# Organic Compounds Containing Nitrogen MLL Questions and Answers

#### 1 Mark Questions

- 1) Write the structure of N-Methylethanamine.
- 2) Write the structure of Prop-2-en-1-amine
- 3) Why do amines behave as nucleophiles?
- 4) Why is an alkylamine more basic than ammonia?
- 5) Arrange the following compounds in increasing order of basic strength in their aqueous solutions:NH<sub>3</sub>, CH<sub>3</sub>NH<sub>2</sub>, (CH<sub>3</sub>)<sub>3</sub>NH, (CH<sub>3</sub>)<sub>2</sub>NH.
- 6) Why is aniline soluble in aqueous HCI?
- 7) What is the role of pyridine in the acylation reaction of amines?
- 8) Why is benzene diazoniumchloridenot stored and is used immediately after its preparation?
- 9) Arrange the following in the increasing order of their solubility in water: C6H5NH2, (C2H5)2NH, C2H5NH2.
- 10) Arrange the following compounds in increasing order of basic strength:  $C_6H_5NH_2$ ,  $C_6H_5N(CH_3)_2$ ,  $(C_6H_5)_2NH$ ,  $C_8H_3NH_2$
- 11) Give the IUPAC name of H<sub>2</sub>N-CH<sub>2</sub>-CH<sub>2</sub>-CH=CH2
- 12) Name one reagent used for the separation of primary, secondary & tertiary amine

#### **Answers of 1 Mark Questions**

- 1) CH<sub>3</sub>NHCH<sub>2</sub>CH<sub>3</sub>
- 2) H<sub>2</sub>NCH<sub>2</sub>CH=CH<sub>2</sub>
- 3) Due to the presence of lone pair of electrons on N atom
- 4) Due to +I effect of alkyl group which increases the electron density on N atom.
- 5) NH<sub>3</sub><(CH<sub>3</sub>)<sub>3</sub>NH<CH<sub>3</sub>NH<sub>2</sub><(CH<sub>3</sub>)<sub>2</sub>NH
- 6) Because of the formation of anilinium ion which is soluble in water.
- 7) To remove the side product, i.e., HCl from the reaction mixture.
- 8) Because it is unstable in nature.
- 9)  $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$  (Hydrogen bonding)
- 10)(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NH<C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub><C<sub>6</sub>H<sub>5</sub>N(CH<sub>3</sub>)<sub>2</sub><CH<sub>3</sub>NH<sub>2</sub>( +I effect of alkyl group and –I effect of Phenyl)
- 11)But-3-en-1-amine
- 12) Hinsberg reagent (benzene sulphonylchloride)

#### .<u>2 Marks Questions</u>

- 1) Give the chemical tests to distinguish between the following pairs of compounds:
  - i) Ethylamine and Aniline
  - ii) Aniline and Benzylamine
- IdentifyA and B in each of the following:
  - i)  $CH_3CH_2CI \xrightarrow{NaCN} A \xrightarrow{Ni/H_2} B$

- $C_6H_5NH_2^{NaNO}/HCI$  A  $C_6H_5NH_2/OH_5$  B ii)
- 3) Give the chemical tests to distinguish between the following pairs of compounds:
- Methylamine and Dimethylamine
- Aniline and N-Methylaniline ii)
- 4) Describe the following giving the relevant chemical equation in each case:
  - Carbylamine reaction i)
  - ii) Hoffmann's bromamide reaction
- 5) Illustrate the following reactions giving equation in each case:
  - Gabriel phthalimide synthesis
  - Coupling reaction ii)
- 6) Complete the following:
  - $C_6H_5N_2^+CI^-+CH_3CH_2OH$ RCONH2  $\xrightarrow{\text{LiAIH }/\text{H }O}$ i)
  - ii)
- 7) In the following cases rearrange the compounds as directed:
  - In decreasing order of basic strength: Aniline, p-nitroaniline, p-toluidine
  - ii) In increasing order of pK<sub>b</sub> values:  $C_6H_5NH_2$ ,  $C_6H_5NHCH_3$ ,  $(C_6H_5)_2NH$ ,  $C_2H_5NH_2$ ,  $(C_2H_5)_2NH$
- 8) Explain by chemical equations:
  - Gattermann reaction
  - Sandmeyer reaction
- 9) Show the mechanism of acylation of ethylamine and write the IUPAC name of the product formed.

# **Answers of 2 Marks Questions**

1) i) These can be distinguished by azodye test.

Aniline forms azo dye while ethylamine does not form dye.

p-Hydroxyazobenzene

(Orange dye) chloride  $CH_3CH_2 - NH_2 + HONO \xrightarrow{0.5^{\circ}C} C_2H_5OH + N_2 T + H_2O$ 

ii)These can be distinguished by azodye test.

Phenol

Benzenediazonium

Aniline forms azo dye while benzylamine does not form dye

Benzenediazonium chloride

$$N = NCI + H$$
 $N = NCI + H$ 
 $N = N + CI + H$ 
 $N$ 

3) i) These can be distinguished by carbylamine test. Methylamine gives this test where as Dimethylamine does not.

(yellow dye)

 $CH_3NHCH_3 + CHCl_3 + 3KOH \xrightarrow{\Delta} No reaction$ Dimethylamine

ii)These can be distinguished by carbylamine test.

Aniline gives this test where as N-Methylaniline does not.

$$C_6H_5 - NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} C_6H_5 - NC + 3KCl + 3H_2O$$
AnIllne (1°) isocyanide (foul smell)

$$C_6H_5NHCH_3 + CHCl_3 + 3KOH \xrightarrow{\Delta} No reaction$$

N-Methylaniline

4i)Carbylamine Reaction:Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines, having unpleasant smell.

$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} R-NC + 3KCl + 3H_2O$$

ii)Hoffmann Bromamide Reaction:This is a method for preparation of primary amines bytreating an amide with bromine in an aqueous or ethanolicsolutionofsodium hydroxide.

$$R - C - NH_2 + Br_2 + 4NaOH \longrightarrow R - NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

5)i)Gabriel Phtahlimide Reaction: This method is used for the preparation of primary amines from phthalimide.

#### ii)) Coupling Reaction:

The reaction of joining two aromatic rings through –N=N- is known as coupling reaction. Arenediazonium salts react with phenols or aromatic amines to form colouredazo compounds.

- 6) i)  $C_6H_6 + N_2 + CH_3CHO + HCI$
- ii) R-CH2NH2
- 7) i) p-toluidine, Aniline , p-nitroaniline
  - ii)  $(C_2H_5)_2NH_1C_2H_5NH_2$ ,  $C_6H_5NHCH_3$ ,  $C_6H_5NH_2$ ,  $(C_6H_5)_2NH_2$

## 8) i) Gatterman reaction:

In this reaction, chlorine or bromine or cyanide can also be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder.

$$ArN_{2}^{+}X \xrightarrow{Cu/HCl} ArCl + N_{2} + CuX$$

$$Cu/HBr ArBr + N_{2} + CuX$$

# ii) Sandmeyer reaction:

In this reaction, chlorine or bromine or cyanide can also be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper(I) ion.

$$ArN_{2}^{+}X \xrightarrow{Cu_{2}Cl_{2}/HCl} ArCl + N_{2}$$

$$Cu_{2}Br_{2}/HBr \rightarrow ArBr + N_{2}$$

$$CuCN /KCN \rightarrow ArCN + N_{2}$$

9)

$$C_{2}H_{5}\overset{\overset{\longleftarrow}{\stackrel{\longleftarrow}}H}\overset{\overset{\longleftarrow}{\stackrel{\longleftarrow}}CH_{3}}{\overset{\longleftarrow}{\stackrel{\longleftarrow}}C} C_{2}H_{5}\overset{\overset{\longleftarrow}{\stackrel{\longleftarrow}}H}\overset{\overset{\longleftarrow}{\stackrel{\longleftarrow}}CH_{3}}{\overset{\longleftarrow}{\stackrel{\longleftarrow}}C} C_{2}H_{5}\overset{\longleftarrow}{\overset{\longleftarrow}}C C_{2}H_{5}\overset{\longleftarrow}{\stackrel{\longleftarrow}}C C_{2}H_{5}\overset{\longleftarrow}{\stackrel}C C_{2}\overset{\longleftarrow}{\stackrel}C C_{2}\overset{\longleftarrow}{\stackrel}{\stackrel}{\stackrel}C C_{2}\overset{\longleftarrow}{\stackrel}C C_{2}\overset{\longleftarrow}{\stackrel}C$$

## Ethanamine

# N-Ethylethanamide

## 3 Marks Questions

- 1) Complete the following reactions:
  - $CH_3CH_2NH_2 + CHCI_3 + alc. KOH$   $C_6H_5N_2^+CI^- \xrightarrow{P O(Room\ Temp.)}$ i)
  - ii)
  - $C_6H_5NH_2 + HCI (aq)$
- 2) Write the main products of the following reactions:
  - $C_6H_5N_2^+CI^$ i)
  - ii)  $C_6H_5NH_2 + Br_2$  (aq)
  - CH<sub>3</sub>CONH<sub>2</sub> Br + NaOH
- 3) Write the main products of the following reactions:
  - CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>
  - C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> + CH<sub>3</sub>COCI ii)
  - iii)  $CH_3CH_2NH_2 + C_6H_5SO_2CI$
- 4) Account for the following:
  - (i) p $K_b$ of aniline is more than that of methylamine.
  - (ii) Ethylamine is soluble in water whereas aniline is not.
  - (iii) Aniline does not undergo Friedel -Craft's reaction.
- 5) State reasons for the following:
  - Primary amines have higher boiling points than tertiary amines. i)

- ii) Although –NH<sub>2</sub> group is an ortho and para directing group, nitration of aniline gives along with ortho and para derivatives meta-derivative also.
- iii) Aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis.
- 6) How are the following conversions carried out?
  - a) Aniline to nitrobenzene
  - b) Ethanamine to N-Ethylethanamide
  - c) Chloroethane to propan-1-amine
- 7) How are the following conversions carried out?
  - a) Nitrobenzene to benzoic acid
  - b) Benzene to m-bromophenol
  - c) Benzoic acid to aniline
- 8) Accomplish the following conversions:
  - i) Aniline to 2,4,6-tribromofluorobenzene
  - ii) Benzyl chloride to 2-phenylethanamine
  - iii) Chlorobenzene to p-chloroaniline

#### **Answers Of 3 Marks Questions**

- 1) i)  $CH_3CH_2NC + KCI + H_2O$ 
  - ii) $C_6H_5OH + N_2 + HCI$
  - iii)C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub><sup>+</sup>Cl<sup>-</sup>
- 2)  $i)C_6H_6 + N_2 + H_3PO_3 + HCI$ 
  - ii) 2,4,6-Tribromoaniline
  - iii)CH<sub>3</sub>NH<sub>2</sub> + Na<sub>2</sub>CO<sub>3</sub> + NaBr + HCl
- 3) i)CH<sub>3</sub>CH<sub>2</sub>OH + N<sub>2</sub> + H<sub>2</sub>O
  - ii)C<sub>6</sub>H<sub>5</sub>NHCOCH<sub>3</sub> + HCl
  - iii)CH<sub>3</sub>CH<sub>2</sub>NHSO<sub>2</sub>C<sub>6</sub>H<sub>5</sub> + HCl
- 4) i) In aniline, lone pair of electrons on N atom is delocalised over the benzene due to which electron density on the nitrogen decreases. On the other hand, electron density on N atom increases in case of methylamine due to +I effect of methy group. So, aniline is less basic than methylamine.and hence pKb value of aniline is more than that of methylamine.

ii)Ethylamine is soluble in water due to intermolecular hydrogen bonding which is very very less in case of aniline due to large hydrocarbon part in aniline.

Ethylamine

iii)Because aniline being lewis base reacts with AlCl<sub>3</sub>, Lewis acid to form salt. Due to this N of aniline acquires + charge and hence acts as strong deactivating group for further reaction.

- 5) i)Due to extensive intermolecular H-bonding in case of primary amines which is absent in tertiary amines
  - ii)Because nitration is carried in acidic conditions and in acidic conditions aniline gets protonated and is converted to anilinium ion which is meta directing group.

iii)Gabriel phthalimide synthesis is used for the preparation of aliphatic primary amines. It involves nucleophilicsubstitution  $(S_N2)$  of alkyl halides by the anion formed by the phthalimide. But aryl halides do not undergo nucleophilic substitution with the anion formed by the phthalimide. Hence, aromatic primary amines cannot be prepared by this process.

6) i) 
$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273-278K} C_6H_5 \stackrel{\uparrow}{N_2} \stackrel{-}{Cl} + NaCl + 2H_2O$$

ii)

Ethanamine

# N-Ethylethanamide

iii) CH<sub>3</sub>CH<sub>2</sub>CI alc. KCN CH<sub>3</sub>CH<sub>2</sub>CN H<sub>2</sub>/NiCH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>

NO2 NH2 N=NCI CN CN 
$$H_2/Pd$$
 NaNO2 + HCI  $273 - 278 \text{ K}$  Senzenediazonium Benzonitrile Benzonitrile Benzonitrile

Aniline

Benzenediazonium chloride

Benzonitrile

Benzoic ac

ii)

8) i)

m-Bromoaniline

2, 4, 6-Tribromoaniline

2, 4, 6-Tribromobenzeni diazonium chloride

2, 4, 6-Tribromof

iii)

$$\begin{array}{c|c} CI & CI \\ \hline & HNO_3/H_2SO_4 \\ \hline & (Nitration) \end{array} \qquad \begin{array}{c} CI \\ \hline & H_2/Pd \\ \hline & Ethanol \end{array}$$
 Chlorobenzene 
$$\begin{array}{c} CI \\ \hline & H_2/Pd \\ \hline & NH_2 \end{array}$$
 
$$\begin{array}{c} P\text{-Nitrochlorobenzene} \end{array} \qquad \begin{array}{c} P\text{-Chloroaniline} \end{array}$$