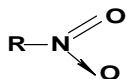


## 13. COMPOUNDS CONTAINING NITROGEN

### 1. What are Nitro Compounds?

Ans. Nitro compounds are organic compounds that contain one or more nitro functional groups ( $-\text{NO}_2$ ).

The **structure** of the nitro-compounds is depicted as follows:



### 2. How are nitroalkanes prepared from (1) Alkanes (2) alkyl halides (3) salts of $\alpha$ -halogeno carboxylic acid (4) Primary amines (5) $\alpha$ - nitroalkanes (6) Oximes?

#### 1) By direct nitration of Alkanes:

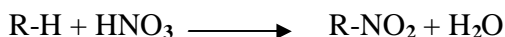
Replacement of H-atom from alkane by  $-\text{NO}_2$  group is known as Nitration.

Two techniques are used for the direct nitration of Alkanes, are as follows:-

##### a) Liquid-phase nitration:-

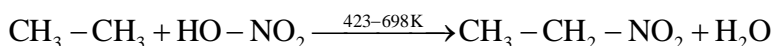
The hydrocarbon is heated with concentrated nitric acid under pressure at  $140^\circ$ . This is a slow reaction and a large amount of polynitro-compounds are produced.

General reaction:-

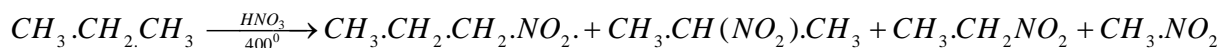


##### (b) Vapors-phase nitration:-

Nitration of alkane is done by heating vapours of alkanes and  $\text{HNO}_3$  at about  $400^\circ\text{C}$  to give nitroalkanes. This is known as vapour phase nitration.



During nitration, of higher alkanes, C-C bonds of alkanes are also broken due to strong oxidant nature of  $\text{HNO}_3$  to produce all possible nitroalkanes.



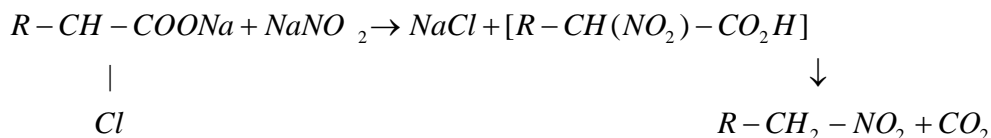
### 2. From alkyl halides:

This reaction is carried out by heating an alkyl halide with silver nitrite in aqueous ethanolic solution. This reaction is an example of a nucleophilic substitution reaction.



### From $\alpha$ -halogeno-carboxylic acid:

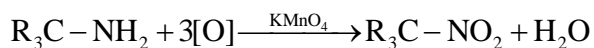
Nitroalkane is prepared by boiling an aqueous solution of sodium nitrite with sodium salt of  $\alpha$ -halogeno-carboxylic acid. e.g.,



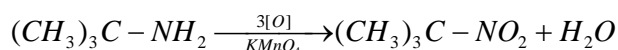
### 4) From primary amines:-

Tertiary nitro compounds can be obtained by the oxidation of primary amines containing amino group linked to tertiary carbon, with acidified potassium permanganate.

General Reaction:-



Example:-

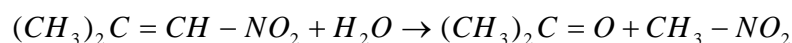


**2-Methyl propan-2-amine      2-Methyl-2-nitropropane**

### 5) From $\alpha$ -nitro alkenes:

Hydrolysis of  $\alpha$ -nitro alkenes with water yields Nitroalkanes.

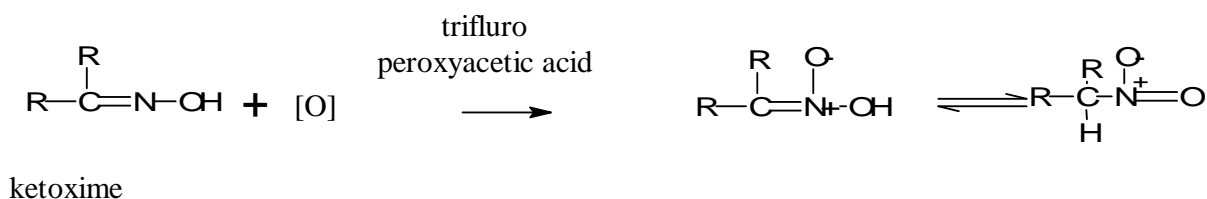
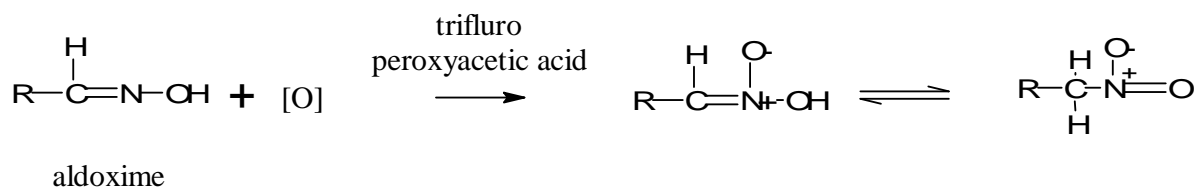
For example: - 2-methyl-1-nitroprop-1-ene gives acetone and nitromethane on hydrolysis with water.



### 6) From Oximes

Primary and secondary nitroalkanes are prepared by oxidizing aldoximes and ketoximes by trifluoroperoxyacetic acid

Eg.

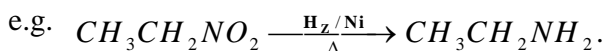
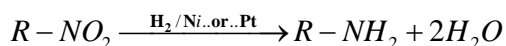


### Q.3 Explain reduction of nitroalkanes

The extent of reduction depends on the nature of the reducing agent as well as on the pH of the medium.

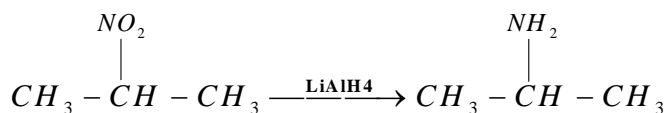
#### a) Catalytic reduction:

Both aliphatic and aromatic nitro compounds are reduced to primary amines when reacted with  $H_2/Ni$  or  $H_2/Pt$  or  $H_2/Pd$ .



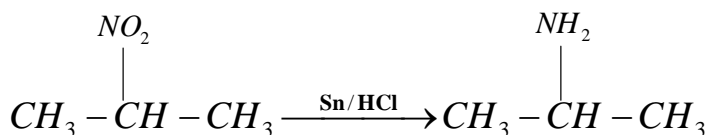
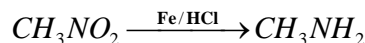
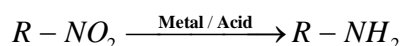
#### b) Reduction with $LiAlH_4$ (Lithium aluminium hydride):-

Nitroalkanes are reduced to primary amines.



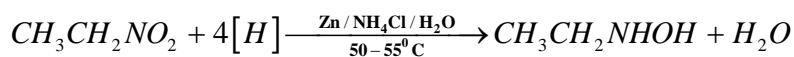
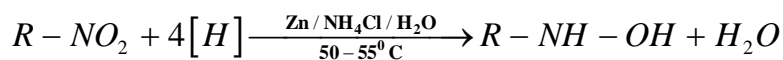
#### c) Reduction in acidic medium:

Aliphatic nitro compounds are reduced to primary amines by metal and acid, e.g.  $Zn/HCl$ ,  $Fe/HCl$  or  $Sn/HCl$



#### d) Reduction in neutral medium:

In neutral medium, the nitro group is reduced to  $-NHOH$ , thus giving substituted hydroxylamines as the product.

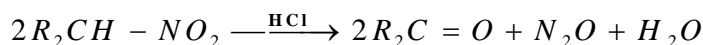


### 2) Hydrolysis of nitro alkanes:

Primary nitro-alkanes are hydrolyzed by boiling hydrochloric acid or by sulphuric acid to give a mixture of carboxylic acid and hydroxylamine.



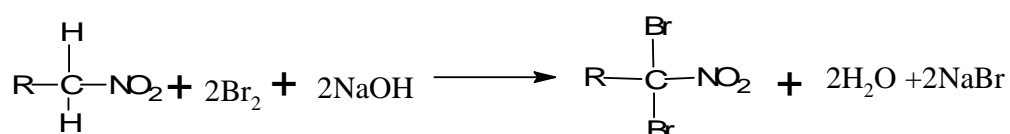
Secondary nitro-alkanes are hydrolysed by boiling hydrochloric acid to give a mixture of ketone and nitrous oxide.



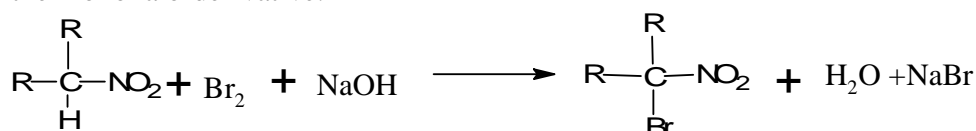
Tertiary nitro-alkanes do not undergo hydrolysis.

#### 4. What is the action of halogen in the presence of sodium Hydroxide on primary, secondary and tertiary nitroalkanes?

When primary and secondary nitro-alkanes are reacted with halogen in the presence of base,  $\alpha$ -halogenation takes place.



Primary nitro-alkanes can form the mono- as well as dihalo-derivatives, but secondary nitroalkanes form only the monohalo-derivative.



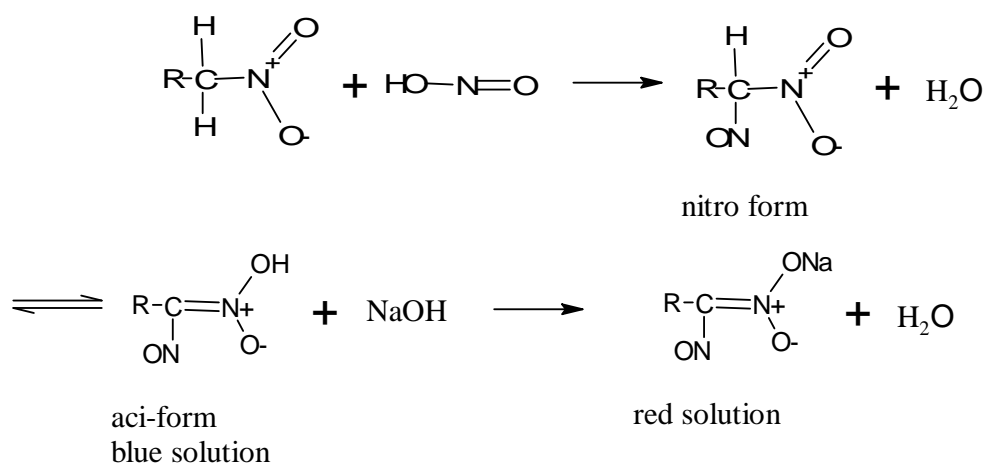
Nitromethane can form the trihalo-derivative.

Tertiary nitroalkanes do not react.

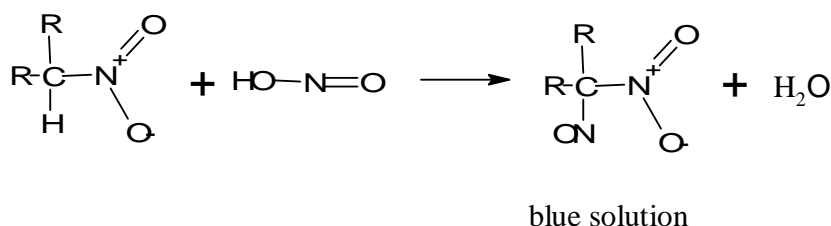
#### 5. How are primary, secondary and tertiary nitroalkanes distinguished?

Nitro-compounds react with nitrous acid, the product formed depending on the nature of the nitro compound.

Primary nitro-alkanes react with nitrous acids to form blue coloured solution (aci form) which dissolve in sodium hydroxide to give red solutions.



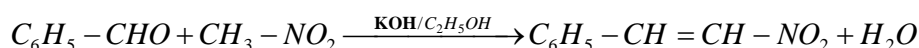
Secondary nitro-alkanes react with nitrous acid to form blue coloured nitroso nitroalkanes, which no more contain  $\alpha$ -hydrogen atom hence are insoluble in NaOH (no red colour)



Tertiary nitro-alkanes do not react with nitrous acid since they have no  $\alpha$ -hydrogen atom.

### Q.6 Explain condensation of nitroalkane with aldehydes and ketones

Owing to the presence of active  $\alpha$ -hydrogen atoms, primary and secondary nitro-compounds undergo condensation with aldehydes; this is similar to Aldol condensation. e.g., Nitromethane condenses with benzaldehyde in the presence of ethanolic potassium hydroxide e.



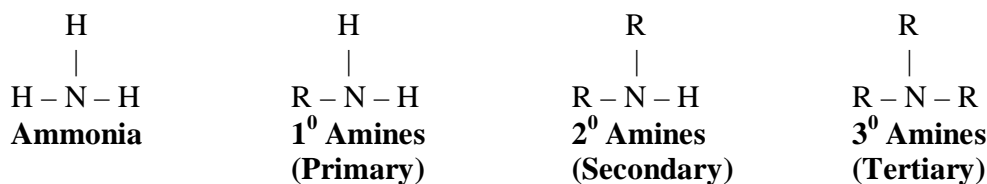
## Amines:

### Q.1 What are amines? Give examples.

(2 marks)

**Ans.** “Amines are the alkyl or organic derivatives of ammonia in which one, two or all the three hydrogen atoms attached to nitrogen are replaced by same or different alkyl (R) or aryl groups”.

**For ex.**



e.g.  $\text{CH}_3-\text{NH}_2$  (methylamine),  
 $(\text{CH}_3)_3\text{N}$  (trimethylamine).

$\text{CH}_3-\text{NH}-\text{CH}_3$  (dimethylamine),

### Q.2 How are amines classified? Give examples.

(2-3 marks)

**Ans.** Amines are alkyl derivatives of ammonia. Depending upon the number of alkyl groups joined to nitrogen atom, they are classified as primary, secondary or tertiary amines.

#### 1. Primary amines (1<sup>o</sup>):

- i) The amines in which only **one hydrogen** atom of ammonia is replaced by an **alkyl or aryl** group are called primary amines.
  - ii) The primary amines are represented as **R – NH<sub>2</sub>**.
  - iii) The functional group of primary amines is **–NH<sub>2</sub> (amino group)**.
- e.g.  $\text{CH}_3-\text{NH}_2$  (methylamine),  $\text{C}_2\text{H}_5-\text{NH}_2$  (ethylamine).

2. **Secondary amines ( $2^0$ ):**

i) The amines in which **two** hydrogen atoms of ammonia are replaced by two **same or different alkyl or aryl groups** are called secondary amines.

ii) The secondary amines are represented as  **$R_2NH$** .

iii) The functional group of secondary amines is  **$>NH$  (imino group)**.

e.g.  $CH_3 - NH - CH_3$  (**dimethyl amine**),  
 $(C_2H_5)_2NH$  (**diethyl amine**),  
 $C_2H_5 - NH - CH_3$  (**ethyl methyl amine**).

3. **Tertiary amines ( $3^0$ ):**

i) The amines in which **all the three** hydrogen atoms of ammonia are replaced by three same or different alkyl or aryl group are called tertiary amines.

ii) The tertiary amines are represented as  **$R_3N$** .

iii) The functional group of tertiary amines is  $\begin{array}{c} | \\ -N- \end{array}$  (**tertiary nitrogen atom**).

$\begin{array}{c} CH_3 \\   \\ CH_3 - N - CH_3 \end{array}$ <b>Trimethyl amine</b>	$\begin{array}{c} C_2H_5 \\   \\ C_2H_5 - N - C_2H_5 \end{array}$ <b>Triethyl amine</b>	$\begin{array}{c} CH_3 \\   \\ C_2H_5 - N - CH_3 \end{array}$ <b>Ethyl dimethyl amine</b>
---	--	--

Secondary and tertiary amines may be further classified as:

i. **Simple amines (Symmetrical amines)**

The amines in which **same** alkyl groups are attached to the nitrogen atom are called simple amines.

e.g.  $(C_2H_5)_2NH$  **diethyl amine**,  $(C_2H_5)_3N$  **triethyl amine**.

ii. **Mixed amines: (Unsymmetrical amines)**

The amines in which **different** alkyl groups are attached to the nitrogen atom are called mixed amines.

e.g.  $CH_3 - CH_2 - NH - CH_3$  **ethyl methyl amine**  
 $(C_2H_5)_2N - CH_3$  **diethyl methyl amine**

**Q.3 How are amines named by common system?**

(2 marks)

**OR**

**How are amines named by IUPAC system?**

(2 marks)

**Ans.**

1. **Common names:**

- i) The aliphatic amines are named as "**Alkyl amines**".
- ii) The common name of primary amine is obtained by writing the name of **alkyl** group followed by the word '**amine**'.
- iii) **Symmetrical secondary and tertiary amines** are named by adding prefix '**di**' and '**tri**' respectively to the name of alkyl group.
- iv) **Unsymmetrically substituted secondary and tertiary amines** are named by writing the names of **alkyl** groups in **alphabetical order** followed by the word **amine**.

## 2. IUPAC names:

- i) According to IUPAC system, aliphatic amines are named as “**Alkanamines**”.
- ii) The name of amine is obtained by replacing the suffix ‘e’ from the name of **parent alkane** by ‘**amine**’.
- iii) The **position of amino group** is indicated by the **lowest possible number**.
- iv) In case of **secondary or tertiary amines**, the **largest alkyl group** is considered as the **parent alkane** and **other alkyl** groups as **N – substituents**.

It should be **noted** here that, regardless of the method of nomenclature, the **complete name of amines is always written as one word**.

Amine	Common Name	IUPAC Name
<b>(a) Primary amines</b>	<b>Alkylamines</b>	<b>Alkanamines</b>
i. $\text{CH}_3\text{--NH}_2$	Methylamine	Methanamine
ii. $\text{CH}_3\text{--CH}_2\text{--NH}_2$	Ethylamine	Ethanamine
iii. $\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--NH}_2$	n-propylamine	Propan-1-amine
iv. $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{--CH--NH}_2 \end{array}$	isopropylamine	Propan-2-amine
v. $\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--NH}_2$	n-butylamine	Butan-1-amine
vi. $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{--CH}_2\text{--CH--NH}_2 \end{array}$	sec-butylamine	Butan-2-amine
vii. $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{--CH--CH}_2\text{--NH}_2 \end{array}$	isobutylamine	2-Methylpropan-1-amine
viii. $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{--C--NH}_2 \\   \\ \text{CH}_3 \end{array}$	tert-butylamine	2-Methylpropan-2-amine

Amine	Common Name	IUPAC Name
<b>(b) Secondary amines</b>	<b>Alkylamines</b>	<b>Alkanamines</b>
i. $\text{CH}_3\text{--NH--CH}_3$	dimethylamine	N-Methylmethanamine
ii. $\text{CH}_3\text{--CH}_2\text{--NH--CH}_3$	ethylmethylamine	N-Methylethanamine
iii. $\text{CH}_3\text{--CH}_2\text{--NH--CH}_2\text{--CH}_3$	diethylamine	N-Ethylethanamine
iv. $\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--NH--CH}_3$	methyl-n-propylamine	N-Methylpropan-1-amine
v. $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{--CH--NH--CH}_3 \end{array}$	isopropylmethyl amine	N-Methylpropan-2-amine
<b>(c) Tertiary amines</b>		
i. $(\text{CH}_3)_3\text{N}$	Trimethylamine	N, N-Dimethylmethanamine
ii. $(\text{C}_2\text{H}_5)_3\text{N}$	Triethylamine	N, N-Diethylethanamine
iii. $\text{C}_2\text{H}_5)_2\text{N--CH}_3$	Diethylmethylamine	N-Ethyl-N- methylethanamine
iv. $(\text{CH}_3)_2\text{N--C}_2\text{H}_5$	Ethyl dimethylamine	N, N-Dimethylethanamine

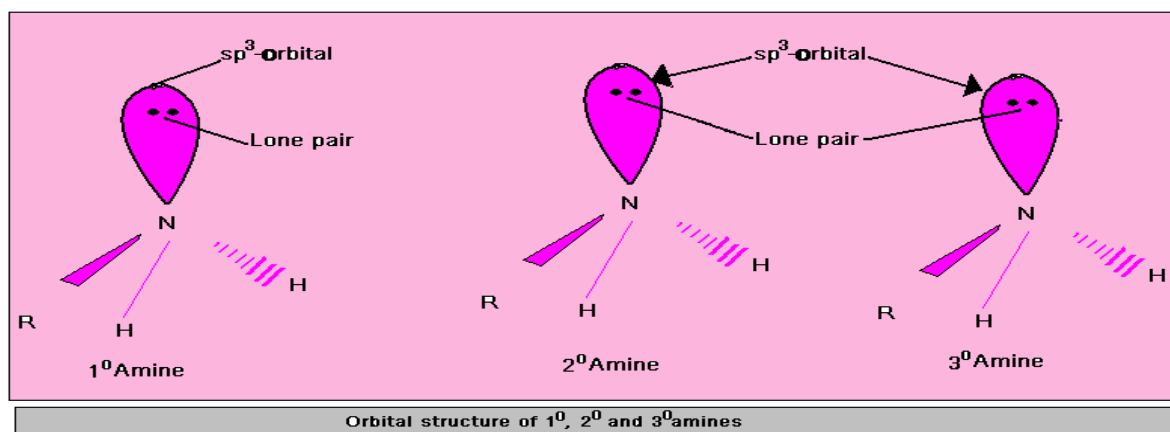
## STRUCTURE OF AMINE: -

Like ammonia, the N atom in amines is also  $sp^3$ - hybridized.

**In  $1^0$  amines**, one of the three half filled  $sp^3$  – orbitals of N overlaps with  $sp^3$  – hybridized orbital of the carbon atom of the alkyl group (or  $sp^2$  – hybridized orbital of the carbon atom of the aryl group) and the remaining two overlap with s – orbitals of hydrogen atoms thereby forming one C – N and two N – H,  $\sigma$  - bonds.

**In  $2^0$  amines**, two of the three  $sp^3$ - hybridized orbital of the carbon atom of the alkyl group ( or  $sp^2$  – hybridized orbitals of carbon atoms of two aryl groups) and one with s- orbital of the H- atom thereby forming two C – N and one N – H,  $\sigma$  bonds . **In  $3^0$  amines**, all the three  $sp^3$ - hybridized orbitals of N overlap with  $sp^3$  – hybridized orbitals of carbon atoms of three alkyl groups (or  $sp^2$ - hybridized orbitals of the carbon atoms of three aryl groups) thereby forming three C – N,  $\sigma$ - bonds.

In all these, three times, the fourth  $sp^3$ - orbital contains the lone pair of electrons as shown in Fig. given below:-



Since lone pair- bond pair repulsions are much greater than bond pair-bond repulsions, therefore, the bond angle between any two adjacent H-atoms or alkyl group decreases from the tetrahedral angle of  $109.28^\circ$  to  $107^\circ$  in  $1^0$  and  $2^0$  amines. However, in case of  $3^0$  amines, due to steric hindrance between the three bulky groups, the bond angle increases from  $107^\circ$  in ammonia to  $108^\circ$  in trimethylamine. Thus, all the types of amines ( $1^0$ ,  $2^0$ , or  $3^0$ ) like  $NH_3$  have pyramidal shape.



### METHODS OF PREPARATION OF PRIMARY AMINES:

**Q.4 Write a note on Hoffmann's synthesis.** (2 marks)

**OR**

**Write a note on Hoffmann's ammonolysis reaction of amines.** (2 marks)

**OR**

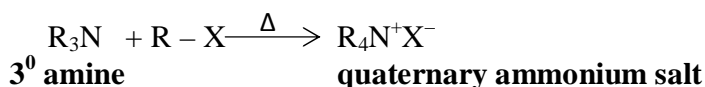
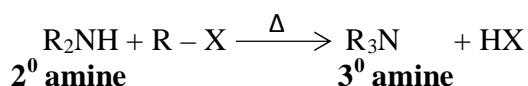
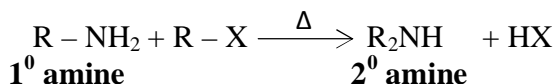
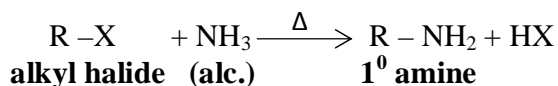
**Explain ammonolysis of alkyl halides.** (2 marks)

**OR**

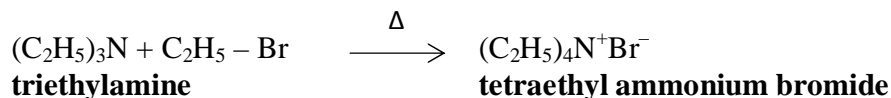
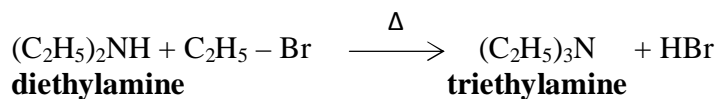
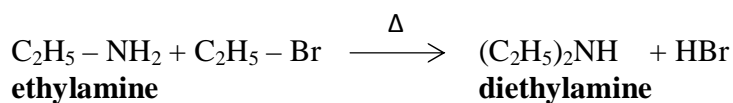
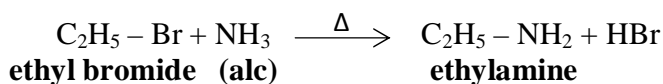
**How will you prepare tetraethyl ammonium bromide from ethyl bromide.** (2 marks)

**Ans.**

When an alkyl halide is heated with **alcoholic ammonia under pressure** at 373K (**100°C**) it gives a mixture of primary, secondary and tertiary amines along with quaternary ammonium salts. This method is known as **Hoffmann Synthesis or ammonolysis of alkyl halide**.



e.g. When ethyl bromide is heated with alcoholic ammonia at 373K it gives a mixture of ethylamine, diethylamine and triethylamine along with tetraethyl ammonium bromide.



**Note:**

- i) **Practically, primary amines are not prepared in laboratory by this method** because a mixture of primary, secondary and tertiary amines along with quaternary ammonium salt is obtained which is difficult to separate.  
However, primary amines can be obtained as major product by using excess of ammonia.

- ii) **Tert-butylamine cannot be prepared by the action of alcoholic ammonia on tert-butyl bromide**, because tertiary alkyl halides on treatment with alcoholic base undergo **elimination** in preference to substitution.

**2. By reduction of oximes, alkyl cyanides and nitroalkanes:**

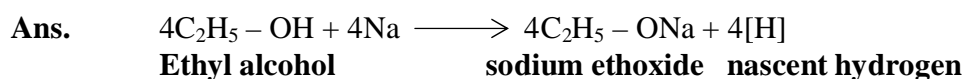
- i) Oximes, alkyl cyanides and nitroalkanes can be catalytically reduced to the corresponding primary amines.  
 ii) They may also be reduced by using  $\text{LiAlH}_4$ .  
 iii) Oximes and alkyl cyanides are reduced by using sodium and ethyl alcohol, while nitroalkanes are particularly reduced by using tin and concentrated.  $\text{HCl}$  to give primary amines.

**a) Reduction of oximes:**

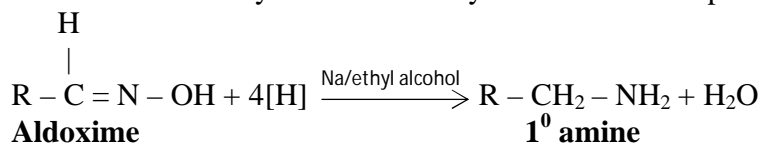
**Q.5 How will you prepare primary amine from aldoxime?** (2 marks)

**OR**

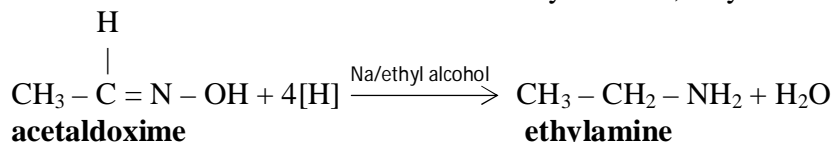
**How will you prepare ethylamine from acetaldoxime?** (1 mark)



Aldoximes are converted by sodium and ethyl alcohol to corresponding primary amines.



When acetaldoxime is treated with sodium and ethyl alcohol, ethylamine is formed.

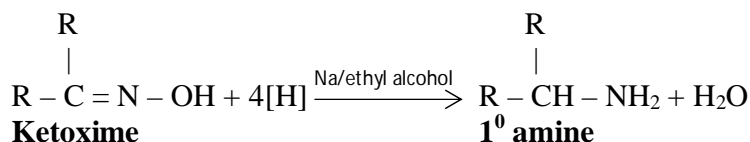


**Q.6 What is the action of Na metal and ethyl alcohol on ketoxime?** (2 marks)

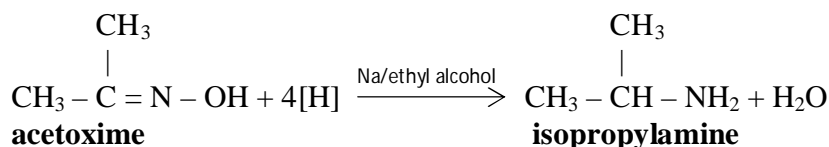
**OR**

**What is the action of Na metal and ethyl alcohol on acetoxime?** (1 mark)

**Ans.** Ketoximes are converted by sodium and ethyl alcohol to the corresponding primary amines.



When acetoxime is treated with sodium and ethyl alcohol, isopropylamine is formed.

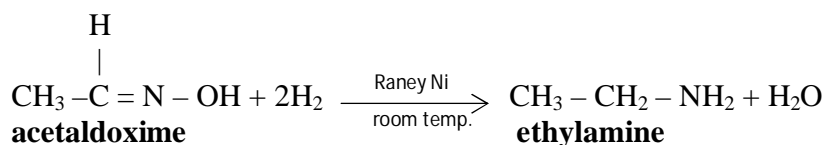
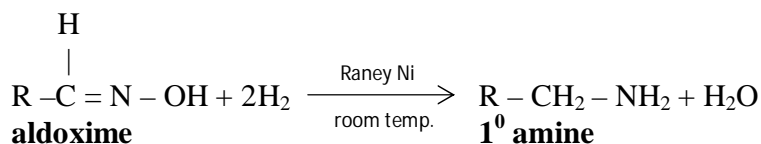


**Q. 7 Explain catalytic hydrogenation of aldoxime using Raney Nickel. (2 marks)**

**OR**

**Explain catalytic hydrogenation of acetaldoxime using Raney Nickel. (1 mark)**

**Ans.** Oximes can be converted into primary amines by catalytic hydrogenation.

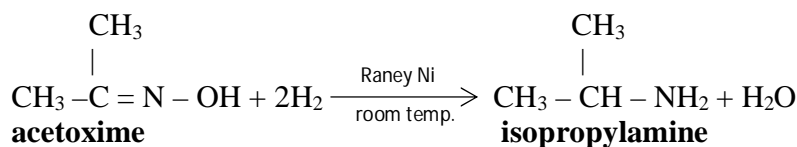
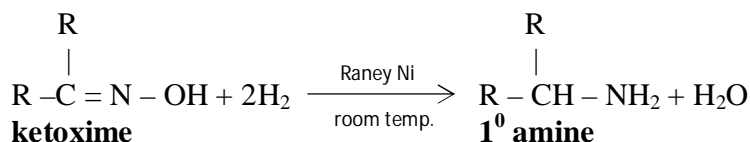


**Q Explain catalytic hydrogenation of ketoxime using Raney Nickel. (2 marks)**

**OR**

**Explain catalytic hydrogenation of acetoxime using Raney Nickel. (1 mark)**

**Ans.**



**b) Reduction of alkyl cyanides (nitriles):**

**Q.8 What is the action of Na metal and alcohol on alkyl cyanides? (2 marks)**

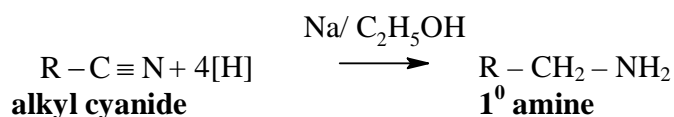
**OR**

**How will you obtain ethyl amine from acetonitrile? (1 mark)**

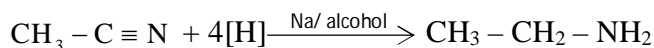
**OR**

**What is the action of Na metal and alcohol on propionitrile? (1 mark)**

**Ans.** Alkyl cyanides are reduced by sodium and ethyl alcohol to the corresponding primary amines. The reaction is called **Mendius reduction**



When acetonitrile is reduced by sodium and alcohol, ethylamine is formed.



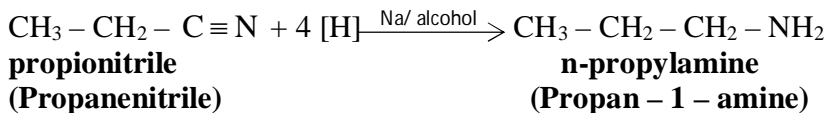
acetonitrile

**(Ethanenitrile)**

ethylamine

**(Ethanamine)**

When propionitrile is reduced by sodium and alcohol, n-propylamine is formed.



**Q.9** Explain catalytic hydrogenation of alkyl cyanides using Raney Ni. (2 marks)

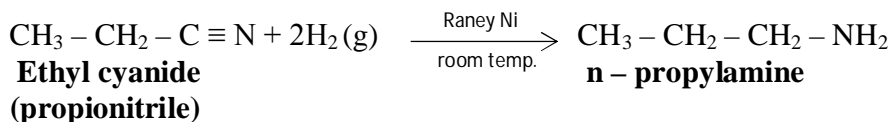
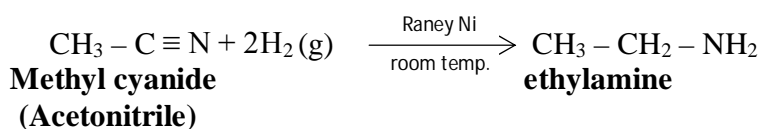
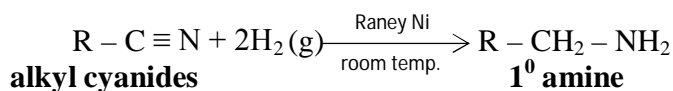
**OR**

What happens on catalytic hydrogenation of acetonitrile in presence of Raney Ni? (1 mark)

**OR**

What is the action of  $\text{H}_2$  (g) and Raney Ni on propionitrile? (1 mark)

**Ans.** Alternatively, alkyl cyanides can be catalytically reduced to primary amines.



**c) Reduction of nitroalkanes:**

**Q.10** What is the action of Sn and conc. HCl on nitroalkanes? (2 marks)

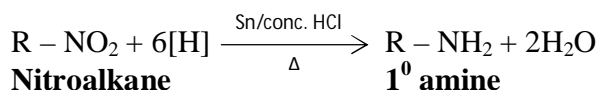
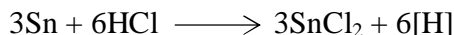
**OR**

What is the action of Sn and conc. HCl on nitromethane? (1 mark)

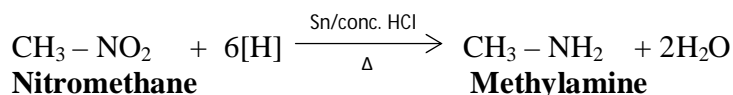
**OR**

What happens when nitroethane is refluxed with Sn and conc. HCl? (1 mark)

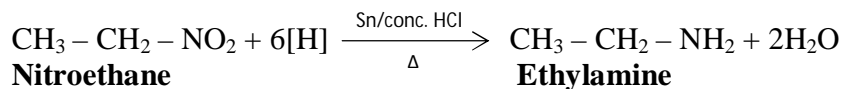
**Ans.** When nitroalkanes are refluxed with tin or iron and concentrated HCl, they give corresponding primary amines.



e.g. When nitromethane is treated with tin or iron and concentrated hydrochloric acid, methylamine is formed.



When nitroethane is refluxed with tin or iron and concentrated hydrochloric acid, it gives ethylamine.



**Q. 11 Explain catalytic hydrogenation of nitroalkanes using Raney Ni. (2 marks)**

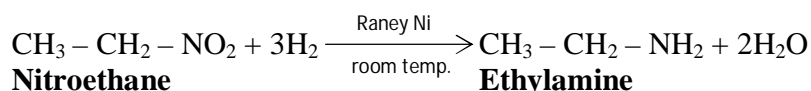
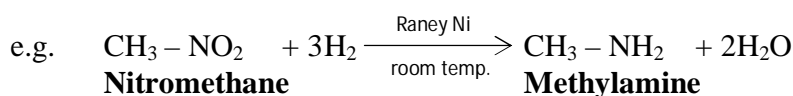
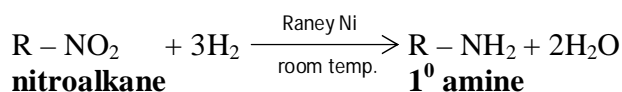
**OR**

**What is the action of  $\text{H}_2$  (g) and Raney Ni on the following:**

**i) Nitromethane (1 mark)**

**ii) Nitroethane (1 mark)**

**Ans.** Nitroalkanes can be catalytically hydrogenated to primary amines.



### REACTIONS OF AMINES:

**Q.12 Explain basic nature of amines. (2 marks)**

**OR**

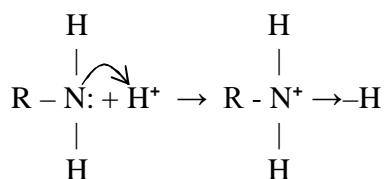
**Explain “amines are weak bases than alkalies”. (1-2 marks)**

**OR**

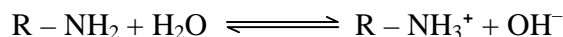
**Explain “Aliphatic amines are stronger bases than ammonia”. (1-2 marks)**

**Ans.**

According to **Lewis theory**, the species which **donates a pair of electrons** is called **base**. The **nitrogen atom** in ammonia carries a **lone pair of electrons**, which can be donated for the formation of a **co-ordinate bond**. Thus **amines are basic in nature and are Lewis bases**.



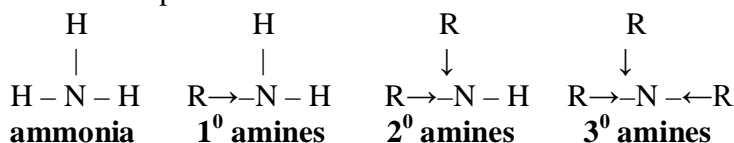
Following equilibrium exists in aqueous solution of amines.



$\text{OH}^-$  is stronger base than amines, hence equilibrium shifts more towards left hand side.

Thus there is low concentration of  $\text{OH}^-$  ions in an aqueous solution of an amine. **Hence, amines are weaker bases than alkalies like NaOH or KOH.**

**Aliphatic amines are stronger bases than ammonia**, due to **electron releasing inductive effect (+I effect)** of the alkyl groups. Electron density on the nitrogen atom increases and the lone pair of electron becomes readily available for protonation.

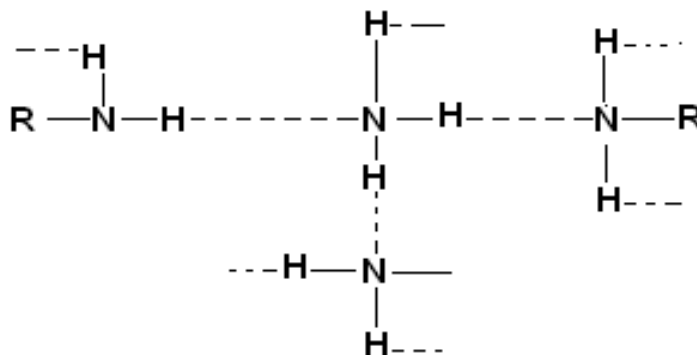


Amines react with mineral acids to form corresponding water soluble salts.

### Physical Properties of Amines: -

Some important physical properties of amines are discussed below:

**1. Colour and odour:** Pure amines are almost colourless but develop colour on keeping in air for long time. This is due to reason that amines, especially aromatic, are readily oxidized in air to form coloured oxidation products. Lower aliphatic amines are gases like ammonia. Primary amines with three or more carbon atoms are liquids with fishy odours. Lower aromatic amines are liquids having amines, in general, are toxic.

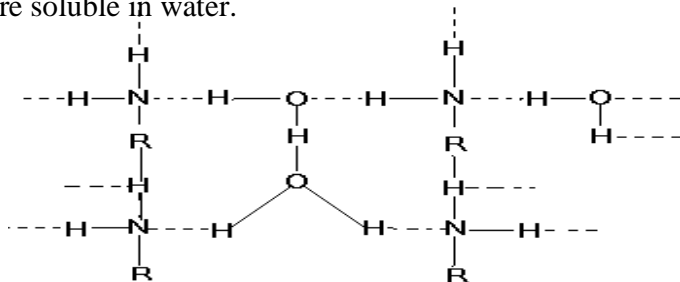


**(Where R is any alkyl or aryl group)**

**2. Boiling Points:** Amines have higher boiling points than hydrocarbons of comparable molecular masses. This is due to the reason that amines being polar, form intermolecular H-bonds (except tertiary amines which do not have hydrogen atoms linked to the nitrogen atom). Primary and secondary amines are engaged in intermolecular association due to hydrogen bonding between nitrogen of one molecule and hydrogen of another molecule. This intermolecular association is more in primary amines than in secondary amines as there are two hydrogen atoms available for hydrogen bond formation in it. Tertiary amines do not have intermolecular association due to the absence of hydrogen atom available for hydrogen bond formation. Therefore, the order of boiling points of isomeric amines is as follows:

Primary > Secondary > Tertiary

**3. Solubility:** All the three classes of aliphatic amines ( $1^0$ ,  $2^0$ , and  $3^0$ ) form H-bonds with water. As a result, lower aliphatic amines are soluble in water.



Methylamine and ethylamine are gases but they are highly soluble in water. However, as the size of the alkyl group increases, solubility decreases (with increase in molecular mass.). The solubility decreases due to a corresponding increase in the hydrocarbon carbon atoms in the molecule. However, amines are quite soluble in organic solvents such as benzene, ether, alcohol, etc. Aromatic amines on the other hand, are insoluble in water. This is due to the larger hydrocarbon part which tends to retard formation of H- bonds. Thus aniline is almost insoluble in water.

**a) Action of dilute hydrochloric acid:**

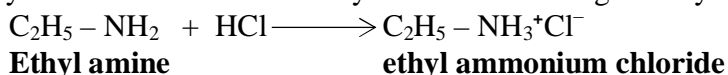
**Q.13** What is the action of dil. HCl on the following:

(i) ethyl amine (ii) diethyl amine (iii) triethyl amine

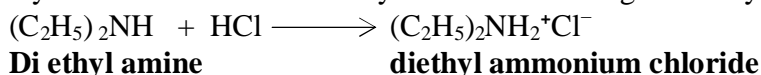
(1 mark each)

**Ans.**

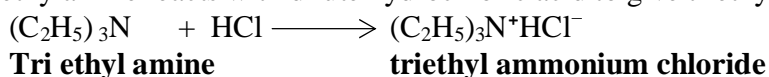
- (i) Ethylamine reacts with dilute hydrochloric acid to give ethyl ammonium chloride.



- (ii) Diethylamine reacts with dilute hydrochloric acid to give diethyl ammonium chloride.



- (iii) Triethylamine reacts with dilute hydrochloric acid to give triethyl ammonium chloride.



**b) Action of dilute sulphuric acid:**

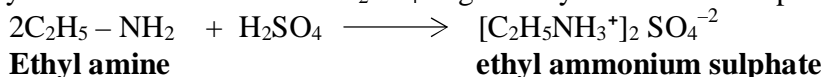
**Q.14** What happens when dil.  $\text{H}_2\text{SO}_4$  reacts with the following:

(i) ethyl amine (ii) diethyl amine (iii) triethyl amine

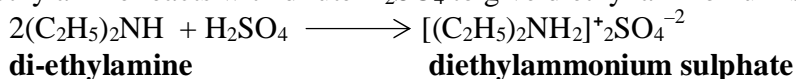
(1 mark each)

**Ans.**

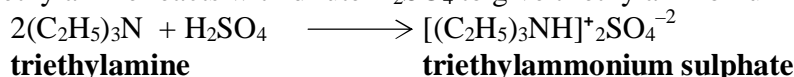
- (i) Ethylamine reacts with dilute  $\text{H}_2\text{SO}_4$  to give ethyl ammonium sulphate.



- (ii) Diethylamine reacts with dilute  $\text{H}_2\text{SO}_4$  to give diethyl ammonium sulphate.



- (iii) Triethylamine reacts with dilute  $\text{H}_2\text{SO}_4$  to give triethylammonium sulphate.



**i) Action of nitrous acid (Distinguishing test):**

**Q.15** *How will you distinguish between primary, secondary and tertiary amines?*  
(2-3 marks)

**OR**

*What is the action of nitrous acid on the following:*

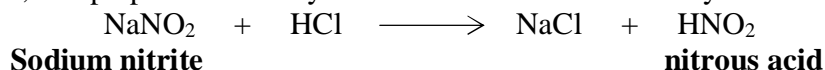
- |       |                  |             |
|-------|------------------|-------------|
| (i)   | Primary amines   | (1-2 marks) |
| (ii)  | Secondary amines | (1-2 marks) |
| (iii) | Tertiary amines  | (1-2 marks) |

**OR**

*What happens when nitrous acid reacts with the following:*

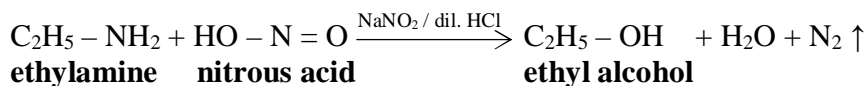
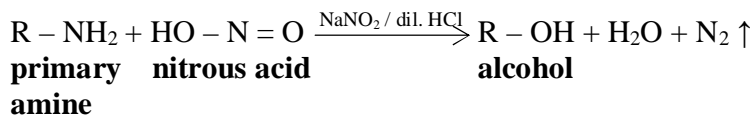
- |       |                |          |
|-------|----------------|----------|
| (i)   | Ethyl amine    | (1 mark) |
| (ii)  | Diethyl amine  | (1 mark) |
| (iii) | Triethyl amine | (1 mark) |

**Ans.** Primary, secondary and tertiary amines react differently with nitrous acid. Since nitrous acid is unstable, it is prepared in situ by the action of cold and dilute hydrochloric acid on sodium nitrite.

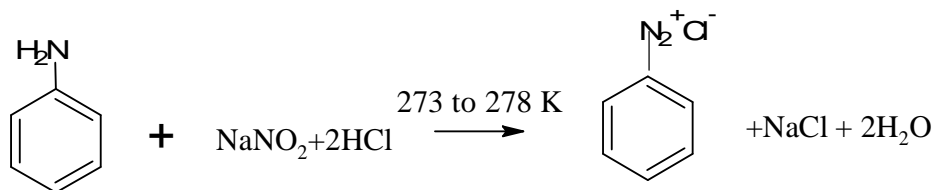


**a) Primary amines:**

**Except methyl amine**, primary amines react with nitrous acid in cold condition (273-278K) to give alcohol and nitrogen gas.



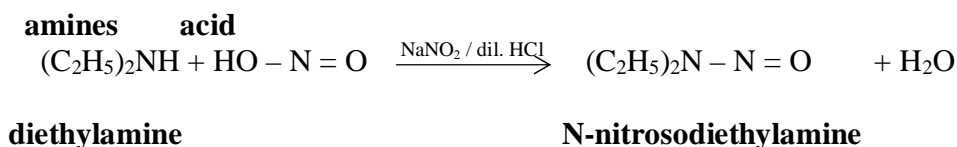
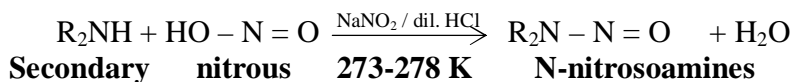
**Aromatic primary amines react with nitrous acid in cold to give diazonium salts**





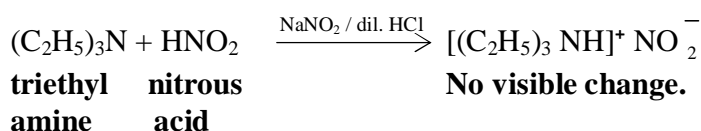
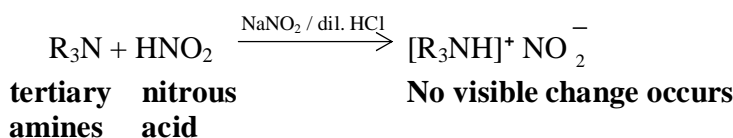
**b) Secondary amines:**

Secondary amines react with nitrous acid to give the N-nitrosoamines which are generally pale yellow oils.



**c) Tertiary amines:**

Tertiary amines react with nitrous acid to form water soluble nitrite salts. As no visible change is observed, it is said that there is no reaction.



**ii) Acetylation of amines:**

**Q.16      Explain acetylation reaction of amines.      (2 marks)**

**Ans.**

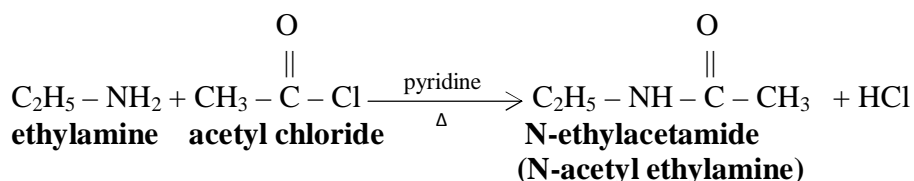
- i)** When – H attached to nitrogen in amines is replaced by acyl group (R – CO –), it is called **acylation of amines**.
- ii)** Primary and secondary amines undergo the acylation on treatment with acid anhydrides or acid chlorides.
- iii)** Tertiary amines do not undergo acylation as there is no hydrogen atom directly attached to the nitrogen atom.
- iv)** Amines can also be distinguished by the action of acetyl chloride or acetic anhydride.
- v)** On reaction with acetyl chloride or acetic anhydride, primary amines give **monoacetyl derivatives (amides)** easily as they are usually well defined crystalline solids.
- vi)** It is difficult to prepare diacetyl derivatives; excess of acetylating agent and high temperature yield diacetyl derivatives.
- vii)** Secondary amines give only **monoacetyl derivatives**.
- viii)** Tertiary amines do not react with acetic anhydride or acetyl chloride due to absence of replaceable hydrogen atom.

**a) Action of acetyl chloride:**

Acid chlorides react rapidly with primary and secondary amines to give **amides**. The base pyridine is added to neutralize the HCl produced.

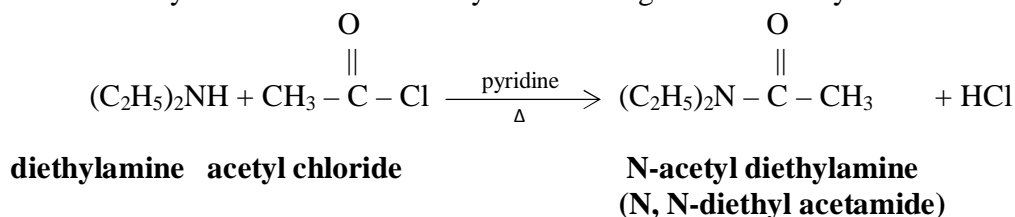
**Q.17** What happens when ethylamine reacts with acetyl chloride? (1 mark)

**Ans.** Ethylamine reacts with acetyl chloride to give monoacetyl derivative.

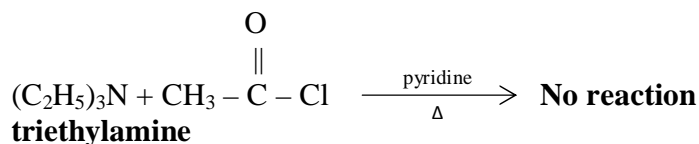


**Q.18** What happens when diethylamine reacts with acetyl chloride? (1 mark)

**Ans.** When diethylamine reacts with acetyl chloride it gives monoacetyl derivative.



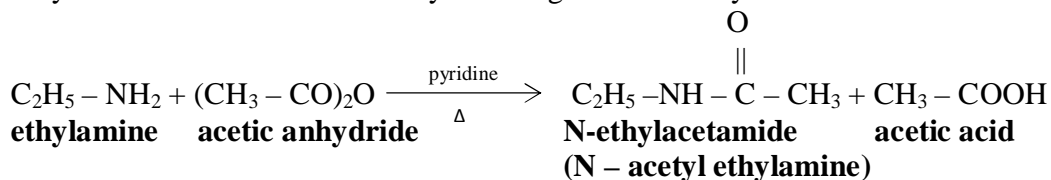
**Note:**



**b) Action of acetic anhydride:**

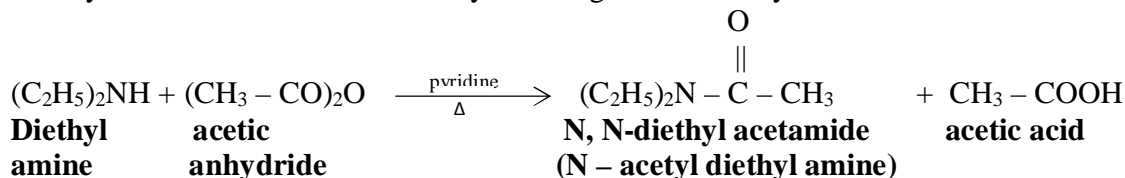
**Q.19** What is the action of acetic anhydride on ethyl amine? (1 mark)

**Ans.** Ethylamine reacts with acetic anhydride to give monoacetyl derivative.



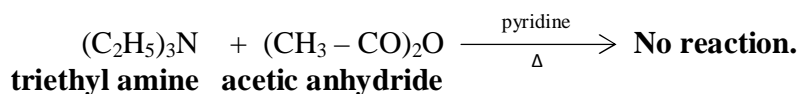
**Q.20** What is the action of acetic anhydride on diethyl amine? (1 mark)

**Ans.** Diethyl amine reacts with acetic anhydride to give monoacetyl derivative.



**Note:**

- i) Acetylation can distinguish 3<sup>0</sup> amines from 1<sup>0</sup> and 2<sup>0</sup> amines, but it cannot distinguish 1<sup>0</sup> and 2<sup>0</sup> amines.
- ii) Triethyl amine does not reacts with acetic anhydride.



**iv) Hofmann's Exhaustive Methylation:**

**Q.21** Write a note on “Hofmann’s Exhaustive Methylation” (2 marks)

**OR**

What happens when methylamine is heated with excess of methyl iodide? (1 mark)

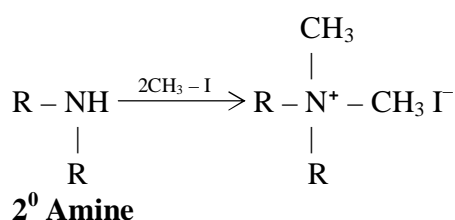
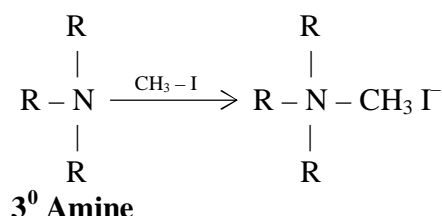
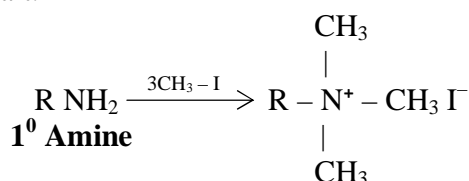
**OR**

How will you prepare diethyl amine from ethylamine? (1 mark)

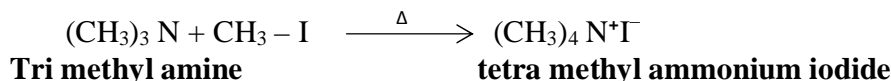
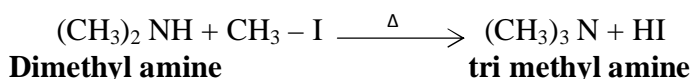
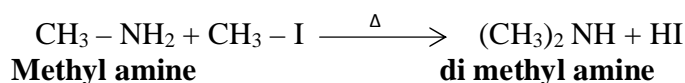
**OR**

How will you obtain diethyl amine from ethyl iodide? (1 mark)

- Ans.**
- The process of introducing an alkyl group in amines is called **alkylation of amines**.
  - The reaction in which a hydrogen atom attached to the nitrogen atom in amines is replaced by methyl group is called **methylation of amines**.
  - Methyl iodide is used as methylating agent.
  - Primary, secondary or tertiary amines react with alkyl halides to give quaternary ammonium halides.
  - 1<sup>o</sup> amine consumes 3 moles of CH<sub>3</sub>I to form its quaternary salt; a 2<sup>o</sup> amine consumes 2 moles of CH<sub>3</sub>I and 3<sup>o</sup> amine consumes only one mole of CH<sub>3</sub>I to form the quaternary salt.



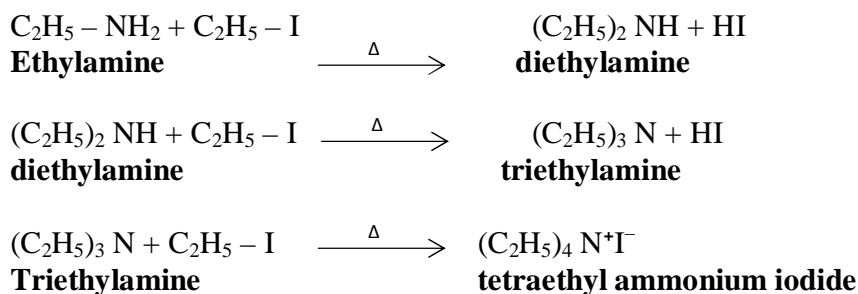
- i) When methylamine is heated with methyl iodide, it gives dimethylamine and trimethylamine along with tetramethyl ammonium iodide.



“The process of converting a primary, secondary or tertiary amine into quaternary ammonium halide on treatment with excess of alkyl halide is called **exhaustive alkylation of amines**.”

However, if the alkyl halide is methyl iodide, it is called **exhaustive methylation of amines**.

- ii) When ethylamine is heated with ethyl iodide, it gives diethylamine and triethylamine along with tetraethyl ammonium iodide.



iii) Quaternary ammonium salts:

*Q.22 How are quaternary ammonium salts formed? (2 marks)*

**OR**

*What happens when tertiary amine is heated with alkyl halide? (2 marks)*

**OR**

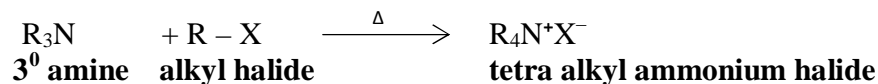
*What is the action of methyl iodide on trimethylamine? (2marks)*

**OR**

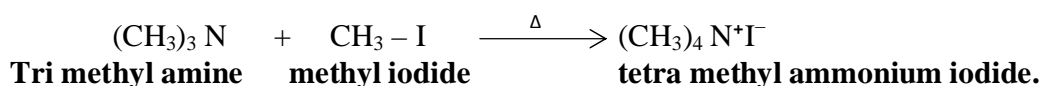
*What happens when ethyl chloride is heated with triethylamine? (2marks)*

**Ans.**

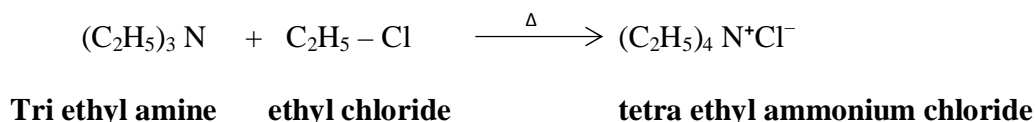
- i) The tetra alkyl ammonium salts are called **quaternary ammonium salts**.
- ii) *“The tetra alkyl derivatives of ammonium salts in which all the four hydrogen atoms are replaced by four same or different alkyl groups are called quaternary ammonium salts.”*
- iii) They are represented as  **$\text{R}_4\text{N}^+\text{X}^-$** .
- iv) **Primary, secondary or tertiary amines** react with excess of alkyl halides to give finally quaternary ammonium halides.
- v) When a **tertiary amine** ( $3^0$ ) is heated with alkyl halide, it gives **quaternary ammonium halide**.



- a) When tri methyl amine is heated with methyl iodide, it gives tetra methyl ammonium iodide.



- b) When triethyl amine is heated with ethyl chloride, it gives tetraethyl ammonium chloride.





## USES OF AMINES:

1. Low molecular mass aliphatic amines such as diethylamine, triethylamine, etc. are used:
  - (i) As reagents in organic synthesis.
  - (ii) As solvents in the laboratory and industry
  - (iii) As intermediates in the manufacture of drugs.
  
2. The quaternary ammonium salts derived from long chain aliphatic tertiary amines are used as detergents.  
For example,  $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Cl}^-$  **n-Hexadecyltrimethylammonium chloride**
  
3. Aromatic amines such as amines are widely used:-
  - (i) In the manufacture of dyes and drugs.
  - (ii) As additives (antioxidants) and vulcanization accelerators in rubber industry.
  - (iii) For the preparation of arenediazonium salts which, in turn, are widely used for preparation of a variety of aromatic compounds via substitution and coupling reactions.
  - (iv) For the preparation of arenediazonium salts which, in turn, are widely used for preparation of a variety of aromatic compounds *via* substitution and coupling reactions.

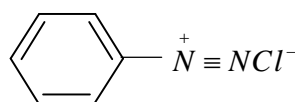
### Questions based on the topic Amines-

- |  |             |
|--|-------------|
| 1) Explain the physical properties of amines.                                | (2/3 Marks) |
| 2) Draw and explain the structure of amines.                                 | (2 Marks)   |
| 3) Give the distinguishing tests for primary, secondary and tertiary amines. | (3 Marks)   |
| 4) Give uses of amines.  | (2/3 Marks) |

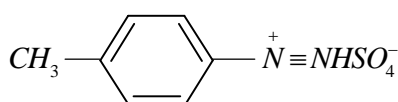
## DIAZONIUM SALTS

Arenediazonium salts were discovered by John Peter Griess in 1958. They have the general formula,  $\text{Ar N}_2^+ \text{X}^-$  where Ar stands for the aryl group and  $\text{X}^-$  may be any anion such as  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{HSO}_4^-$ ,  $\text{BF}_4^-$ , etc.

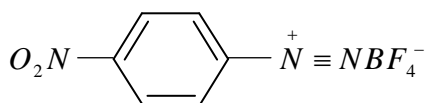
Diazonium salts are named by adding the suffix diazonium to the name of the aromatic hydrocarbon from which they are derived followed by the name of the anion. For example,



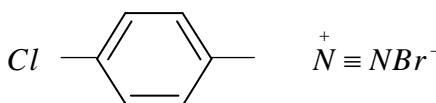
**Benzenediazonium chloride**



**p-Toluenediazonium hydrogen sulphate**



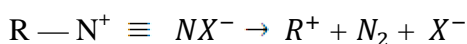
**p-Nitrobenzenediazonium fluoroborate**



**p-Chlorobenzenediazonium bromide**

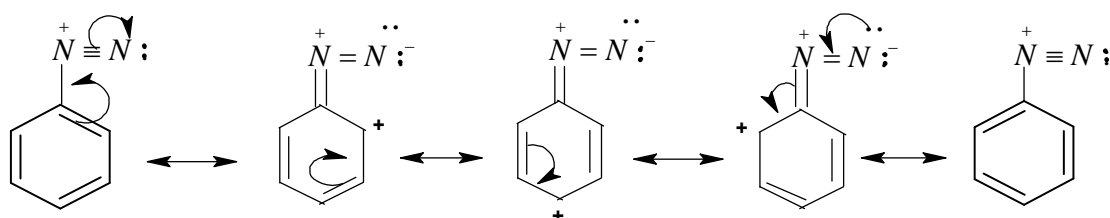
## Stability of Diazonium Salts

Primary aliphatic amines form highly unstable alkanediazonium salts. They rapidly decompose even at low temperatures ( $< 273 - 278 \text{ K}$ ) forming carbocations and nitrogen gas.

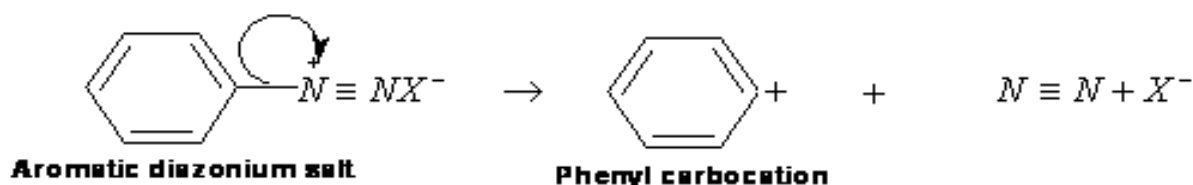


Carbocation

Primary aromatic amines, on the other hand, form arenediazonium salts, which are stable for a short time in solution at low temperatures ( $273 - 278 \text{ K}$ ). Thus, aromatic diazonium (arenediazonium) salts are much more stable than aliphatic diazonium (alkanediazonium) salts. The stability of arenediazonium salts is due to the dispersal of the positive charge over the benzene ring as shown below:



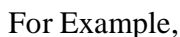
Alternatively, the instability of alkanediazonium salt is due to their tendency to eliminate an exceptionally stable molecule of nitrogen to form carbocations. i.e.,



Since the phenyl (or aryl) carbocation is much less stable than alkyl carbocations, therefore, aromatic diazonium salts have much lower tendency to eliminate nitrogen than aliphatic diazonium salts. In other words, aromatic diazonium salts, are much more stable than aliphatic diazonium salts.

## Preparation of Diazonium Salts:

Aromatic diazonium salts are generally prepared by adding a cold aqueous solution of sodium nitrite to the solution or suspension of a primary aromatic amine in an acid at  $273 - 278 \text{ K}$ .



**General procedure for diazotization:** -

$$\text{NH}_2\text{CONH}_2 + 2 \text{HONO} \rightarrow 2 \text{N}_2 \uparrow + \text{CO}_2 \uparrow + 3\text{H}_2\text{O}$$

Since diazonium salts slowly decompose even at low temperature (273 – 278 K), they are used immediately after preparation.

Arenediazonium salts are generally colourless crystalline solids, highly soluble in water. Many diazonium salts especially nitrates are dangerously explosive in the dry state. Therefore, they are never isolated but are usually prepared *in situ* and used immediately after their preparation. However, certain diazonium salts such as fluoroborates are relatively insoluble in water and are stable enough to be dried and stored. Some diazonium salts also form complexes with metallic salts such as zinc chloride e.g.,  $(\text{ArN}_2^+)_2 \text{ZnCl}_4^{2-}$ . These complexes are generally insoluble.

Arenediazonium salts are highly reactive compounds. Their high reactivity arises due to excellent leaving ability of the diazo group as nitrogen gas,  $N_2$ . They are, therefore, extremely useful synthetic reagents in organic chemistry. The reactions of diazonium salts are broadly divided into two categories:

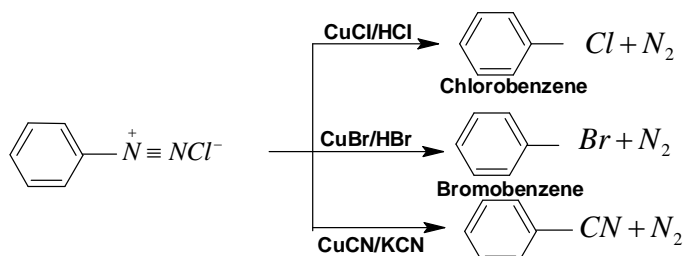
- (a) Reactions involving displacement of diazo group by monovalent atoms or groups.
- (b) Reactions involving retention of diazo group.



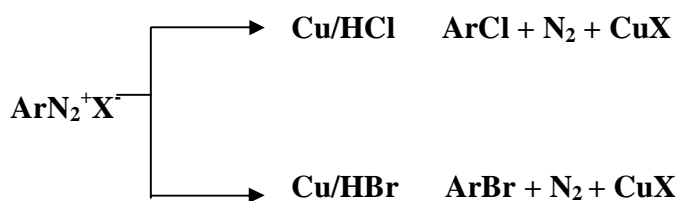
### (a) Reactions involving Displacement of Diazo Group by Monovalent Atoms or group:

Some important reactions of this category along with their synthetic applications are discussed below:

**1. Replacement by Cl, Br, and CN group:** - The  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{CN}^-$  nucleophiles can easily be introduced in the benzene ring in the presence of Cu (I) ion. This reaction is called **Sandmeyer reaction**.

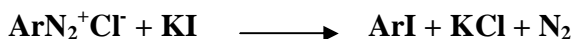


Alternatively, chlorine or bromine can also be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder. This is referred as halogen acid in the presence of copper powder. This is referred as **Gatterman reaction**.

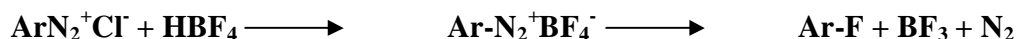


The yield in Sandmeyer reaction is found to be better than Gattermann reaction.

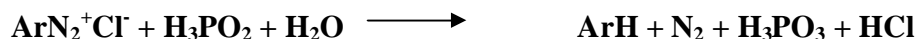
**2. Replacement by iodide ion:** Iodine is not easily introduced into the benzene ring directly. But when the diazonium salt solution is treated with potassium iodide, iodobenzene is formed.



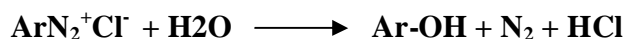
**3. Replacement by fluoride ion:** When arenediazonium chloride is treated with fluoroboric acid, arene diazonium fluoroborate is precipitated which on heating decomposes to yield aryl fluoride.



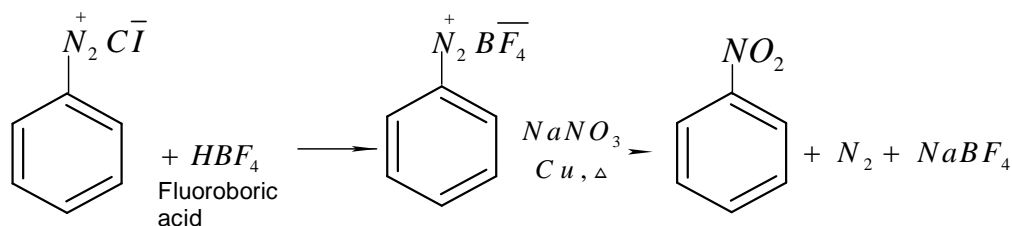
**4. Replacement by H:** Certain mild reducing agents like hypophosphorous acid (phosphinic acid) or ethanol; reduce diazonium salts to arenes and themselves get oxidised to phosphorous acid and ethanol respectively



**5. Replacement by hydroxyl group:** If the temperature of the diazonium salt solution is allowed to raise upto 283 K. the salt gets hydrolyzed to phenol.

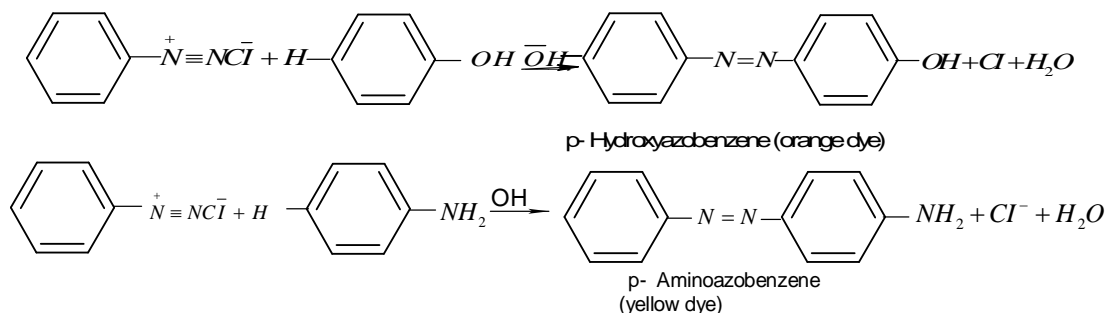


**6. Replacement by –NO<sub>2</sub> group:** When diazonium fluoroborate is heated with aqueous sodium nitrate sodium in the presence of copper, the diazonium group is replaced by –NO<sub>2</sub> group.



**(b) Reactions involving retention of Diazo Group:** -

The azo products obtained have an extended conjugate system having both the aromatic rings joined through the –N = N – bond. These compounds are often coloured and are used as dyes. Benzene diazonium chloride reacts with phenol in which the phenol molecule at its Para position is coupled with the diazonium salt to form p-hydroxyazobenzene. This type of reaction is known as coupling reaction. Similarly the reaction of diazonium salt with aniline yield p-aminoazobenzene. This is an example of electrophilic substitution reaction.



**Importance of Diazonium Salts in the Synthesis of Aromatic Compounds**

- i) From the chemical properties of Diazonium salt we can say that, diazonium salts are very good intermediates for the introduction of –F, –Cl, –Br, –I, –OH, and –NO<sub>2</sub> group into the aromatic ring.
- ii) We know that aryl fluorides and iodides cannot be prepared by direct halogenations but can be easily prepared *via* diazonium salts. Similarly, cyano group cannot be introduced by nucleophilic substitution of chlorine in chlorobenzene but benzonitrile (cyanobenzene) can be easily prepared from diazonium salts.
- iii) Likewise –OH group cannot be directly introduced into the benzene ring. However, these can be easily prepared through diazonium salts.
- iv) Thus, replacement of diazo group by a number of other monovalent groups gives us a useful method for preparing those substituted aromatic compounds which otherwise cannot be prepared either by direct substitution in benzene or the substituted benzene.

### BOARD QUESTIONS

1. Write a short note on Hoffmann bromamide degradation. (March 2013)
2. What is the action of bromine in alkaline medium on