	Secondary
(6) CH ₃ CHNHCH ₃	N-Methyl-2-aminopropane	N-Methylethanamine	Secondary
(7) CH ₃ CH ₂ NHC ₂ H ₅	N-Ethyl aminoethane	N-Ethylethanamine	Secondary
(8) CH ₃ CH ₂ N CH ₃	N, N-Dimethylaminoethane	N,N-Dimethylethanamine	Tertiary

Use your brain power! (Textbook Page No 283)

Question 1.

Write chemical equations for

(i) reaction of alc. NH with C₂H₅I.

Answer:

(1)
$$CH_3 - CH_2 - I + NH_3 \xrightarrow{\Delta} CH_3 - CH_2 - NH_2 + HI$$

ethyl bromide (alc.) ethylamine

(2)
$$CH_3 - CH_2 - NH_2 + CH_3 - CH_2 - I \xrightarrow{\Delta} (CH_3 - CH_2 -)_2 NH + HI$$

ethylamine diethylamine

(3)
$$(CH_3 - CH_2)_2NH + CH_3 - CH_2 - I \xrightarrow{\Delta} (C_2H_5)_3N + HI$$

diethylamine triethylamine

(4)
$$(CH_3 - CH_2)_3N + CH_3 - CH_2 - I \xrightarrow{\Delta} (CH_3 - CH_2)_4N\overline{I}$$

triethyl amine tetraethylammonium iodide (quaternary ammonium salt)

(ii) Amonolysis of benzyl chloride followed by the reaction with 2 moles of CH3I. Answer:

(2) Ammonolysis of alkyl halides is not suitable method to prepare primary amines. Answer:

- Arjun
- Digvijay

In the laboratory, ammonolysis of alkyl halides is not a suitable method to prepare primary amines as it gives a mixture of primary, secondary, tertiary amines and quaternary ammonium salts. (Refer to the reaction in answer to Question 16). The separation of primary amine becomes difficult.

Problem 13.1: (Textbook Page No 285)

Question 1.

Write reaction to convert methyl bromide into ethyl amine? Also, comment on the number of carbon atoms in the starting compound and the product.

Solution:

Methyl bromide can be converted into ethyl amine in two stage reaction sequence as shown below.

$$CH_3 - Br + KCN \longrightarrow CH_3 - CN + KBr$$

$$CH_3 - CN \xrightarrow{Na/C_2H_5OH} CH_3 - CH_2 - NH_2$$

The starting compound methyl bromide contains one carbon atom while the product ethylamine contains two carbon atoms. A reaction in which number of carbons increases involves a step up reaction. The overall conversion of methyl bromide into ethyl amine is a step up conversion.

Use your brain power! (Textbook Page No 285)

Identify 'A' and 'B' in the following conversions.

(1)
$$CH_3 - I \xrightarrow{KCN} A \xrightarrow{Na/C_2H_5OH} B$$
 (2) $CH_3 - Br \xrightarrow{AgNO_2} A \xrightarrow{Sn/HCl} B$

(2)
$$CH_3 - Br \xrightarrow{AgNO_2} A \xrightarrow{Sn/HCl} B$$

(3)
$$C_2H_5 - I \xrightarrow{AgCN} A \xrightarrow{Na/C_2H_5OH} B$$

(1)
$$CH_3 - I \xrightarrow{KCN} CH_3CN \xrightarrow{Na/C_2H_5OH} CH_3 - CH_2 - NH_2$$
Acetonitrile
(A) Respectively.

$$A = CH_3CN$$

$$B = CH_3 - CH_2 - NH_2$$

(2)
$$CH_3 - Br \xrightarrow{AgNO_2} CH_3 - NO_2 \xrightarrow{Sn/HCl} CH_3 - NH_2 + 2H_2O$$
(A) (B)

$$A = CH_3 - NO_2$$

$$nitromethane$$

$$B = CH_3 - NH_2$$

$$methyl amine$$

Use your brain power! (Textbook Page No 286)

Question 1.

Write the chemical equations for the following conversions:

- (1) Methyl chloride to ethylamine.
- (2) Benzamide to aniline.
- (3) 1, 4-Dichlorobutane to hexane-1, 6-diamine.
- (4) Benzamide to benzylamine.

Answer:

(1) Methyl chloride to ethylamine

$$CH_3 - Cl + KCN \xrightarrow{alc.} CH_3 - CN + KCl$$

$$\text{CH}_5\text{CN} + 4(\text{H}) \xrightarrow{\text{Na/C}_2\text{H}_5\text{OH}} \text{CH}_3 - \text{CH}_2 - \text{NH}_2$$

Methyl chloride

(2) Benzamide to aniline

- Arjun
- Digvijay

CONH₂

$$+ Br_2 + 4KOH \xrightarrow{\Delta} + K_2CO_3 + 2KBr + 2H_2O$$

(3) 1, 4-Dichlorobutane to hexane-1, 6-diamine

Adiponitrile

$$\begin{array}{c} \operatorname{CH_2} - \operatorname{CH_2} - \operatorname{CH_2} - \operatorname{CH_2} - \operatorname{CH_2} - \operatorname{CH_2} \\ | \\ \operatorname{NH_2} \\ \text{Hexamethylene diamine} \end{array}$$

(4) Benzamide to benzylamine

CONH₂

$$+ 4 [H] \xrightarrow{\text{LiAlH}_4/\text{ether}} + H_2O$$
Benzamide
$$+ 4 [H] \xrightarrow{\text{benzyl amine}} + H_2O$$

Use your brain power! (Textbook Page No 287)

Question 1.

Arrange the following:

- (1) In decreasing order of the boiling point C₂H₅ OH, C₂H₅ NH₂, (CH₃)₂ NH
- (2) In increasing order of solubility in water: C₂H₅ NH₂, C₃H₇ NH₂, C₆H₅ NH₂ Answer:
- (1) Decreasing order of the boiling point: C2H5 OH, C2H5 NH2, (CH3)2 NH
- (2) Increasing order of solubility in water: C6H5NH2, C3H7 NH2, C2H5 NH2

Use your brain power! (Textbook Page No 288)

Question 1.

Refer to pKb values and answer which compound from the following pairs is the stronger base?

- (1) CH₃ NH₂ and (CH₃)₂ NH
- (2) (C₂H₅)₂ NH and (C₂H₅)₃ N
- (3) NH₃ and (CH₃)₂ CH NH₂

Answer:

- (1) CH₃ -NH₂ and (CH₃)₂ NH
- (CH₃)₂ NH is a stronger base

(2) $(C_2H_5)_2$ NH and $(C_2H_5)_3$ N $(C_2H_5)_2$ NH is a stronger base

(3) NH₃ and (CH₃)₂ CHNH₂ (CH₃)₂ CHNH₂ is a stronger base

Use your brain power! (Textbook Page No 290)

Question 1.

Arrange the following amines in decreasing order of their basic strength:

NH₃, CH₃ – NH₂, (CH₃)₂ NH, C₆H₅NH₂

Answer:

Decreasing order of basic strength:

(CH₃)₂NH, CH₃ -NH₂, NH₃, C₆H₅NH₂

Use your brain power! (Textbook Page No 291)

- Arjun

- Digvijay

Question 1.

$$(1) C2H5 - NH2 + C2H5 - I \xrightarrow{\Delta} ?$$

(2)
$$(C_2H_5)_2NH + CH_3 - I \xrightarrow{\Delta} ?$$
excess

(3)
$$C_6H_5 - NH_2 + CH_3 - I \xrightarrow{\Delta}$$
?

Answer:

(1)
$$C_2H_5NH_2 + C_2H_5I \xrightarrow{\Delta} C_2H_5 - NH - C_2H_5 + C_2H_5 - I \xrightarrow{\Delta} C_2H_5 - N + C_2H_5I \xrightarrow{\Delta} (C_2H_5)_4N^+I^-$$
Ethyl amine excess Diethyl amine C_2H_5 Die

(2)
$$(C_2H_5)_2$$
 NH + CH₃I $\xrightarrow{\Delta}$ C_2H_5 - N - CH₃ + CH₃ - I \longrightarrow
$$\begin{bmatrix} C_2H_5 \\ C_2H_5 \\ C_2H_5 - N - CH_3 \end{bmatrix}^+$$
 IDiethyl amine

Diethyl amine

Diethylmethyl amine (tert. amine)

Diethyl dimethyl ammonium iodide

(3)
$$C_6H_5 - NH_2 + CH_3 - I \xrightarrow{\Delta}_{-HI} C_6H_5 - NH - CH_3 + CH_3I \xrightarrow{\Delta}_{-HI} C_6H_5 - N < CH_3 \xrightarrow{\Delta}_{-HI} CH_3I \xrightarrow{CH_3} \begin{bmatrix} CH_3 & \Delta & -HI \\ CH_3 & CH_3I & CH_3I \\ CH_3 & CH_3I & CH_3I \end{bmatrix} = \begin{bmatrix} CH_3 & \Delta & -HI \\ CH_3 & CH_3I & CH_3I \\ CH_3 & CH_$$

Use your brain power! (Textbook Page No 291)

Question 1.

Complete the following reaction:

$$CH_3 - CH_2 - \stackrel{+}{N}(CH_3)_3 I \stackrel{-}{\longrightarrow} \stackrel{Moist}{\longrightarrow} ? \stackrel{\Delta}{\longrightarrow}$$

Answer:

$$\begin{bmatrix} CH_{3} \\ | & \alpha & \beta \\ CH_{3}-N^{+}-CH_{2}CH_{3} \\ | & CH_{3} \end{bmatrix}I^{-} + AgOH \xrightarrow{Ag_{2}O/H_{2}O} \begin{bmatrix} CH_{3} \\ | & \alpha & \beta \\ CH_{3}-N^{+}-CH_{2}-CH_{3} \\ | & CH_{3} \end{bmatrix}OH^{-} + AgI$$

Ethyltrimethyl ammonium iodide

Ethyltrimethyl ammonium hydroxide

$$\begin{bmatrix}
CH_3 & \beta \\
CH_3 - N^+ - CH_2 - CH_2 \\
CH_3 & H
\end{bmatrix}
OH^- \xrightarrow{\Delta} CH_2 = CH_2 + (CH_3)_3N + H_2O$$
Ethylene trimethyl amine

Use your brain power! (Textbook Page No 292)

(1)
$$CH_3 - NH_2 + Ph - CO - Cl \longrightarrow ?$$

(2)
$$(CH_3)_3N + Ph - CO - Cl \longrightarrow ?$$

Answer:

(1)
$$CH_1 - NH_2 + Ph - CO - Cl \rightarrow$$

(1)
$$CH_3 - NH_2 + Ph - CO - Cl \longrightarrow$$

O

 $CH_3 - NH_2 + Cl - C - Ph \xrightarrow{Pyridine} CH_3 - NH - C - ph$

N-methyl benzamide

(2)
$$(CH_3)_3N + Ph - CO - Cl \longrightarrow$$

 $(CH_3)_3N + Ph - CO - Cl \longrightarrow No reaction$

Use your brain power! (Textbook Page No 292)

- Arjun
- Digvijay

Question 1.

Write the carbylamine reaction by using aniline as starting material.

$$C_6H_5-NH_2+CHCl_3+3KOH \xrightarrow{\Delta} C_6H_5NC+3HCl+3H_2O$$
Aniline (alc.) Phenyl isocyanide

Aniline

Phenyl isocyanide

Can you tell? (Textbook Page No 292)

- (1) What is the formula of nitrous acid?
- (2) Can nitrous acid be stored in bottle?

Answer:

- (1) Formula of nitrous acid : H O N = O
- (2) Nitrous acid cannot be stored in bottle.

Use your brain power! (Textbook Page No 294)

Question 1.

How will you distinguish between methyl amine, dimethylamine and trimethylamine by Hinsberg's test?

(1) Methyl amine (primary amine) reacts with benzene sulphonyl chloride to form N-methylbenzene sulphona- mide

(2) Dimethyl amine reacts with benzene sulphonyl chloride to give N, N – dimethylbenzene sulphonamide.

$$\begin{array}{c|c} O & O \\ \parallel & S - Cl + H - N - CH_3 \\ O & CH_3 \\ \hline O & CH_3 \\$$

(3) Trimethyl amine does not react with benzene sulphonyl chloride and remains insoluble in KOH

O
$$S - Cl + (CH_3)_3N$$
No reaction
(insoluble in KOH)

Problem 13.1: (Textbook Page No 295)

Question 1.

Write the scheme for preparation of p-bromoaniline from aniline. Justify your answer.

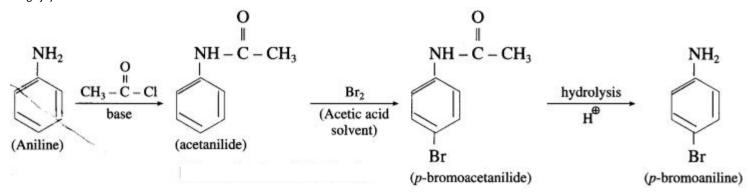
NH₂ – group in aniline is highly ring activating and o - /p – directing due to involvement of the lone pair of electrons on 'N' in resonance with the ring. As a result, on reaction with Br2 it gives 2,4,6-tribromoaniline. To get a monobromo product, it is necessary to decrease the ring activating effect of – NH2 group. This is done by acetylation of aniline. The lone pair of 'N' in acetanilide is also involved in resonance in the acetyl group. To that extent, ring activation decreases.

$$\begin{array}{c}
O \\
NH = C - CH_3
\end{array}$$

$$\begin{array}{c}
O \\
NH = C - CH_3
\end{array}$$

Hence, acetanilide on bromination gives a monobromo product p-bromoacetanilide. After monobromination the original – NH2 group is regenerated. The protection of – NH2 group in the form of acetyl group is removed by acid catalyzed hydrolysis to get p-bromoaniline, as shown in the following scheme.

- Arjun
- Digvijay



Use your brain power! (Textbook Page No 296)

Question 1.

- (1) Can aniline react with a Lewis acid?
- (2) Why aniline does not undergo Frledel Craft's reaction using aluminium chloride? Answer:
- (1) Aniline reacts with a Lewis acid, forms salt.
- (2) Aniline does not undergo Friedcl-Crafr's reaction (alkylation and acetylation) due to salt formation with aluminium chloride (Lewis acid), which is used as catalyst. Due to this, nitrogen of anime acquires + ve charge and hence acts as strong deactivating effect on the ring and makes it difficult for electrophilic attack.

Can you tell? (Textbook Page No 294)

- (1) Do tertiary amines have 'H' bonded to 'N?
- (2) Why do tertiary amines not react with benzene sulfonyl chloride? Answer:



- (1) Tertiary amines
- \mathbf{R} do not have 'H' bonded to 'N'.
- (2) Tertiary amine does not undergo reaction with benzene sulphonyl chloride as it does not have any H atom attached to nitrogen atom of amine.