CHAPTER / 20

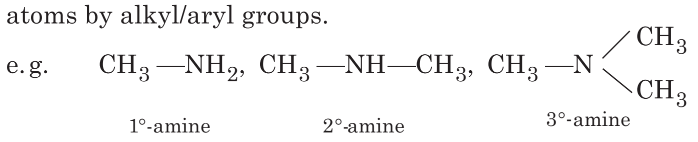
Amines

Topics Covered

Classification, Structure, Nomenclature and Preparation of Amines
- Classification of Amines
- Structure
- Nomenclature
- General Methods of Preparation

Properties and Uses of Amines
- General Properties
- Physical Properties
- Chemical Properties
- Tests
- Uses

Amines are the derivatives of ammonia, obtained by the replacement of one, two or three hydrogen atoms by alkyl/aryl groups.



e.g. $\underset{1^\circ\text{-amine}}{CH_3—NH_2}$, $\underset{2^\circ\text{-amine}}{CH_3—NH—CH_3}$, $\underset{3^\circ\text{-amine}}{CH_3—N(CH_3)_2}$

The simplest arylamine/ aromatic amine in which the —NH_2 group is directly attached to the benzene ring is called **aniline.**

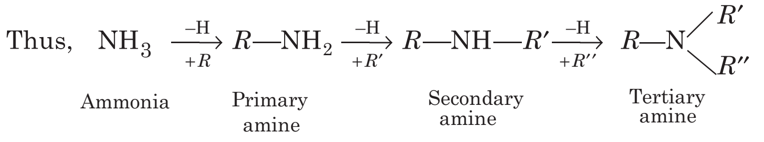
TOPIC~01 Classification, Structure, Nomenclature and Preparation of Amines

Classification of Amines

Amines are classified into following types:

1. Aliphatic Amines

Aliphatic amines are classified as primary (1°), secondary (2°) and tertiary (3°) depending upon the number of hydrogen atoms in ammonia molecule which get replaced by alkyl (R) or aryl (Ar) groups.



Thus, $$\underset{\text{Ammonia}}{NH_3} \xrightarrow[+R]{-H} \underset{\text{Primary amine}}{R—NH_2} \xrightarrow[+R']{-H} \underset{\text{Secondary amine}}{R—NH—R'} \xrightarrow[+R'']{-H} \underset{\text{Tertiary amine}}{R—N\begin{smallmatrix}R'\\R''\end{smallmatrix}}$$

2. Aryl Amines

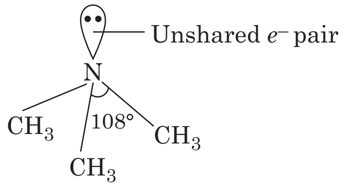
Amines in which 'N' atom is attached to the benzene ring are called aromatic amines. Here 'NH_2' group of amines is directly attached to the benzene ring. They are named as derivative of aniline or benzene amine.

Structure

Nitrogen atom of amines is trivalent and carries an unshared pair of electrons.

Like ammonia, the nitrogen atom in amines is sp^3-hybridised and the geometry of amines is pyramidal. i.e., one $2s$ and three $2p$-orbitals of N are hybridised to form four sp^3- hybridised orbitals, three of them have one electron and the fourth orbital has one lone pair of electrons. Each of the three sp^3-hybridised orbitals of nitrogen overlap with orbitals of carbon or hydrogen depending upon the composition of the amines.

Due to presence of lone pair of electrons on nitrogen, amines act as a nucleophile.



Pyramidal shape of trimethylamine

Nomenclature

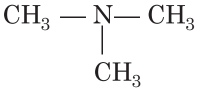
Rules and steps to be followed, while naming the amines are given below:

1. Common System

(i) In common system, an aliphatic amine is named by adding suffix 'amine' to the name of the alkyl group attached to the nitrogen atom (e.g. methylamine).

(ii) In 2° and 3° amines, when two or more groups are same, the prefix *di* or *tri* is used before the name of the alkyl group.

e.g.



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_3$$

Trimethyl amine

2. IUPAC Name

(i) In IUPAC system, amines are named as alkanamines, derived by the replacement of '*e*' of alkane by word 'amine'.

e.g. CH_3NH_2 , Methanamine

$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{N}}-CH_3$$

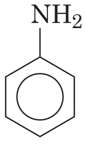
N, N- dimethylmethanamine

(ii) If more than one amino group is present at different positions, then by assigning number, their positions are specified to the carbon atoms bearing $—NH_2$ groups and the terminal 'e' of the name of the parent hydrocarbon is retained.

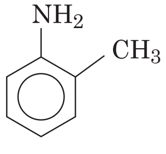
e.g. $H_2N—CH_2—CH_2—NH_2$

Ethane-1, 2- diamine

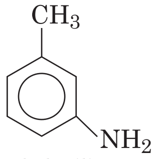
(iii) The substituted aromatic amines are named as derivatives of aniline.



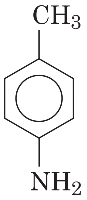
Aniline



2-methylaniline

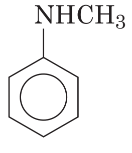


3-methylaniline

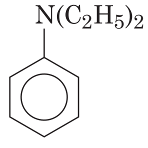


4-methylaniline

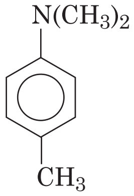
N- or C- substituted aromatic amines are named as derivatives of aniline or toluidine.



N-methyl aniline



N,N-diethyl aniline

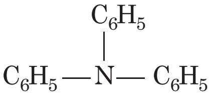


N,N-dimethyl *p*-toluidine

Diaryl and triaryl amines are named, like aliphatic amines by putting names of aryl groups directly attached to nitrogen before the word 'amine'.

$C_6H_5—NH—C_6H_5$

Diphenyl amine



$$C_6H_5-\overset{\displaystyle C_6H_5}{\overset{|}{N}}-C_6H_5$$

Triphenyl amine

General Methods of Preparation

Amines are prepared by the following methods:

(i) By the Reduction of Nitroalkanes and Nitroarenes

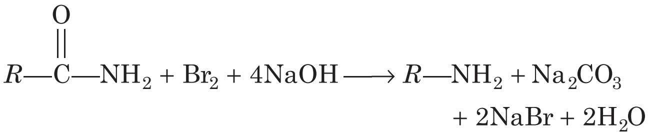
Aliphatic and aromatic primary amines can be prepared by the reduction of nitro compounds either catalytically with H_2 in the presence of Raney Ni, Pt or Pd or chemically with active metal in acidic medium.

e.g.
$$\underset{\text{Nitromethane}}{CH_3NO_2} + 3H_2 \xrightarrow[\text{Ethanol}]{\text{Raney Ni/Pt}} \underset{\text{Methylamine}}{CH_3NH_2} + 2H_2O$$

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 3H_2 \xrightarrow[\text{or Fe + HCl}]{\text{Sn + HCl}} \underset{\text{Aniline}}{C_6H_5NH_2} + H_2O$$

(ii) By Hoffmann Bromamide Degradation Reaction

This reaction is used for preparing amine containing one carbon less than the starting amide. This method was developed for preparation of primary amines by reacting an amide with Br_2 / Cl_2 in NaOH/KOH. In this reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the N-atom.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

e.g. $CH_3CH_2CONH_2 + Br_2 + 4NaOH \longrightarrow CH_3CH_2NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

(iii) By the Reduction of Alkyl or Aryl Cyanides

Reduction of nitriles with lithium aluminium hydride ($LiAlH_4$) or by sodium and alcohol (Mendius reaction) or by catalytic hydrogenation produces primary amines. This method is used to prepare amines containing one carbon atom more than the starting amine.

$$R-C\equiv N \xrightarrow[\substack{\text{or } LiAlH_4 \\ \text{or Na + alcohol}}]{\text{Raney Ni}/H_2} R-CH_2-NH_2$$

(iv) Ammonolysis of Alkyl Halides

(Hofmann's Method)

The process of cleavage of C—X bond by ammonia is called **ammonolysis**.

Alkyl or benzyl or aryl halides on reaction with alcoholic solution of ammonia in a sealed tube give **primary amines**.

$$\underset{\text{Alkyl halide}}{R-X} + \underset{\text{Ammonia}}{H-NH_2} \longrightarrow \underset{1°\text{amine}}{RNH_2} + HX$$

Primary amines react with another molecule of alkyl halide to form **secondary amine**.

$$\underset{\text{Alkyl halide}}{R-X} + \underset{\text{Ammonia}}{H\ \ HNR} \longrightarrow \underset{2°\text{amine}}{R_2NH} + HX$$

Secondary amines combine with another molecule of alkyl halide to form a **tertiary amine**, which in turn can combine with another molecule of alkyl halide to form quaternary ammonium salt.

$$RX + HNR_2 \longrightarrow \underset{3°\text{amine}}{R_3N} + HX$$

$$RX + R_3N \longrightarrow \underset{\substack{\textit{Tetra}\text{-alkyl} \\ \text{ammonium halide}}}{R_4NX}$$

(v) Ammonolysis of Alcohols and Phenols

When vapours of an alcohol and ammonia are passed over a dehydrating catalyst such as thoria or alumina at 300°C, a mixture of 1°, 2° and 3° amine is formed.

$$R-OH + H-NH_2 \xrightarrow{ThO_2} RNH_2 + H_2O;$$

$$R-OH + H-NHR \xrightarrow{300°C} R_2NH + H_2O$$

$$R-OH + H-NR_2 \longrightarrow R_3N + H_2O$$

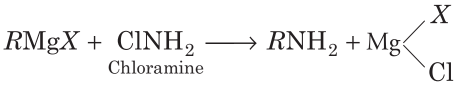
Phenols react with ammonia in the presence of zinc chloride at about 300° C to form corresponding amines.

$$Ar-OH + NH_3 \xrightarrow[300°C]{ZnCl_2} Ar-NH_2 + H_2O\,;$$

$$\underset{\text{Phenol}}{C_6H_5-OH} + NH_3 \xrightarrow[300°C]{ZnCl_2} \underset{\text{Aniline}}{C_6H_5-NH_2} + H_2O$$

(vi) From Grignard Reagent

Alkyl magnesium halides (Grignard reagent) react with chloramine to form primary amines.



$$RMgX + \underset{\text{Chloramine}}{ClNH_2} \longrightarrow RNH_2 + Mg\begin{matrix} X \\ Cl \end{matrix}$$

(vii) From Isocyanate

Acyl azides on heating produces isocyanates. When alkyl isocyanates are boiled with alkali, they undergo hydrolysis to form primary amines. This is known as **Curtius reaction.**

***Step* I** $RCOCl + NaN_3 \longrightarrow RCON_3 + NaCl$

***Step* II** $RCON_3 \xrightarrow{\text{Heat}} R-N=C=O$

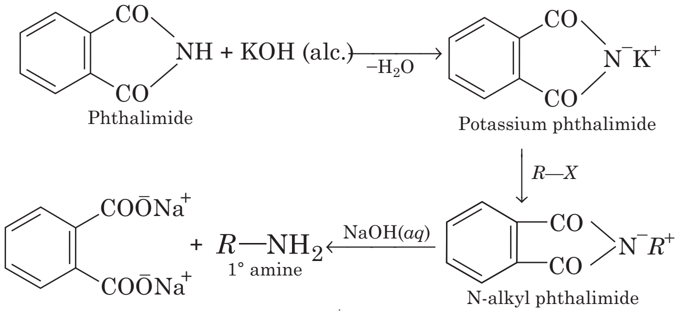
***Step* III** $R-N=C=O \xrightarrow{H_2O} RNH_2 + CO_2$

Carboxylic acids react with hydrazoic acid to form primary amines. This is called **Schmidt reaction**.

$$RCOOH + HN_3 \xrightarrow[\text{Heat}]{H_2SO_4} RNH_2 + N_2\uparrow + CO_2$$

(viii) Gabriel Phthalimide Synthesis

When a phthalimide is treated with ethanolic KOH, it forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis forms corresponding primary amines.



This method produces only primary amines without the traces of secondary or tertiary amines. So, this method is preferred for the synthesis of primary amines.

PRACTICE QUESTIONS

Exams', Textbook's Other Imp. Questions

1 MARK *Questions*

Exams' Questions

Q.1 Which product is obtained when methyl cyanide is reduced by sodium and ethyl alcohol? **[2019]**

Sol When methyl cyanide is reduced by sodium and ethyl alcohol, it gives primary amine. i.e.

$$CH_3-C\equiv N \xrightarrow{Na,\ C_2H_5OH} CH_3-CH_2-NH_2$$

Na/ethanol provides nascent H for reduction.

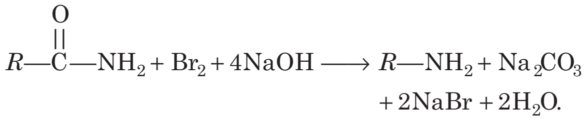
Q.2 In Hofmann-bromamide reaction an amide is converted to **[2016]**

(i) primary amine (ii) secondary amine

(iii) tertiary amine (iv) aldehyde

Sol (i) In Hofmann-bromamide reaction, an amide is converted into primary amine.

e.g.



$$R-\overset{\overset{O}{||}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O.$$

Q.3 $R-CH_2-CN$ on reduction with H_2/Ni forms .... **[2013]**

Sol RCH_2CN on reduction with H_2/Ni forms primary amines.

Reaction is given as follows:

$$RCH_2CN \xrightarrow{H_2/Ni} \underset{\text{Primary amines}}{RCH_2CH_2NH_2}$$

Q.4 .... is obtained by treating acetamide with Br_2 and excess of NaOH solution. **[2012 Instant]**

Sol Methylamine is obtained by treating with Br_2 and excess of NaOH solution. This reaction is known as Hofmann bromamide degradation reaction.

Q.5 Which product is formed when methyl isocyanide is reduced? **[2003]**

Sol Dimethylamine is formed. The reaction is given as: below: $CH_3-N\equiv C + 4H \xrightarrow{LiAlH_4} CH_3NHCH_3$

Important Questions

Q.6 Reduction of nitrobenzene by which of the following reagent gives aniline? **[Textbook]**

(a) Sn/HCl (b) $LiAlH_4$

(c) Zn/NH_4OH (d) $SnCl_2$

Sol (*a*) Reduction of nitrobenzene with Sn/HCl gives aniline. The reaction is given below:

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 3H_2 \xrightarrow{Sn/HCl} \underset{\text{Aniline}}{C_6H_5NH_2} + H_2O$$

Q.7 $C_6H_5NO_2 \xrightarrow{Sn/HCl} C_6H_5X$

In the above reaction 'X' is **[Textbook]**

(a) Cl (b) NH_2

(c) $NH_3^+Cl^-$ (d) $\overset{+}{N_2}-Cl^-$

Sol The reaction is given as:

$$C_6H_5NO_2 \xrightarrow{Sn/HCl} C_6H_5NH_2$$

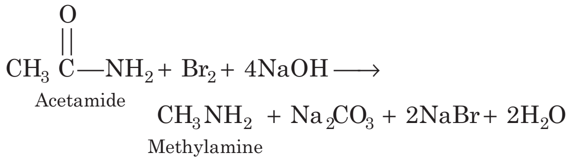
$\therefore X$ is $-NH_2$ (amine group).

Q.8 Acetamide is treated separately with the following reagent. Which of these would give methylamine? **[Textbook]**

(a) PCl_5 (b) NaOH + Br_2

(c) Soda lime (d) Hot conc. H_2SO_4

Sol (b)



$$\underset{\text{Acetamide}}{CH_3\overset{\overset{O}{||}}{C}-NH_2} + Br_2 + 4NaOH \longrightarrow \underset{\text{Methylamine}}{CH_3NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

Q.9 Which of the following reactions will not give a primary amine?

(a) $CH_3CONH_2 \xrightarrow{Br_2/KOH}$ (b) $CH_3CN \xrightarrow{LiAlH_4}$

(c) $CH_3NC \xrightarrow{LiAlH_4}$ (d) $CH_3CONH_2 \xrightarrow{LiAlH_4}$

Sol (*c*) CH_3NC gives secondary amine on reduction, and not primary amine.

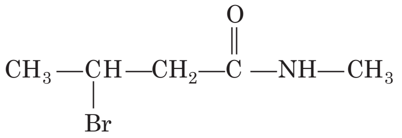
$$\underset{\text{Methyl isocyanide}}{CH_3NC} + 4H \xrightarrow{LiAlH_4} \underset{\text{Dimethyl amine}}{CH_3NHCH_3}$$

Q.10 Write the IUPAC name for $C_6H_5N(CH_3)_2$. **[Textbook]**

Sol N, N-dimethylaniline.

Q.11 Write the IUPAC name of $CH_3CH(Br)CH_2CONHCH_3$.

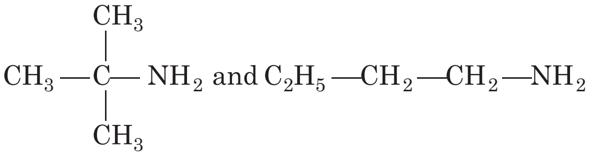
Sol



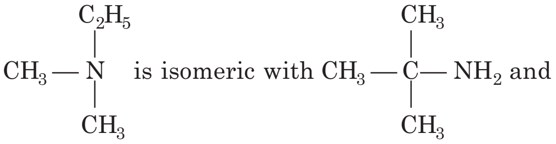
$$CH_3-\underset{\underset{Br}{|}}{CH}-CH_2-\overset{\overset{O}{||}}{C}-NH-CH_3$$

3-bromo-N-methylbutanamide

Q.12 Name a tertiary amine in IUPAC system which is isomeric with **[Textbook]**



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-NH_2 \text{ and } C_2H_5-CH_2-CH_2-NH_2$$

Sol 

$$CH_3-\overset{\overset{\displaystyle C_2H_5}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N}} \text{ is isomeric with } CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-NH_2 \text{ and}$$

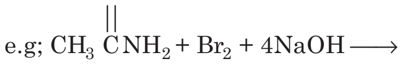
$C_2H_5CH_2CH_2NH_2$. It's IUPAC name is N,N-dimethyl ethanamine.

2 MARK *Questions*

Exams' Questions

Q.13 Explain the Hofmann bromamide reaction with one example. **[2018]**

Sol **Hoffmann bromamide reaction** Hofmann developed a method for the preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. In this degradation reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom. The amine, so formed contains one carbon less than that present in the amide.



e.g; $CH_3\overset{\overset{\displaystyle O}{||}}{C}NH_2 + Br_2 + 4NaOH \longrightarrow$

$$CH_3NH_2 + Na_2CO_3 + 2NaBr + 2H_2O \quad \textbf{(2)}$$

Q.14 How can you convert acetic acid to methyl amine? **[2008 Instant]**

Sol Conversion of acetic acid into methylamine.

$$\begin{tikzcd}[column sep=small] \underset{\text{Acetic acid}}{CH_3COOH} \arrow[r, "NH_3"] & CH_3COONH_4 \arrow[r, "\Delta"] & \underset{\text{Acetamide}}{CH_3CONH_2} \arrow[d, "Br_2/KOH"] \\ & & \underset{\text{Methylamine}}{CH_3NH_2} \end{tikzcd} \quad \textbf{(2)}$$

Q.15 What happens, when propanamide is heated with KOH and Br_2? **[2006]**

Sol Ethylamine is formed. Reaction is given as follows:

$$CH_3CH_2CONH_2 + Br_2 + 4KOH \text{ (alc).}$$
$$\xrightarrow{\Delta} CH_3CH_2NH_2 + 2KBr + K_2CO_3 + 2H_2O \quad \textbf{(2)}$$

Important Questions

Q.16 Give a method of preparation of primary amine. **[Textbook]**

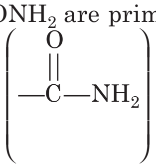
Sol Both aliphatic and aromatic primary amines can be prepared by the reduction of nitro compound. Reaction is given as below:

$$CH_3NO_2 + 3H_2 \xrightarrow[\text{Ethanol}]{\text{Raney Ni / Pt}} \underset{\text{Methyl amine}}{CH_3NH_2} + 2H_2O \quad \textbf{(2)}$$

Q.17 Name the functional group in the following compounds.

$CH_3CH_2NH_2$ and CH_3CONH_2. **[Textbook]**

Sol Functional groups are present in $CH_3CH_2NH_2$ and CH_3CONH_2 are primary amine ($-NH_2$) and acid



amide $\left(-\overset{\overset{\displaystyle O}{||}}{C}-NH_2\right)$ respectively. **(2)**

Q.18 What happens when nitromethane is reduced? **[Textbook]**

Sol Reduction of nitro compounds either catalytically with H_2 in the presence of Raney Ni, Pt or Pd or chemically with active metal in acidic medium gives primary amines (aromatic or aliphatic).

Reaction is given below:

$$\underset{\text{Nitromethane}}{CH_3NO_2} + 3H_2 \xrightarrow[\text{Ethanal}]{\text{Raney Ni / Pt}} \underset{\text{Methylamine}}{CH_3NH_2} + 2H_2O \quad \textbf{(2)}$$

Q.19 Identify A and B in the following sequence.

$$CH_3COOC_2H_5 \xrightarrow{NH_3} A \xrightarrow{Br_2/KOH} B$$

Sol $\underset{\text{Ethyl ethanoate}}{CH_3COOC_2H_5} \xrightarrow{NH_3} \underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{Br_2/KOH} \underset{\text{Methylamine}}{CH_3NH_2}$

Therefore, A and B are acetamide and methylamine respectively. **(2)**

Q.20 Why aromatic amines cannot be prepared by Gabriel phthalimide synthesis.

Sol The main step in the Gabriel phthalimide synthesis is a S_N2 reaction in which the nucleophile, phthalimide anion displaces the halide ion from alkly halides to form N-alkyl phthalimide which by subsequent acid or alkaline hydrolysis gives the corresponding aliphatic primary amine.

However, in aryl halides nucleophilic substitution reaction does not occur easily due to resonance in Ar — X. That is why, aromatic primary amines cannot be prepared by Gabriel phthalimide reaction. **(2)**

3 MARK *Questions*

Important Questions

Q.21 Complete the following equation and balance.

$$C_2H_5OH \xrightarrow{PCl_5} A \xrightarrow{KCN} B \xrightarrow{H_3O^+} C \xrightarrow{NH_3} D$$

[Textbook]

Sol

$$\begin{tikzcd}[column sep=small] C_2H_5OH \arrow[r, "PCl_5"] & \underset{\text{Ethyl chloride}}{C_2H_5Cl} \arrow[r, "KCN"] & \underset{\text{Ethane nitrile}}{C_2H_5CN} \arrow[d, "H_3O^+"] \\ \underset{\text{Ammonium salt}}{C_2H_5COO^-NH_4^+} & & \underset{\text{Propanoic acid}}{C_2H_5COOH} \arrow[ll, "NH_3"'] \end{tikzcd} \quad \textbf{(3)}$$

Q.22 How will you prepare ethylamine from

(i) methyl cyanide (ii) propanamide **[Textbook]**

Sol (i) Refer to text on page 302 (Reduction of alkyl or aryl cyanides).

(ii) Refer to text on pages 301 and 302 (By Hofmann bromamide degradation reaction). **(3)**

7 MARK *Questions*

Q.23 (i) An aromatic compound *A* on treatment with aqueous ammonia and heating forms compound *B* which on heating with Br_2 and KOH forms a compound *C* of molecular formula C_6H_7N.

Write the structures and IUPAC names of compounds *A*, *B* and *C*.

(ii) How will you synthesise amines by ammonolysis of alkyl halides?

Sol (i) As the compound *C* with molecular formula C_6H_7N is formed from compound *B* on treatment with $Br_2 + KOH$ (i.e. Hofmann bromamide reaction), compound *B* must be an amide and *C* must be an amine. The amine having the molecular formula C_6H_7N is $C_6H_5NH_2$ (aniline or benzenamine). **(2)**

(ii) Since, *C* is aniline, the amide *B* from which it is formed must be benzamide ($C_6H_5CONH_2$).

$$\underset{(B)}{\underset{\text{Benzamide}}{C_6H_5CONH_2}} \xrightarrow[\text{(Hofmann bromamide reaction)}]{Br_2/KOH} \underset{(C)}{\underset{\text{Benzenamine}}{C_6H_5NH_2}}$$

Since, compound *B* is formed from compound *A* with aqueous ammonia and heating, compound *A* must be benzoic acid, as acids on treatment with NH_3, subsequent heating form amides.

$$\underset{(A)}{\underset{\text{Benzoic acid}}{C_6H_5COOH}} \xrightarrow[\text{(ii) }\Delta]{\text{(i) Aq. }NH_3} \underset{(B)}{\underset{\text{Benzamide}}{C_6H_5CONH_2}}$$

$\therefore$ $A = C_6H_5COOH$ (Benzoic acid)

$B = C_6H_5CONH_2$ (Benzamide)

$C = C_6H_5NH_2$ (Benzenamine) **(3)**

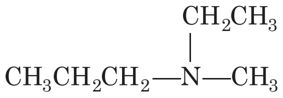
(ii) Refer to text on page 302. **(2)**

TOPIC TEST 1

1. Which of the following halide will give highest yeild in ammonolysis?

(a) Primary halides
(b) Secondary halides
(c) Tertiary halides
(d) Quaternary salts of amines

2. The IUPAC nomenclature for the following compound is



$CH_3CH_2CH_2—N(CH_2CH_3)—CH_3$

(a) ethyl methyl propylamines
(b) N-ethyl-N methyl-1-propanamine
(c) N-methyl-N-ethyl-1-propanamine
(d) None of the above

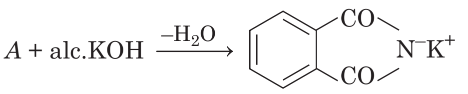
3. Gabriel phthalimide synthesis is used in the preparation of

(a) 1° amines (b) 2° amines
(c) 3° amines (d) mixture of all amines

4. When ……… are reduced by sodium and alcohol, primary amines are produced.

5. Carboxylic acids react with ……… to form primary amines

6. Give the structure of *A* in the following reaction:



7. How benzene is converted into aniline?

8. Explain any one method which is used for preparing amine containing one carbon less than the reactant?

9. Complete the following reactions:

(i) $CH_3MgBr + ClNH_2 \longrightarrow$

(ii) $CH_3—N=C=O \xrightarrow{H_2O}$

(iii) $RCOOH + NH_3 \xrightarrow[\text{Heat}]{H_2SO_4}$

10. Name the reagent used in the following reactions:

(i) $R—C\equiv N \xrightarrow{A} RCH_2NH_2$

(ii) $CH_3CH_2CONH_2 \xrightarrow{B} CH_3CH_2NH_2 + Na_2CO_3 + 2NaBr$

(iii) $C_6H_5NO_2 + 3H_2 \xrightarrow{C} C_6H_5NH_2 + 2H_2O$

TOPIC ~02 Properties and Uses of Amines

General Properties

Some of the general properties of amines are discussed below:

Basic Character of Amines

(Aliphatic and aromatic)

Amines have unshared pair of electrons over the nitrogen atom and, hence they behave as Lewis base. They readily react with mineral acids to form soluble salts.

$$R—\ddot{N}H_2 + H—X \rightleftharpoons \underset{\text{(Salt)}}{R—\overset{+}{N}H_3X^-}$$

Basic character of amines can be better understood in terms of their K_b and pK_b values as explained below:

$$R—\ddot{N}H_2 + H_2O \rightleftharpoons R—\overset{+}{N}H_3 + \overset{-}{O}H$$

$$K = \frac{[R—\overset{+}{N}H_3][\overset{-}{O}H]}{[R—NH_2][H_2O]} \text{ or } K[H_2O] = \frac{[R—\overset{+}{N}H_3][\overset{-}{O}H]}{[R—NH_2]}$$

$$K_b = \frac{[R—\overset{+}{N}H_3]\,[\overset{-}{O}H]}{[R—NH_2]}\ ;\ pK_b = -\log K_b$$

Larger the value of K_b or smaller the value of pK_b, stronger is the base.

e.g. K_b $\underset{12.0\times10^{-10}}{p\text{-toluidine}} > \underset{5\times10^{-10}}{m\text{-toluidine}} > \underset{4.2\times10^{-10}}{\text{aniline}} > \underset{2.6\times10^{-10}}{o\text{-toluidine}}$

$$pK_b\ \underset{3.27}{(CH_3)_2NH} > \underset{3.38}{CH_3NH_2} > \underset{4.22}{(CH_3)_3N}$$

Basicity of Aliphatic Amines

Aliphatic amines are stronger bases than ammonia due to $+I$ effect of alkyl group due to which electron density on nitrogen atom increases and hence they can easily donate their electrons.

- Order of basicity of amines in gaseous phase follows the expected order:

  Tertiary amine > Secondary amine > Primary amine > Ammonia

- Basicity of an amine in aqueous solution depends upon the stability of ammonium cation formed by accepting proton from water.

  The ammonium cation stability depends upon following three factors:

  (i) $+I$ effect (alkyl group)

  H-bonding with water molecules

  (ii) Steric effects (alkyl groups)

  (iii) Solvation effect

Basic Character of Aromatic Amines

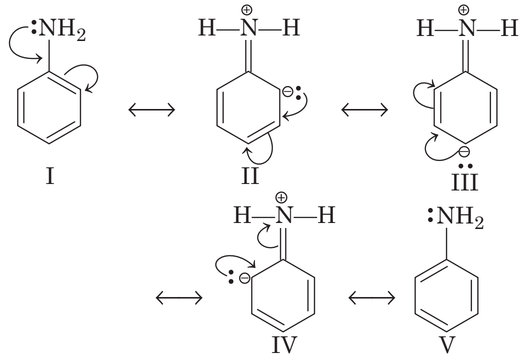
Aromatic amines are weaker bases than ammonia due to electron withdrawing nature of aryl group. pK_b value of aniline is quite high because $—NH_2$ group is directly attached to benzene ring.

Basic character of aromatic amines in comparison to aliphatic amines are discussed below:

(i) Due to resonance in aniline, lone pair of electrons gets delocalised inside the benzene ring and, thus it is less available for protonation. Therefore, aromatic amines (aniline) are weaker bases than ammonia.

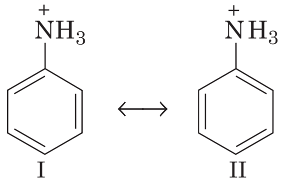
(ii) Greater the number of resonating structures, greater is the stability.

The resonating structures of aniline are as follows :



Resonating structures of aniline

(iii) In anilinium ion, there are only two resonating structures, therefore it is less stable than aniline (five resonating structures).



Resonating structures of anilinium ion

(iv) In case of substituted aniline, electron releasing groups, like $—CH_3$, $—OCH_3$, $—NH_2$ increase the basic strength and electron withdrawing groups like $—NO_2$, $—X$, $—COOH$ decrease the basic strength.

Physical Properties

Physical properties of amines are as follows :

1. Colour and Odour

Pure amines are colourless but develop colour on keeping in air or on storage due to atmospheric oxidation.

The lower aliphatic amines are gases and smell, like ammonia. Primary amines with three or more carbon atoms are liquids with fishy odours and higher ones are solid.

Aromatic amines are colourless liquids or solids having characteristic unpleasant smell.

2. State

The lower members of amines are gases. Amines containing three to eleven carbon atoms are liquids at ordinary temperature, while higher members are solid.

3. Density

Aliphatic amines are less dense than H_2O, having densities in the range of 0.63 to $0.74\,g/cm^3$, while aromatic amines are slightly heavier than H_2O.

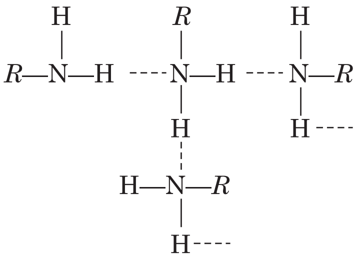
4. Solubility

Lower aliphatic amines can form hydrogen bonds with water molecules and, hence are soluble in water. Solubility of amines decreases with increase in molar mass due to increase in the hydrophobic part which retard the formation of H–bonds and, hence aromatic amines are insoluble in water.

5. Boiling Points

Amines are polar and, hence form intermolecular H-bonds and, therefore they have higher boiling points. This intermolecular association depends upon the extent of H-bonding.

1° amines have two, 2° amines have one while 3° amines have no hydrogen linked to nitrogen. Therefore, the order of boiling point of amines are:
1°-amines > 2°-amines > 3°-amines.



Intermolecular hydrogen bonding in primary amines

Since, the electronegativity of nitrogen (3.0) is lower than oxygen (3.5), amines form weaker H-bond than alcohols and carboxylic acids.

Chemical Properties

Amines are very reactive due to the difference in electronegativity between nitrogen and hydrogen atoms. Due to the presence of unshared pair of electrons over N-atom, amines behave as nucleophile.

The different chemical reactions shown by amines are given below :

1. Reaction with Alkyl Halides

Amines undergo alkylation on reaction with alkyl halides.

$$\underset{\text{Ethylamine}}{CH_3CH_2NH_2} + \underset{\text{Ethyl bromide}}{CH_3CH_2Br} \longrightarrow \underset{\text{Diethylamine}}{(CH_3CH_2)_2NH} + HBr$$

$$\underset{\text{Diethylamine}}{(CH_3CH_2)_2NH} + CH_3CH_2Br \longrightarrow (CH_3CH_2)_3N + HBr$$

$$\Big\downarrow{\scriptstyle CH_3CH_2Br}$$

$$\underset{\text{Tetraethyl ammoniumbromide}}{(CH_3CH_2)_4\overset{+}{N}\,Br^-}$$

Like aliphatic 1° amines, aniline also react with alkyl halides to give successively 2°, 3° and quaternary ammonium salts.

2. Reaction with Water

Amines combine with water to form alkyl ammonium hydroxide which ionise to give protonated amines and hydroxide ion.

$$\underset{\text{Amine}}{RNH_2} + H_2O \longrightarrow \underset{\text{Alkyl ammonium hydroxide}}{RNH_3OH} \rightleftharpoons \underset{\text{Protonated amine}}{RNH_3^+} + OH^{\cdot\cdot}$$

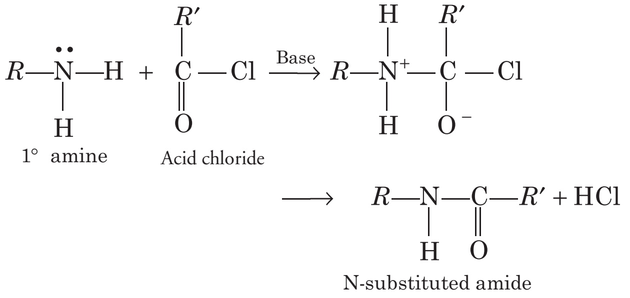
3. Reaction with Acid Chlorides

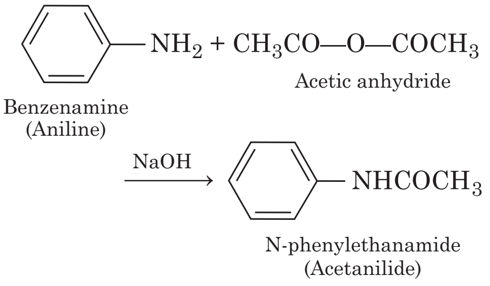
Aliphatic primary and secondary amines react with acid chlorides. Anhydrides and esters by nucleophilic substitution reaction.

This reaction is considered as replacement of hydrogen atom of $—NH_2$ or $>NH$ group by acyl group.

This reaction is known as **acylation**.

The reaction is carried out in the presence of a base stronger than amine like pyridine which removes HCl, so formed and shift the equilibrium towards right hand side.

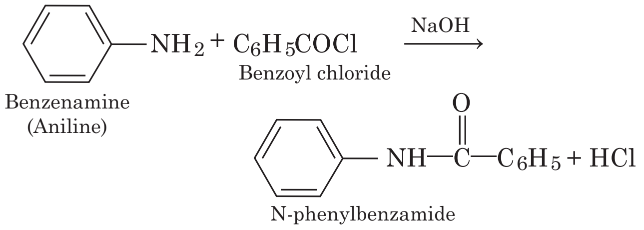




4. Benzoylation

The process of introducing $C_6H_5-\overset{\overset{O}{\|}}{C}-$ group in a molecule by treating amines with benzoyl chloride in the presence of base is known as benzoylation.

Benzoylation of amines in the presence of NaOH is known as **Schotten-Baumann reaction**.



5. Reaction with Nitrous Acid

Primary, secondary and tertiary amines react differently with nitrous acid which is prepared in *situ* from a mineral acid and sodium nitrite.

(i) **Primary amines** When primary amines react with nitrous acid, diazonium salts are formed which being unstable liberate nitrogen gas quantitatively and alcohols.

$$R-NH_2 + HNO_2 \xrightarrow{NaNO_2\ +\ HCl} \left[R-\overset{+}{N}_2\overset{-}{Cl}\right] \xrightarrow{H_2O} R-OH + N_2\uparrow + HCl$$

Aromatic primary amines also react with nitrous acid but at low temperatures (273-278 K) to form diazonium salts.

$$\underset{\text{Aniline}}{C_6H_5NH_2} \xrightarrow[\text{273 K-278 K}]{NaNO_2 + 2HCl} \underset{\text{Benzene diazonium chloride}}{C_6H_5-\overset{+}{N}_2\overset{-}{Cl}} + NaCl + 2H_2O$$

(ii) **Secondary amines** These react with nitrous acid to form a yellow green oily layer of N-nitrosoamines.

$$R_2NH + HONO \longrightarrow \underset{\substack{\text{N-Nitrosoamine}\\ \text{(Yellow oil)}}}{R_2N-N=O} + H_2O$$

(iii) **Tertiary amines** These readily dissolve in nitrous acid forming crystalline trialkyl ammonium nitrite.

$$R_3N + HNO_2 \longrightarrow \underset{\text{Trialkyl ammonium nitrite}}{[R_3\overset{+}{N}H]NO_2^-}$$

Now a days, benzene sulphonyl chloride is replaced by *p*-toluene sulphonyl chloride.

6. Carbylamine Reaction

Primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which have foul smell. This reaction is called carbylamine reaction or isocyanide test. This reaction is used to test primary amine.

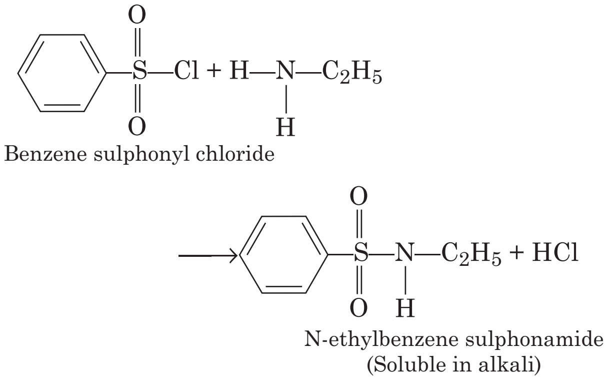
$$\underset{\text{Amine}}{R-NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH \xrightarrow{\Delta} \underset{\text{Isocyanide}}{R-N\overset{\rightarrow}{\equiv}C} + 3KCl + 3H_2O$$

e.g. $$\underset{\text{Methylamine}}{CH_3-NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\text{Methyl isocyanide}}{CH_3-NC} + 3KCl + 3H_2O$$

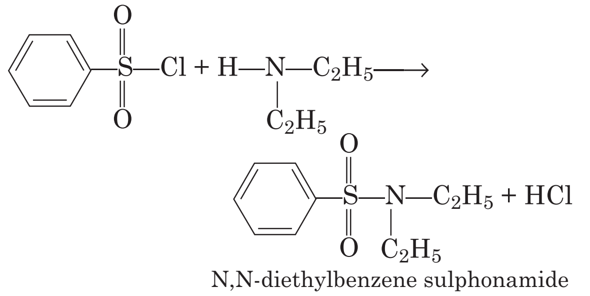
7. Reaction with Benzene Sulphonyl Chloride

(Hinsberg's Method)

(i) **Primary amine** When reacts with benzene sulphonyl chloride (Hinsberg's reagent), it yields N-ethylbenzene sulphonamide. Hydrogen attached to nitrogen is strongly acidic due to the presence of strong electron withdrawing sulphonyl group, hence it is soluble in alkali.



(ii) **Secondary amine** When reacts with benzene sulphonyl chloride, it yields N,N-dimethylbenzene sulphonamide. It does not have any H-atom attached to N-atom. It is not acidic and, hence it is insoluble in alkali.



(iii) **Tertiary amine** does not react with benzene sulphonyl chloride. This reaction is used for the distinction of 1°, 2° and 3° amines and also for the separation of a mixture of amines.

8. Reaction with Grignard Reagent

Primary amines react with Grignard reagent to form hydrocarbons.

$$RNH_2 + R'MgX \longrightarrow R'H + RNHMgX$$

9. Formation of Schiff's Base

Primary amines react with aldehydes to form imine or Schiff's base. This reaction is catalysed by acids.

$$RNH_2 + R'CHO \xrightarrow{H^+} \underset{\text{Schiff's base}}{R{-}N{=}CH{-}R'} + H_2O$$

10. Reaction with Acids

Amines react with strong acids to form ammonium salts.

$$\underset{1°\text{amine}}{R\,NH_2} + HCl \longrightarrow \underset{\text{Alkyl ammonium chloride}}{R\overset{+}{N}H_3Cl^-}$$

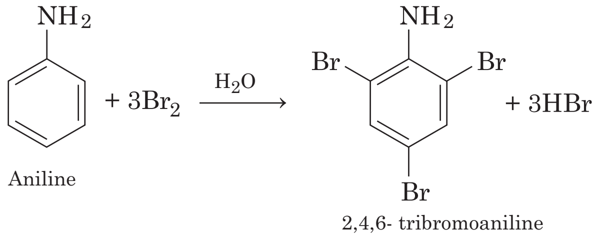
$$\underset{2°\text{amine}}{R_2\,NH} + HCl \longrightarrow \underset{\text{Dialkyl ammonium chloride}}{R_2NH_2Cl}$$

$$\underset{3°\text{amine}}{R_3\,N} + HCl \longrightarrow \underset{\text{Trialkyl ammonium chloride}}{R_3NHCl}$$

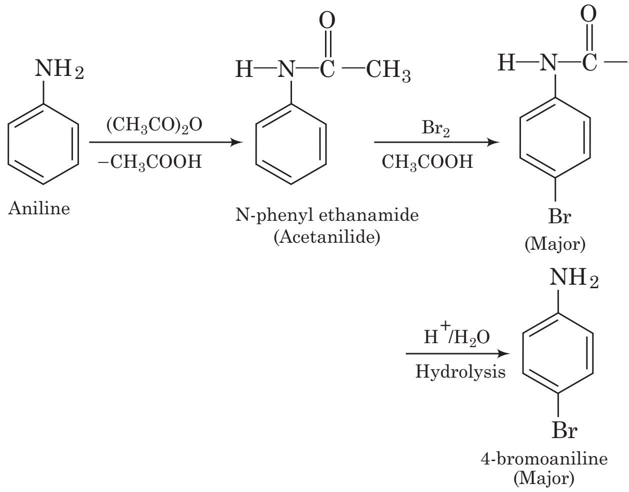
11. Electrophilic Substitution Reactions

In aniline, electron density at *ortho* and *para* positions to the —NH_2 is high. Therefore, —NH_2 group is *ortho* or *para* directing and a powerful activating.

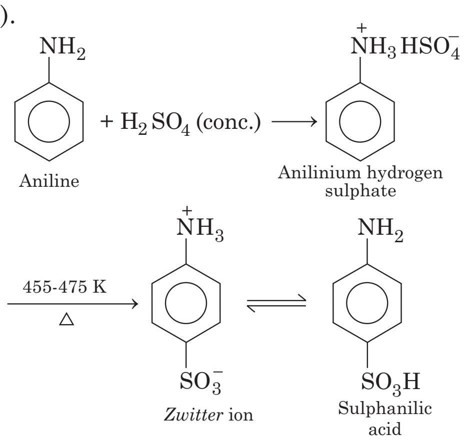
(i) **Halogenation** (Bromination) In the absence of catalyst, aniline on treatment with bromine water forms 2, 4, 6-tribromoaniline.



In order to get a monohalogenated derivative by protecting the —NH_2 group by acetylation, activating effect of —NH_2 group can be controlled, therefore we get desired product.

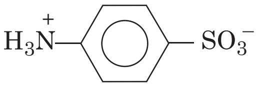


(ii) **Sulphonation** Aniline when react with concentrated H_2SO_4, it forms anilinium hydrogen sulphate which on heating with H_2SO_4 at 455-475 K forms *p*-aminobenzene sulphonic acid (sulphanilic acid).



Note *Zwitter ion* The ions which contains both positive and negative ions, also it contains acidic and basic groups in the same molecule is called *Zwitter ion*.

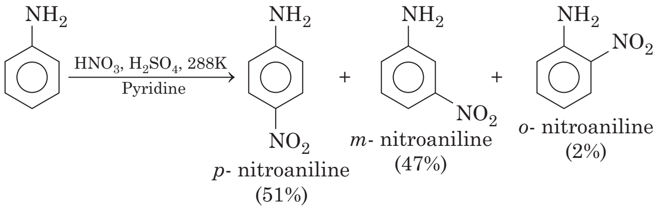
e.g.



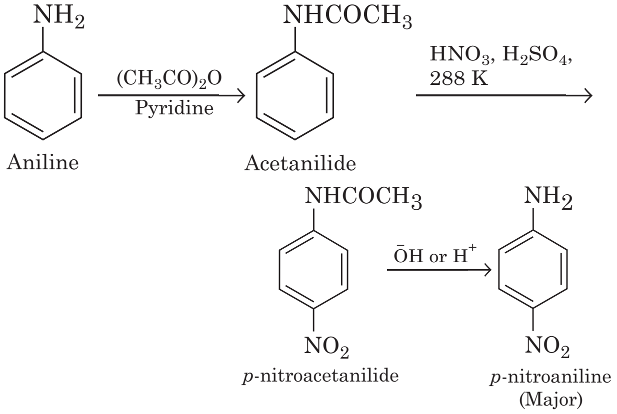
Structure of *Zwitter* ion

(iii) **Nitration** In strongly acidic medium, aniline on nitration gives a mixture of ortho, para and significant amount of meta-nitroaniline.

The formation of unexpected *m*-nitroaniline occurs under strongly acidic conditions, aniline protonated to form anilinium ion which is *m*-directing group.



By protecting the —NH_2 group by acetylation, it gives only *p*-nitro derivative as the major product.



Tests

(i) The aqueous solution of water soluble amine turn red litmus paper to blue which show their basic character.

(ii) When aqueous solution of sodium nitrite is added to a solution of amine in dilute HCl then primary amine give alcohols with rapid effervescence of nitrogen, secondary amines give water insoluble yellow oil and tertiary amines give nitrite addition salts.

(iii) **Carbylamine test** This test is particularly for primary amine. When aliphatic or aromatic primary amine is heated with chloroform and alcoholic KOH, an alkyl isocyanide is formed (having unpleasant smell).

(iv) **Liebermann nitroso reaction** N-nitrosoamines on warming with a crystal of phenol and a few drops of conc. H_2SO_4 form a green solution which when made alkaline with *aq.* NaOH turns deep blue and then red on dilution. This reaction is called Liebermann's nitroso reaction and used as a test for secondary amines.

Distinction of 1°, 2° and 3° Amines

Distinction between Three Types of Amines has been Summarised in Table

S.No.	Test	1° amine	2° amine	3° amine
1.	Carbylamine test	Unpleasant smell of alkyl isocyanide is obtained.	2° amine does not give this reaction.	3° amine does not give this reaction.
2.	Reaction with HNO_2 (nitrous acid)	N_2 is evolved	Oily nitrosoamine is formed	Only dissolves, forming $R_3NH^+\ NO_2^-$
3.	Hinsberg's test [with benzene sulphonyl chloride i.e. $C_6H_5SO_2Cl$]	N-alkyl benzene sulphonamide is formed. It is soluble in alkali.	N,N-dialkyl benzene sulphonamide is formed. It is insoluble in alkali.	No reaction
4.	Action of methyl iodide	Three molecules of CH_3I react to form quaternary salt.	Two molecules of CH_3I react to form quaternary salt.	One molecule of CH_3I reacts to form quaternary salt.
5.	Action of acetyl chloride	Forms N-alkyl amide	Forms N, N-dialkylamide.	No reaction

Uses

(i) Aliphatic amines are used as solvents and intermediates in the manufacture of drugs.

(ii) They are used as reagents in organic synthesis.

(iii) Aromatic amines are used for the formation of polymers, dyes and drugs.

(iv) Quaternary salts of amines are formed from long chain tertiary amines which are used as detergents. e.g. *n*-hexadecyl trimethylammonium chloride.

(v) N, N-dimethylaniline (DMA) is used in the preparation of dyes.

PRACTICE QUESTIONS

Exams', Textbook's Other Imp. Questions

1 MARK *Questions*

Exams' Questions

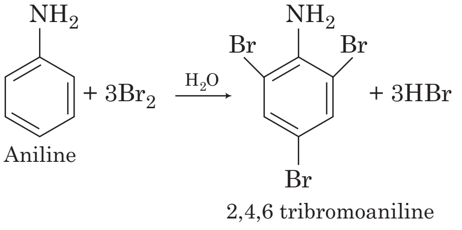
Q.1 Nitration of nitrobenzene yields **[2016]**

(a) *o*-dinitrobenzene
(b) *m*-dinitrobenzene
(c) *p*-dinitrobenzene
(d) 1, 2, 3-trinitrobenzene

Sol (*b*) The directing effect of the nitro group (EWG) of nitrobenzene results in the formation of *meta*-dinitrobenzene.

Q.2 Name the compound precipitated when excess of bromine water is added to aniline. **[2016]**

Sol 2, 4, 6-tribromoaniline is precipitated when excess of bromine water is added to aniline.



Q.3 Reaction between primary amine, $CHCl_3$ and alcoholic KOH is called **[2015, 2012]**

(a) aldol condensation (b) Friedel-Crafts reaction
(c) Cannizzaro's reaction (d) carbylamine reaction

Sol (*d*) All primary amines react with chloroform and aqueous KOH solution to form alkyl isocyanide which has a foul smell.

$$\underset{1^\circ \text{ amine}}{RNH_2} + CHCl_3 + 3KOH \xrightarrow{\text{Heat}} \underset{\substack{\text{Alkyl}\\\text{isocyanide}}}{RN \overset{\rightarrow}{=} C} + 3KCl + 3H_2O$$

This reaction is known as carbylamine reaction.

Q.4 Complete the following reaction and name the products formed.

$$C_6H_5NH_2 + HNO_2 + HCl \xrightarrow{273\text{-}278\text{ K}} \ldots + \ldots$$

[2014]

Sol $C_6H_5NH_2 + HNO_2 + HCl \xrightarrow{273\text{-}278\text{ K}} \underset{\substack{\text{Benzene}\\\text{diazonium}\\\text{chloride}}}{C_6H_5\overset{+}{N}_2\overset{-}{Cl}} + 2H_2O$

Q.5 Ethylamine on reaction with acetyl chloride gives **[2012 Instant, Textbook]**

(a) acetamide (b) N-methylacetamide
(c) N-ethylacetamide (d) ethyl acetate

Sol (*c*) $\underset{\text{Ethyl amine}}{CH_3CH_2NH_2} + \underset{\text{Acetyl chloride}}{CH_3COCl} \xrightarrow{-HCl} \underset{\text{N-ethylacetamide}}{CH_3CH_2NHCOCH_3}$

Q.6 Complete the reaction:

$$C_2H_5NH_2 + \ldots\ldots + 3KOH \longrightarrow C_2H_5N \overset{\rightarrow}{=} C + 3KCl + \ldots\ldots$$

[2011]

Sol $C_2H_5NH_2 + CHCl_3 + 3KOH \longrightarrow C_2H_5N \overset{\rightarrow}{=} C + 3KCl + 3H_2O$

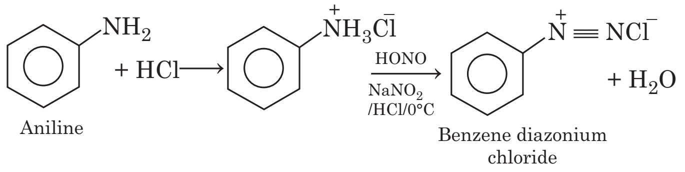
Q.7 Electrophilic substitution reaction in aniline takes place

(a) *m*-position (b) only *o*-position
(c) only *p*-position (d) *o* and *p*-position **[2010]**

Sol (*d*) Electrophilic substitution reaction in aniline takes place at *o* and *p*-position.Because in aniline, electron density at *ortho* and *para* positions is high.

Q.8 Name the main product formed, when aniline is allowed to react with $NaNO_2$ and dil. HCl at low temperature. **[2009]**

Sol Benzene diazonium chloride is formed.



Q.8 Out of primary, secondary and tertiary aliphatic amines, which one is the most basic? **[2002]**

Sol Secondary aliphatic amine is most basic among the primary, secondary and tertiary aliphatic amines.
(Refer to text page on page 214)

Important Questions

Q.9 The compound on reaction with aq.HNO_2 at low temperature produces oily ntirosoamine is,

(a) methylamine (b) diethylamine **[Textbook]**
(c) ethylamine (d) triethylamine

Sol (*b*) Secondary amines (aliphatic or aromatic) reacts with HNO_2 to form a yellow green oily layer of N-nitrosoamines. Reaction is given as follows:

$$(C_2H_5)_2NH + HONO \longrightarrow \underset{\substack{\text{N-nitrosoamine}\\\text{(yellow oil)}}}{(C_2H_5)_2\text{—}N\text{—}N = O} + H_2O$$

Q.10 The correct increasing order of basic strength for aniline (I), *p*-nitroaniline (II), and *p*-toluidine (III) is .... **[Textbook]**

(a) II < III < I (b) III < I < II
(c) III < II < I (d) II < I < III

Sol (*d*) The correct increasing order of basic strength for aniline (I), *p*-nitroaniline (II) and *p*-toluidine (III) is II < I < III

This is because, in case of substituted aniline, electron releasing groups, like —CH_3 increase the basic strength and electron withdrawing groups, like —NO_2 decreases the basic strength.

Q.11 Complete the following reaction and give the names of the products? **[Textbook]**

(i) $CH_3CH_2NH_2 + HNO_2 \longrightarrow \ldots + \ldots ?$

(ii) What happens, when an alkyl cyanide is reduced by sodium metal in ethanol?

Sol (i) $CH_3CH_2NH_2 + HNO_2 \longrightarrow \underset{\text{Ethanol}}{CH_3CH_2OH} + \underset{\substack{\text{Nitrogen}\\\text{gas}}}{N_2\uparrow} + \underset{\substack{\text{Hydrogen}\\\text{chloride}}}{HCl}$

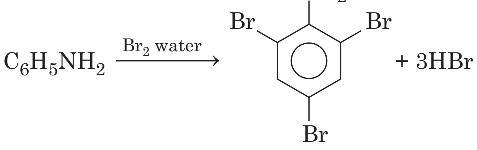
(ii) Refer to text on page 209.

Q.12 Why aniline is soluble in *aq*. HCl? **[Textbook]**

Sol Aniline is an amine and all amines are basic in nature. Therefore, it dissolves in aq.HCl which is an acid.

Q.13 Complete the reaction, $C_6H_5NH_2 \xrightarrow{Br_2 \text{ water}}$ **[Textbook]**

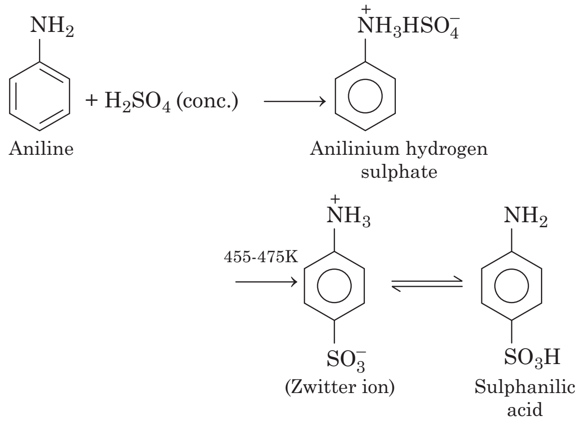
Sol



2, 4, 6- tribromophenylamine

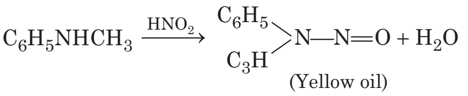
Q.14 Complete the reaction, $C_6H_5NH_2 \xrightarrow{\text{Sulphonation}}$ **[Textbook]**

Sol



Q.15 Complete the reaction, $C_6H_5NHCH_3 \xrightarrow{HNO_2}$ **[Textbook]**

Sol



$$C_6H_5NHCH_3 \xrightarrow{HNO_2} \begin{matrix} C_6H_5 \\ C_3H \end{matrix}\!\!>N-N=O + H_2O$$

(Yellow oil)

Q.16 Benzoylation of amines in the presence of NaOH is known as

Sol Benzoylation of amines in the presence of NaOH is known as Schotten-Baumann reaction.

Q.17 Tetraalkyl ammonium salts are called ……… **[Textbook]**

Sol Tetraalkyl ammonium salts are called **quaternary ammonium salts.**

Q.18 Amine salts are soluble in ……… but insoluble in ……… like ether.

Sol Amine salts are soluble in water but insoluble in organic solvent like ether.

Q.19 Aniline reacts with nitrous acid at 0-5°C to give ………. **[Textbook]**

Sol Aniline reacts with nitrous acid at 0 -5°C to give benzene diazonium chloride.

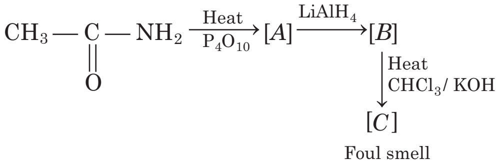
Q.20 Aniline on treatment with bromine water gives ……… . **[Textbook]**

Sol Aniline on treatment with bromine water gives 2, 4, 6-tribromoaniline.

2 MARK *Questions*

Exams' Questions

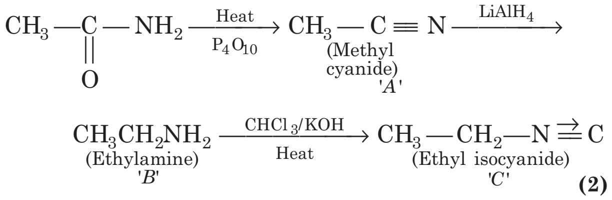
Q.21 Identify *A*, *B*, *C* and name the reaction involved in the transformation of *B* to *C*. **[2016]**



$$CH_3-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow[P_4O_{10}]{Heat} [A] \xrightarrow{LiAlH_4} [B] \xrightarrow[CHCl_3/\,KOH]{Heat} [C]$$

Foul smell

Sol



$$CH_3-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow[P_4O_{10}]{Heat} \underset{\substack{\text{(Methyl}\\ \text{cyanide)}\\ 'A'}}{CH_3-C\equiv N} \xrightarrow{LiAlH_4} \underset{\substack{\text{(Ethylamine)}\\ 'B'}}{CH_3CH_2NH_2} \xrightarrow[Heat]{CHCl_3/KOH} \underset{\substack{\text{(Ethyl isocyanide)}\\ 'C'}}{CH_3-CH_2-N \overset{\rightarrow}{=} C}$$

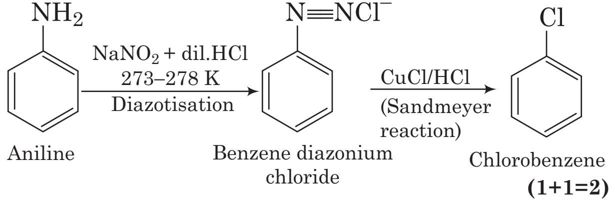
(2)

Q.22 Why aniline is less basic than methylamine? **[2014, 2012, 2011, Textbook]**

Sol Due to resonance in aniline, lone pair of electrons gets delocalised over benzene ring and, therefore is less available for protonation. Thus, aniline is weaker bases than methylamine. **(2)**

Q.23 How will you convert aniline to chlorobenzene? **[2013]**

Sol



(1+1=2)

Q.24 How is methylamine converted to trimethyl amine? **[2012, 2011]**

Sol

$$\underset{\substack{\text{Methyl}\\ \text{amine}}}{CH_3\,NH_2} + \underset{\substack{\text{Methyl}\\ \text{bromide}}}{CH_3\,Br} \longrightarrow \underset{\text{Dimethyl amine}}{(CH_3)_2NH} + HBr$$

$$\downarrow CH_3Br$$

$$\underset{\text{Trimethyl amine}}{(CH_3)_3\,N} + HBr$$

(2)

Q.25 How can you convert ethylamine to ethyl alcohol? **[2006]**

Sol Ethylamine is treated with HNO_2 (i.e. $NaNO_2$ + cold dil. HCl) to form alcohol.

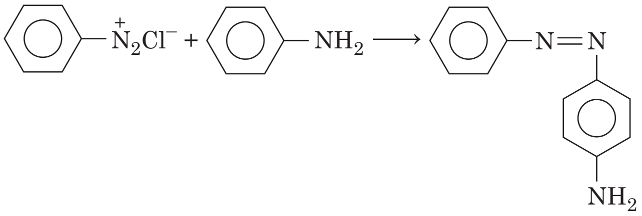
$$\underset{\text{Ethylamine}}{CH_3CH_2NH_2} + HONO \xrightarrow{NaNO_2/HCl} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + N_2 + H_2O$$

(2)

Important Questions

Q.26 How you will distinguish $C_2H_5NH_2$ and $C_6H_5NH_2$? **[Textbook]**

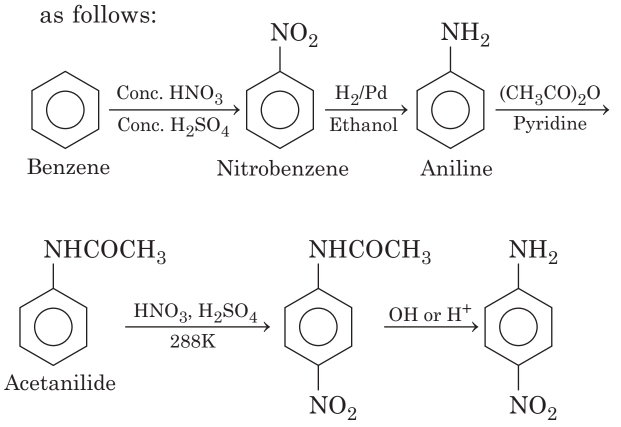
Sol Ethylamine and aniline can be distinguished by using azo-dye test. Benzene diazonium salts react with highly reactive electron rich compounds such as phenols and amines to form bright coloured azo compounds. This is called coupling reaction.



This reaction is not given by ethylamine. **(2)**

Q.27 How will you carry out the conversion of benzene to *p*-nitroaniline?

Sol Conversion of benzene to *p*-nitroaniline takes place as follows:



p-nitroaniline **(2)**

Q.28 Why ethyl amine is more basic than ammonia? **[Textbook]**

Sol Refer to text on page 306. **(2)**

Q.29 Why aniline is less basic than ammonia? **[Textbook]**

Sol Due to resonance in aniline, lone pair of electrons gets delocalised over benzene ring and, thus is less available for protonation. Therefore, aromatic amines or aniline is less basic than ammonia. **(2)**

(Refer to text on page 306).

Q.30 What is carbylamine test? **[Textbook]**

Sol **Carbylamine test** Primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which have foul smell.

This reaction is called carbylamine amine test and it is used to test primary amine.

$$\underset{\text{1°-amine}}{R—NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\text{Isocyanide}}{R—N \overset{\rightarrow}{=} C} + 3KCl + 3H_2O$$ **(2)**

Q.31 Arrange the following in the increasing order of their basic strength in aqueous solution.

CH_3NH_2, $(CH_3)_3N$, $(CH_3)_2NH$

Sol Basicity increases with increase in the number of *R* groups but 3° amine is least basic due to steric hindrance. Thus, increasing order of basicity:

$$\underset{\text{Least basic}}{(CH_3)_3N} < CH_3NH_2 < \underset{\text{Most basic}}{(CH_3)_2NH}$$

Refer to text on page 306. **(2)**

Q.32 Complete the following acid-base reactions and name the products.

(i) $CH_3—CH_2—CH_2—NH_2 + HCl \longrightarrow$

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

Sol (i) $$\underset{n\text{-propyl amine}}{CH_3—CH_2—CH_2—\ddot{N}H_2} + H—Cl \longrightarrow$$

$$\underset{n\text{-propyl ammonium chloride}}{CH_3—CH_2—CH_2—\overset{+}{N}H_3\overset{-}{Cl}}$$ **(1)**

(ii) $$\underset{\text{Triethyl amine}}{(C_2H_5)_3\ddot{N}} + H—Cl \longrightarrow \underset{\text{Triethyl ammonium chloride}}{(C_2H_5)_3\overset{+}{N}HCl^-}$$ **(1)**

Q.33 Arrange the following.

(i) In the increasing order of boiling point
C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$

(ii) In the increasing order of solubility in water
$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$

Sol (i) Order of boiling points

$(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

(Refer to text on page 307.) **(1)**

(ii) Order of solubility

$C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

(Refer to text on page 307.) **(1)**

Q.34 Arrange the following.

(i) In the decreasing order of pK_b values.
$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$.

(ii) In the increasing order of basic strength.
$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2.

Sol (i) The decreasing order of pK_b values is,

$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

Refer to text on page 306.

(ii) The increasing order of basic strength values is,

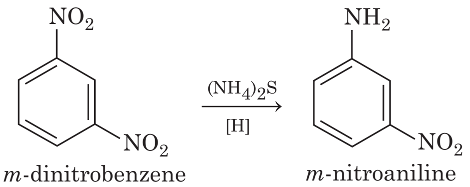
$C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$

Refer to text on page 306. **(1 + 1 = 2)**

Q.35 (i) How will you convert *m*-dinitrobenzene to *m*-nitroaniline?

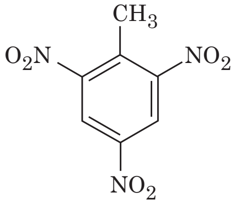
(ii) Draw the structure of trinitrotoluene.

Sol (i)



(1)

(ii)



Trinitrotoluene **(1)**

3 MARK *Questions*

Exams' Questions

Q.36 Write short notes on carbylamine reaction.

[2011, 2009, 2007 Instant]

Sol Refer to the text on page 308. **(3)**

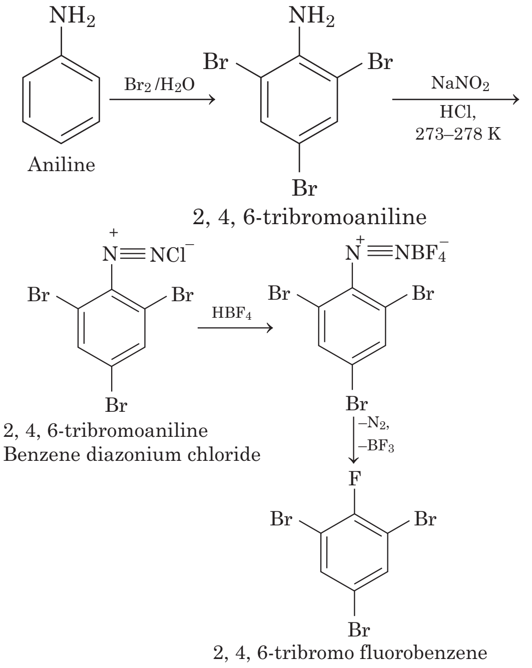
Important Questions

Q.37 Accomplish the following conversions.

(i) Aniline to 2, 4, 6-tribromofluorobenzene
(ii) Benzyl chloride to 2-phenylethanamine
(iii) Chlorobenzene to *p*-chloroaniline

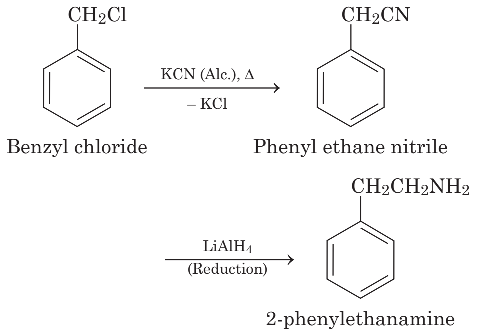
Sol

(i)



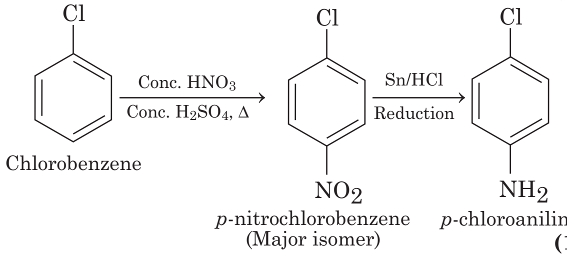
(1)

(ii)



(1)

(iii)



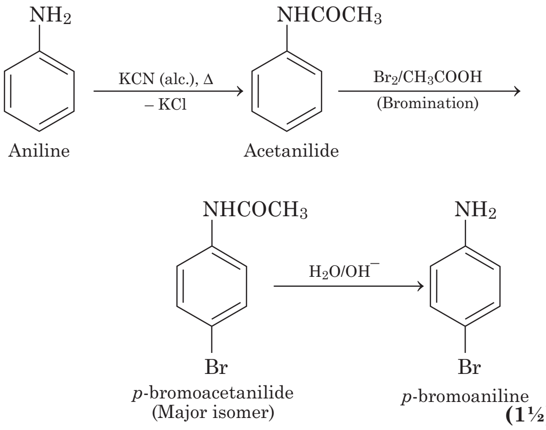
(1)

Q.38 Accomplish the following conversions:

(i) Aniline to *p*-bromoaniline
(ii) Benzamide to toluene

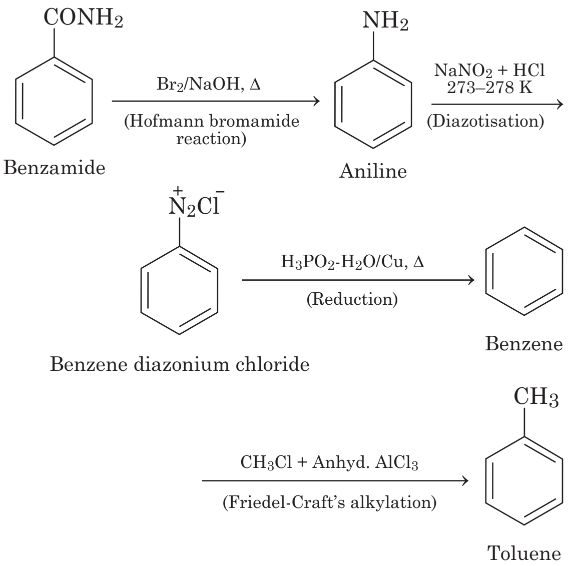
Sol

(i)



(1½)

(ii)

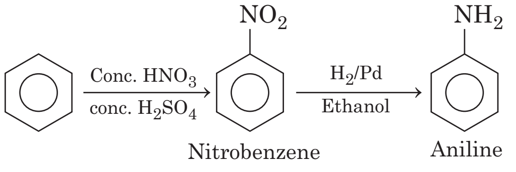


(1½)

Q.39 How will you convert the following: **[Textbook]**

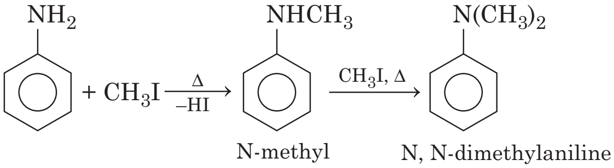
(i) Benzene to aniline
(ii) Aniline to N, N-dimethylaniline?

Sol (i) Conversion of benzene to aniline.



(1½)

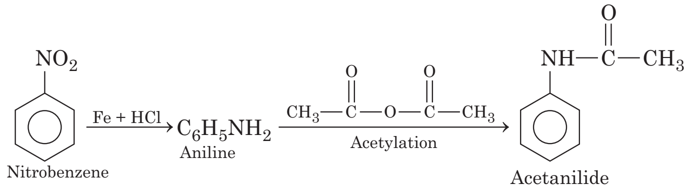
(ii) Conversion of aniline to N, N-dimethylaniline.



(1½)

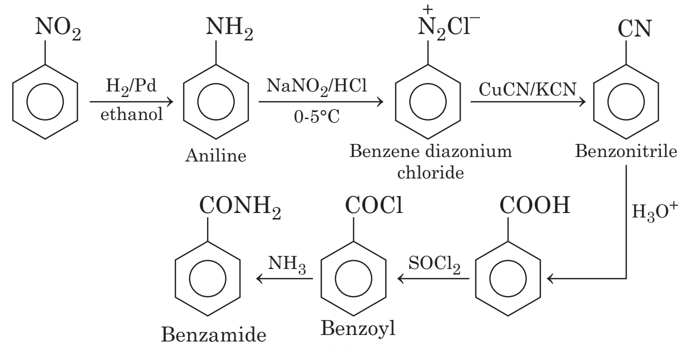
Q.40 How will you convert nitrobenzene to **[Textbook]**
(i) acetanilide (ii) benzamide?

Sol (i) Conversion of nitrobenzene to acetanilide.



(1½)

(ii) Conversion of nitrobenzene to benzamide.



(1½)

Q.41 Arrange the following compounds in decreasing order of basicity, Give reason. **[Textbook]**

Methylamine, dimethylamine, aniline, N-methyl aniline.

Sol The decreasing order of basicity of the given compounds is Dimethylamine > methylamine > N-methylaniline > aniline.

Refer to text on page 306. **(3)**

Q.42 Write the reactions of aromatic and aliphatic primary amines with nitrous acid. **[Textbook]**

Sol Reaction of aromatic and aliphatic primary amines with nitrous acid are:

(i) Aromatic primary amines also react with nitrous acid at low temperatures (273-278K) to form diazonium salts.

$$C_6H_5NH_2 \xrightarrow[273\text{-}278K]{NaNO_2 + 2HCl} \underset{\text{Benzene diazonium chloride}}{C_6H_5\overset{+}{N}_2Cl^-} + NaCl + 2H_2O$$

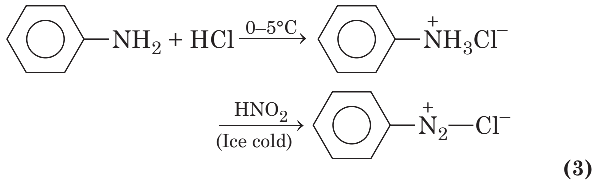
(ii) When primary aliphatic amines react with nitrous acid, diazonium salts are formed which being unstable, liberate nitrogen gas quantitatively and alcohols.

$$R\text{—}NH_2 \xrightarrow{NaNO_2 + HCl} [R\text{—}\overset{+}{N}_2\overset{-}{Cl}] \xrightarrow{H_2O} \underset{\text{Alcohol}}{R\text{—}OH} + N_2\uparrow + HCl$$

(3)

Q.43 How you will prepare benzene diazonium chloride? **[Textbook]**

Sol Benzene diazonium chloride can be prepared by diazotisation reaction. Primary aromatic amines react with HNO_3 under ice cold conditions to form benzene diazonium chloride.



(3)

Q.44 Describe a method for the identification of primary, secondary and tertiary amines?

Sol Refer to text on page 310. **(3)**

7 MARK *Questions*

Exams' equestions

Q.45 (i) Give any two methods for the preparation of primary amine. How does it react with
(a) CH_3COCl and (b) $CHCl_3$? **[2013, 2000]**
(ii) How will you prove that amines are basic compounds?

Sol (i) Refer to text on pages 302, 307 and 308.
(ii) Refer to text on page 308. **(7)**

Q.46 How is methylamine prepared from nitromethane and acetamide? How does it react with (i) acetyl chloride and (ii) chloroform in the presence of alcoholic KOH solution? Compare the basic character of ammonia and methylamine with justification. **[2007 Textbook]**

Sol Refer to text on pages 301, 307, 308 and 306. **(7)**

Q.47 What are different types of aliphatic amines? Describe two general methods of preparation of primary amine. How ethylamine reacts with
(i) methyl bromide? (ii) acetyl chloride? **[2006 Textbook]**

Sol Refer to text on pages 300, 301 and 307. **(7)**

Q.48 (i) Give the structure of *A*, *B* and *C* in the following reactions:

(a) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273\text{ K}]{NaNO_2 + HCl} B \xrightarrow[\Delta]{H_2O/H^+} C$

(b) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$

(c) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273\text{ K}]{HNO_2} B \xrightarrow{C_6H_5OH} C$

(ii) Write the reaction of aromatic amines with nitrous acid.

Sol (i) (a) $\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow{Fe/HCl} \underset{\underset{(A)}{\text{Aniline}}}{C_6H_5NH_2}$

$\xrightarrow[273\text{ K}]{NaNO_2 + HCl} \underset{\underset{(B)}{\text{Benzene diazonium chloride}}}{C_6H_5\overset{+}{N}\equiv NCl^-} \xrightarrow[\Delta]{H_2O/H^+} \underset{\underset{(C)}{\text{Phenol}}}{C_6H_5OH}$ **(2)**

(b) $\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[\Delta]{NH_3} \underset{\underset{(A)}{\text{Ethanamide}}}{CH_3CONH_2}$

$\xrightarrow[\text{(Hofmann's bromamide reaction)}]{NaOBr} \underset{\underset{(B)}{\text{Methanamine}}}{CH_3NH_2}$

$\xrightarrow{NaNO_2/HCl} \underset{\underset{(C)}{\text{Methanol}}}{CH_3OH}$ **(2)**

(c) $\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow{Fe/HCl} \underset{\underset{(A)}{\text{Aniline}}}{C_6H_5NH_2}$

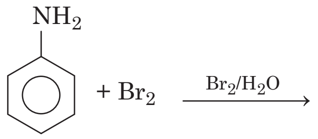
$\xrightarrow[273\text{ K}]{HNO_2} \underset{\underset{(B)}{\text{Benzene diazonium chloride}}}{C_6H_5-\overset{+}{N}\equiv NCl^-}$ **(2)**

(ii) $\underset{\text{Aniline}}{C_6H_5NH_2} \xrightarrow[0\text{-}5^\circ C]{NaNO_2+HCl}$

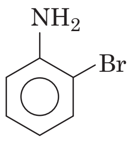
$\underset{\text{Benzene diazonium chloride}}{C_6H_5\overset{+}{N}_2Cl^-} + NaCl + 2H_2O$ **(1)**

TOPIC TEST 2

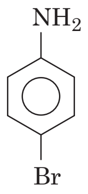
1. Which of the following product is formed in the given reaction?



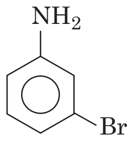
(a)



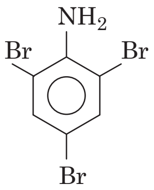
(b)



(c)



(d)



2. N- methylbenzamide is formed when methanamine reacts with benzoyl chloride. This reaction is known as

(a) benzoylation (b) Hinsberg test

(c) Schmidt reaction (d) Curtius reaction

[***Ans.*** **1.** (d), **2.** (a)]

3. Bromination, nitration and sulphonation of aniline are .... reactions. [***Ans.*** electrophilic substitution]

4. Secondary amines react with nitrous acid to form a yellow green oily layer of ....

[***Ans.*** N-nitroso amines]

5. How will you convert the following aniline into N-phenyl ethanamide?

6. Give the chemical test to distinguish between ethylamine and dimethylamine?

7. Account for the following:

(i) Aniline does not undergo Friedel-Crafts reaction.

(ii) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution.

8. Write the structures of A, B and C in the following reactions:

(i) $C_6H_5CONH_2 \xrightarrow{Br_2/aq.KOH} A \xrightarrow{NaNO_2, HCl} B$

(ii) $CH_3Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[alc.KOH]{CH_3Cl_3} C$

9. (i) Arrange the following in the increasing order of their boiling point:

$C_2H_5NH_2, C_2H_5OH, (CH_3)_3N$

(ii) Give a simple chemical test to distinguish between the following pair of compounds $(CH_3)_2NH$ and $(CH_3)_3N$.

10. An aromatic compound (A) of molecular formula $C_7H_6O_2$ undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions.

$$\begin{tikzcd}
\underset{(A)}{C_7H_6O_2} \arrow[r, "NH_3/Heat"] & C_6H_5CONH_2 \arrow[r, "Br_2", "NaOH"'] \arrow[d, "LiAlH_4/Ether"] & {} & \\
& D & B \arrow[r, "(CH_3CO)_2O"] \arrow[d, "Br_2/Ag"] & C \\
& & E &
\end{tikzcd}$$

Chapter Test

1 MARK *Questions*

1 Primary amines on heating with chloroform and ……… form ……… .

2 Which of the following cannot be acetylated?

(a) $C_2H_5NH_2$ (b) $C_6H_5NH_2$
(c) $(CH_3)_2NH$ (d) $(CH_3)_3N$

3 Dehydration of an amide with phosphorus pentoxide yields

(a) ammonia (b) alkyl cyanide
(c) alkyl isocyanide (d) alkyl amine

[***Ans.*** **1.** KOH, carbylamines, **2.**(d), **3.**(b)]

4 Name the product when nitroethane is reduced with tin and hydrochloric acid.

5 Name the following reaction and write balanced equation?

Acetamide with bromine in the presence of potassium hydroxide.

6 Complete the reaction.

$CH_3CH_2Br + NaNO_2 \longrightarrow ……… + NaBr$

[***Ans.*** $CH_3CH_2NO_2$]

7 What is the order of boiling point of amines among: 1°-amines, 2°-amines and 3°-amines?

2 MARK *Questions*

8 Convert nitromethane into methyl alcohol.

9 Account for the following:

(i) Amines are basic substances while amides are neutral.
(ii) *Tert*-butylamine cannot be prepared by the action of NH_3 on *tert*-butylbromide.

10 Although, trimethylamine and *n*-propylamine have the same molecular weight but the former boils at a lower temperature (276 K) than the latter (322 K). Explain.

11 Complete the following reactions:

(i) $C_6H_5NH_2 + CHCl_3 + \text{alc. KOH} \longrightarrow$
(ii) $C_6H_5NO_2 \xrightarrow{Fe/HCl}$

12 Why are the boiling points of amines much lower than those of alcohols of comparable molecular masses?

3 MARK *Questions*

13 What happens, when alcohols react with ammonia in the presence of alumina as a catalyst?

14 An organic compound A with molecular formula C_2H_7N on reaction with nitrous acid gives a compound *B*. *B* on controlled oxidation gives compound *C*. *C* reduces Tollen's reagent to give silver mirror and *D*. *B* reacts with *D* in presence of concentrated sulphuric acid to give sweet smelling compound *E*. Identify *A*, *B*, *C*, *D* and *E*. Give the reaction of *C* with NH_3.

15 Suggest chemical reactions for the following conversions.

(i) 1-hexanenitrile ⟶ 1-aminopentane
(ii) Chloroethane ⟶ Propan-1-amine

7 MARK *Questions*

16 Why do amines exhibit basic character? With suitable explanation, compare the basic strength of 1°, 2° and 3°-amines.

17 What are amines and how are they classified? Give suitable examples alongwith their common and IUPAC names.

18 A compound *A* of molecular formula $C_3H_7O_2N$ on reaction with iron and concentrated HCl gives a compound *B* of molecular formula C_3H_9N. compound *B* on treatment with $NaNO_2$ and HCl gives another compound *C* having molecular formula C_3H_8O. Compound *C* gives effervescence with sodium. On oxidation with CrO_3, compound *C* gives a saturated aldehyde containing three carbon atom. Deduce the structure of compounds *A*, *B* and *C* and write the equations involved?