# NITROGEN COMPOUNDS

## Preface

This is a simple and easy topic. This are called alkyl derivative of $NH_3$. Different amines is formed by replacement of hydrogen of ammonia by alkyl group. This chapter deals with methods of preparation of nitrogen compounds, different functional groups of amine, explaination of different mechanisms of different reactions.

This book consists of theoretical & practical explanations of all the concepts involved in the chapter. Each article followed by a ladder of illustration. At the end of the theory part, there are miscellaneous solved examples which involve the application of multiple concepts of this chapter.

Students are advised to go through all these solved examples in order to develope better understanding of the chapter and to have better grasping level in the class.

Total No.of questions in **Nitrogen Compounds** are -

| | |
|---|---|
| In chapter Examples | 10 |
| Solved Examples | 29 |
| **Total No. of questions** | **39** |

## 1. INTRODUCTION

**(a)** Amines are called alkyl derivative of $NH_3$.

**(b)** If a hydrogen atom of $NH_3$ is replaced by an alkyl group then it is called primary amine and possess $–NH_2$(amino) group.

**(c)** If two hydrogen atoms of $NH_3$ are replaced then it is called secondary amine and it posses > NH (Imino) group.

**(d)** If all hydrogen atoms of $NH_3$ are replaced then it is called tert. amine and has a nitrilo N group.

**(e)** Aliphatic amine was discovered by **'Wurtz'.**

**(f)** Aliphatic and aromatic amine shows chain, position, functional and metamerism.

**(g)** $–NH_2$ group is called Amino group.

**(h)** –NH– group is called Imino group.

**(i)** $-\underset{|}{N}-$ group is called Nitrilo group.

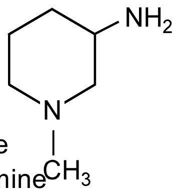
**(j)** N is in $sp^3$ hybridisation and tetrahedral geometry.

**(k)** Bond angle increases from ammonia to 3° amines.

$NH_3$ (107°) < $RNH_2$ < $R_2NH$ < $R_3N$

## Examples based on General Points

**Ex.1** Compound is a -



(A) 1° and 3° amine

(B) Only primary amine

(C) 2° and 3° amine

(D) Only secondary amine **(Ans.A)**

**Sol.** 3–Amino–N–methylpiperidine contains primary and tertiary amino groups.

**Ex.2** The third member of homologous series of dimethyl amine -

(A) $CH_3–CH_2–NH–CH_2–CH_3$

(B) $CH_3–NH–CH_2–CH_2–CH_3$–

(C) $CH_3–NH–CH(CH_3)_2$

(D) 2nd and 3rd are correct **(Ans.D)**

**Sol.** Compounds 2nd and 3rd contains $CH_3$–NH– group.

**Ex.3** Tertiary butyl amine is a-

(A) 1° Amine

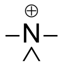
(B) 2° Amine

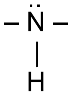
(C) 3° Amine

(D) Quaternary salt **(Ans.A)**

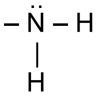
**Sol.** $(CH_3)_3C–NH_2$ is primary amine

**Ex.4** N–atom in quaternary ammonium halide will have the form-

(A) 

(B) 

(C) 

(D) 

**(Ans.A)**

**Sol.** Quaternary ammonium halide is an ionic compound. Hence N carries positive charge.

**Ex.5** $–CONH_2 \xrightarrow{\text{Re duction}} –CH_2NH_2$

In above reaction hybridisation state of carbon changes from ..... → ........

(A) sp ⟶ $sp^2$ (B) sp ⟶ $sp^3$

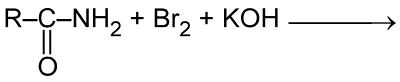
(C) $sp^2$ ⟶ $sp^3$ (D) $sp^2$ ⟶ sp

**(Ans.C)**

**Sol.** Hybridisation state of carbon changes from $sp^2$ to $sp^3$.

## 2. METHODS OF PREPARATION

### 2.1 From Alkanamide :



$$R-\underset{\underset{O}{\|}}{C}-NH_2 + Br_2 + KOH \longrightarrow$$

$$R–NH_2 + KBr + K_2CO_3 + H_2O$$

**Note :** The reaction is called '**Hoffmann Bromamide reaction**' discussed earlier.

### 2.2 From Alkylchloride :

$$R–Cl + H–NH_2 \xrightarrow[200°C]{Cu_2O} R–NH_2 + HCl$$

**Note :** In the above reaction $Cu_2O$ neutralises the evolved HCl in form of $Cu_2Cl_2 + H_2O$ otherwise HCl forms additional salt with amines.

### 2.3 By reduction of Nitro compounds :

Nitro alkanes are reduced catalytically to primary amine.

**(a)** By $LiAlH_4$

**(b)** By Metal and acid (commonly used Sn + HCl or Fe + HCl)

$$RNO_2 \xrightarrow[4H]{\text{reduction}} RNH_2 + 2H_2O$$

**Note : (i)** When reduction with metal is carried out in neutral solution e.g. with Zn dust & $NH_4Cl$ solution, nitro compounds are converted into N-alkyl hydroxyl amine.

$$RNO_2 \xrightarrow[NH_4Cl]{Zn^+} \underset{\text{N-alkylhydroxyl amine}}{RNHOH} + 2H_2O$$

**(ii)** When reduction of nitroalkane is carried out with $SnCl_2$ and conc. HCl, a mixture of N-alkyl hydroxyl amine and oxime are produced.

$$RCH_2NO_2 \xrightarrow[\text{conc. HCl}]{SnCl_2+} \underset{\text{N-Alkyl hydroxy amine}}{RCH_2NHOH} + \underset{\text{Oxime}}{RCH = NOH}$$

**2.4 From Alcohol :**

$$R \boxed{OH + H} NH_2 \xrightarrow[-H_2O]{300°C} R–NH_2 + H_2O$$

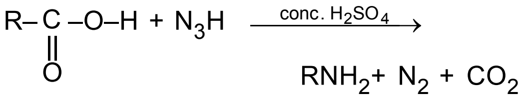
**2.5 From Grignard reagent :**

$$R–Mg–Cl + Cl–NH_2 \longrightarrow R–NH_2 + MgCl_2$$

**2.6 From Alkyl isocyanate (Alkaline Hydrolysis) :**

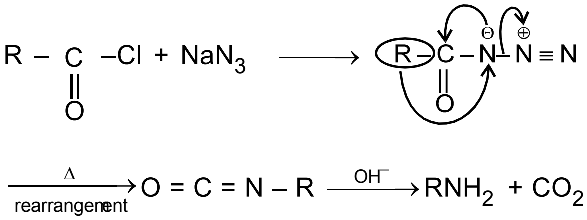
$$R–N=C=O + 2KOH \longrightarrow R–NH_2 + K_2CO_3$$

**2.7 From Alkanoic acid (Schimdt Reaction) :**



$$R–\underset{\underset{O}{\|}}{C}–O–H + N_3H \xrightarrow{\text{conc. } H_2SO_4} RNH_2 + N_2 + CO_2$$

**Note :** Alkyl isocyanate can also be produced by heating the mixture of acyl halide and sodium azide, alkylisocyanate, once it is formed, can easily be hydrolysed into primary amine and $CO_2$.



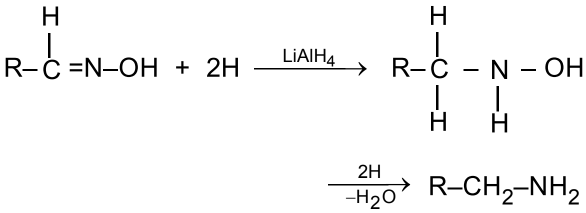
$$R–\underset{\underset{O}{\|}}{C}–Cl + NaN_3 \longrightarrow R–\underset{\underset{O}{\|}}{C}–\overset{\ominus}{N}–\overset{\oplus}{N}\equiv N \xrightarrow[\text{rearrangement}]{\Delta} O = C = N – R \xrightarrow{OH^-} RNH_2 + CO_2$$

**2.8 By Alkyl cyanide (By reduction) :**

$$R–C\equiv N + 4H \xrightarrow[Na+Et\ OH]{LiAlH_4} R–CH_2–NH_2$$

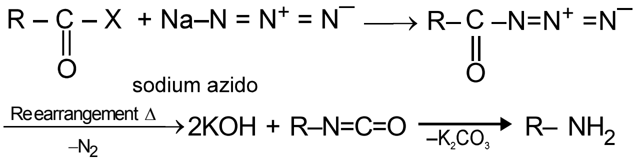
**Note :** When (Na + Et.OH) is used as reducing agent then reaction is called '**Mandius Reaction**'.

**2.9 From Aldoxime (By Reduction) :**



$$R–\overset{\overset{H}{|}}{C}=N–OH + 2H \xrightarrow{LiAlH_4} R–\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}–\underset{\underset{H}{|}}{N}–OH \xrightarrow[-H_2O]{2H} R–CH_2–NH_2$$

**2.10 From Acyl halide :**

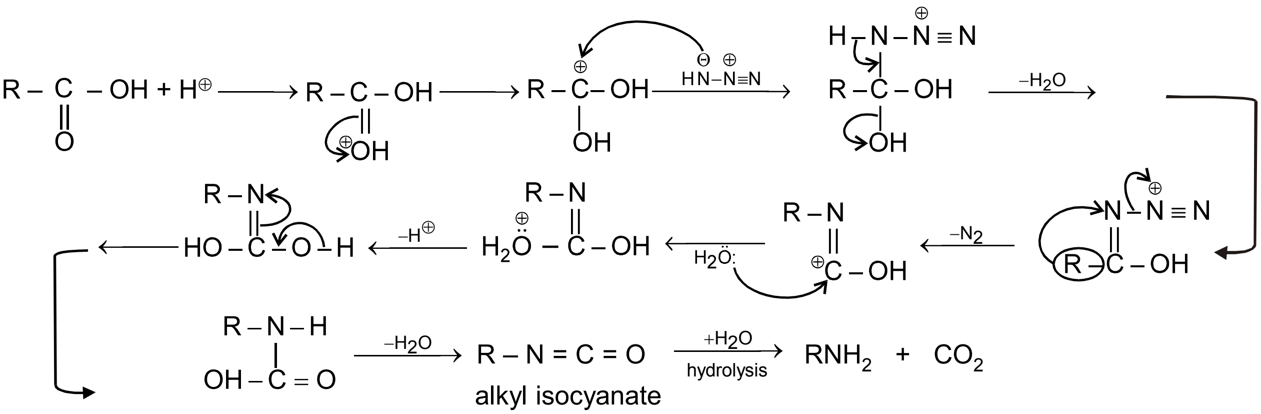


$$R–\underset{\underset{O}{\|}}{C}–X + \underset{\text{sodium azido}}{Na–N = N^+ = N^-} \longrightarrow R–\underset{\underset{O}{\|}}{C}–N=N^+=N^- \xrightarrow[-N_2]{\text{Reearrangement } \Delta} 2KOH + R–N=C=O \xrightarrow{-K_2CO_3} R–NH_2$$

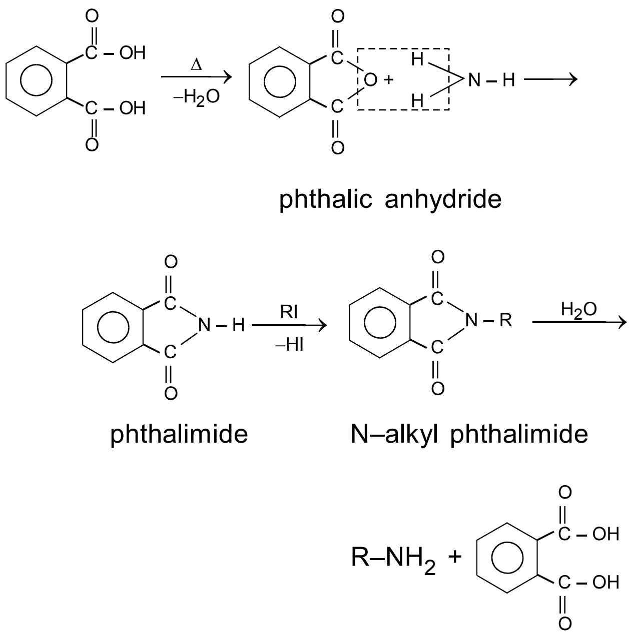
**Note :** It is a good method for preparation of alkyl amine. Reaction is called '**Curtius Reaction**'.

**2.11 From Phthalic acid :**

**Mechanism : –**



$$R–\underset{\underset{O}{\|}}{C}–OH + H^{\oplus} \longrightarrow R–\underset{\underset{\oplus OH}{\|}}{C}–OH \longrightarrow R–\overset{\oplus}{C}–OH \xrightarrow{HN–N\equiv N} R–\overset{H–N–\overset{\oplus}{N}\equiv N}{C}(OH)–OH \xrightarrow{-H_2O} \xrightarrow{-N_2} \xrightarrow{H_2O:} \xrightarrow{-H^{\oplus}} \longrightarrow \underset{OH–C=O}{R–N–H} \xrightarrow{-H_2O} \underset{\text{alkyl isocyanate}}{R–N=C=O} \xrightarrow[\text{hydrolysis}]{+H_2O} RNH_2 + CO_2$$



phthalic anhydride

phthalimide N–alkyl phthalimide

**Note :** It is the best method for preparation of aliphatic amines. The reaction is called '**Gabriel-Phthalimide reaction**'.

**2.12 By Aldehyde or Ketone (reaction with $H_2$ and $NH_3$ in presence of catalyst) :**

Primary amine can be produced by passing a mixture of aldehyde or ketone and large excess of ammonia and hydrogen under pressure (20-150 atm) over raney nickel catalyst at 40-150ºC.

$$R_1R_2C{=}O + NH_3 \xrightarrow{Ni} R_1R_2CHNH_2$$

**Note :** Small amount of secondary and tertiary amines are also produced in this method as by products.

**2.13 By reaction of Aldehyde or Ketones (with ammonium formate or with formamide and subsequent hydrolysis of product)**

Aldehyde and ketones when react with ammonium formate or formamide or the formyl derivative of primary amine on hydrolysis yields primary amine and formate ions.

$$>C = O + 2HCO_2NH_4 \longrightarrow$$

(ammonium formate)

$$>CH - NHCHO + 2H_2O + NH_3 + CO_2$$

$$>C = O + 2HCONH_2 \longrightarrow$$

$$>CH - NH - CHO + CO_2 + NH_3$$

$$>CH - NH - CHO \xrightarrow[\text{in alkaline medium}]{2H_2O}$$

$$>CH - NH_2 + HCOO^{\ominus}$$

## 3. PHYSICAL PROPERTIES

**(a)** Unlike other organic compounds, amines are much more soluble in water. Because All amines form a stronger H- bond with water.

**(b)** Like ammonia, amines are polar compounds and except 3º amines can form intermoleculer H-bonds that's why they have higher boiling points.

**(c)** Boiling points of amines are lesser than alcohols and acids of comparable mol. weight. Because H- bonding in amines is less pronounced in 1º and 2º than that in alcohols and carboxylic acids. Because nitrogen is less electronegative than oxygen.

Thus every question regarding boiling point can be answered on the basis of H - bonding.

**(d)** Boiling points of 1º, 2º and 3º amines follow the order.

1º > 2º > 3º amine.

**(e)** Solubility in water follow the order.

1º > 2º > 3º amine.

This is all due to H- Bonding.

## 4. CHEMICAL PROPERTIES

**(a)** Almost all chemical properties and reactions of amines are governed by basicity of amines.So we should understand it clearly. A lone pair of electron on nitrogen atom in each of amines and ammonia makes them basic in nature.

**(b)** Basicity is nothing but tendency to lose electron.

**(c)** A compound will be more basic, if it can donate electron more readily. Other atoms attached to nitrogn having lone pair of electron, effect it's basicity.

**(d)** Alkyl groups are electron releasing group which increases electron density on nitrogen atom thus, we can expect the order of basicity of ammonia

1º , 2º and 3º amines to be

3º > 2º > 1º > ammonia

**(e)** Some other factors like steric effect, Solvation or hydration and mainly crowding on nitrogen atom by three bulky alkyl groups, decreases the basicity of 3° amines to a great extent and order follows -

$$\underset{(2^\circ)}{R_2NH} > \underset{(1^\circ)}{RNH_2} > \underset{(3^\circ)}{R_3N} > \underset{\text{(ammonia)}}{NH_3}$$

**(f)** This can be also explained on basis of lesser capacity of 3° amine to form H- bonds with water which stabilizes $R_2N^+H$ on because it has only one H-atom

## 5. CHEMICAL REACTIONS

**5.1 Salt formation:** Amine forms salt with mineral acids

$$RNH_2 \xrightarrow{+HCl} [RNH_3]^+ Cl^-$$

$$R_2NH + HCl \longrightarrow [R_2NH_2]^+ Cl^-$$

$$R_3N + HCl \longrightarrow [R_3NH]^+ Cl^-$$

These salts may undergo dealkylation at higher temp.

**For example :** $C_2H_5NH_3^+Cl^- \xrightarrow[\Delta]{} C_2H_5Cl + NH_3$

**5.2 Reaction with water :** Amine gives alkyl ammonium hydroxides which dissociate into ions-

$$RNH_2 + H_2O \rightleftharpoons RNH_3OH \rightleftharpoons RNH_3^+ + OH^-$$

**5.3 Reaction with $HNO_2$ :** This reaction distinguishes 1°, 2° and 3° alcohols.

**(a) Primary Amime :** Except methyl amine, reaction happens at ordinary temp. to evolve $N_2$ Gas.

$$CH_3CH_2NH_2 + HNO_2 \longrightarrow CH_3CH_2OH + N_2 + H_2O$$

Methylamine reacts in different way:

$$CH_3NH_2 + 2HNO_2 \longrightarrow \underset{\text{methyl nitrite}}{CH_3\text{-}O\text{-}N = O} + N_2 + H_2O$$

$$2CH_3NH_2 + 2HNO_2 \longrightarrow \underset{\text{dimethyl ether}}{CH_3\text{-}O\text{-}CH_3} + 2N_2 + 3H_2O$$

**(b) Secondary Amine :** Form nitroso amines with $HNO_2$ (No $N_2$ gas is evolved)

$$R_2NH + HNO_2 \longrightarrow \underset{\text{(yellow)}}{R_2 - N - N = O} + H_2O$$

**Note :** These nitroso amines formed, on warming with phenol and conc. $H_2SO_4$ give a brown or red colour changing to blue or green on further addition of an alkali, colour changes to red . This test is called **Libermann's nitroso test** and used for identification of 2° amines.

**(c) Tertiary Amine :** These are inert to $HNO_2$ but being basic in nature forms salts with it.

$$(CH_3)_3N + HNO_2 \longrightarrow (CH_3)_3\,N - HONO$$

**5.4 Isocyanide test or Carbylamine reaction :**

Primary amines when heated with chloroform and ethanolic KOH solution, alkyl isocyanides is produced which have characteristic foul smell. This reaction is characteristic to the primary amine. This test is known as **carbyl amine test or isocyanide test**.

$$RNH_2 + CHCl_3 + 3KOH \longrightarrow RNC + 3KCl + 3H_2O$$

The reaction proceeds via the formtion of dichloro carbene ($:CCl_2$). In the absence of any lewis base catalyst when $HCCl_3$ reacts only with base, $:CCl_2$ also produced, which is rapidly hydrolysed into CO, $HCO_2^-$ and $Cl^-$.

$$CHCl_3 + OH^\ominus \longrightarrow \underset{\text{(dichloro carbene)}}{:CCl_2} + H_2O + Cl^\ominus$$

$$RNH_2 + :CCl_2 \longrightarrow \underset{\text{(alkyl isocyanide)}}{R - \overset{\oplus}{N} \equiv \overset{\ominus}{C}} + 2HCl$$

$$:CCl_2 \xrightarrow[H_2O]{OH^\ominus} CO + HCO_2^\ominus + 2Cl^\ominus$$

**5.5 Acylation :** 1° and 2° amines react with acetyl chloride or acetic anhydride to form acetyl derivatives.

$$R\text{-}NH_2 + CH_3COCl \longrightarrow RNHCOCH_3 + HCl$$

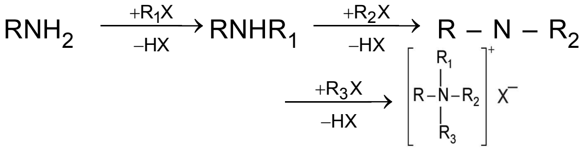
$$R\text{-}NH_2 + (CH_3CO)_2O \longrightarrow RNHCOCH_3 + CH_3COOH$$

$$(CH_3)_2NH + CH_3COCl \longrightarrow (CH_3)_2N - COCH_3 + HCl$$

**Note :** **(a)** Tertiary amines donot undergo this reaction because of absence of replacable H- atom.

**(b)** When Benzoyl chloride is used in place of acetyl chloride reaction is called '**Schotten - Baumann**' reaction.

**5.6 Alkylation :**



$$RNH_2 \xrightarrow[-HX]{+R_1X} RNHR_1 \xrightarrow[-HX]{+R_2X} R - N - R_2 \xrightarrow[-HX]{+R_3X} \left[R-\overset{R_1}{\underset{R_3}{N}}-R_2\right]^+ X^-$$

(quartenary amm. salts.)

**5.7 Oxidation :** All three are oxidised in different ways depending upon conditions of oxidation.

**(a) Primary Amine :** Oxidised to aldehydes and ketones.

$$RCH_2NH_2 \xrightarrow[KMnO_4]{[O]} R\text{-}CH=NH \xrightarrow{H_2O} R\text{-}CHO + NH_3$$

aldimine aldehyde

$$R_2CHNH_2 \xrightarrow[KMnO_4]{[O]} R_2C=NH \xrightarrow{H_2O} R_2C=O + NH_3$$

ketimine ketone

**(b) Secondary Amine :**

$$2R_2NH \xrightarrow[KMnO_4]{[O]} R_2N\text{-}NR_2$$

(tetra-alkyl hydrazine)

$$R_2NH \xrightarrow{\text{caro's acid}} R_2N\text{-}OH$$

(dialkyl hydroxylamine)

**(c) Tertiary Amine :** Resistant to $KMnO_4$ but oxidised by neutral and aqueous $H_2O_2$ in cold to form trialkyl amine oxide.

**Note:** **(i)** $NH_2\text{-}NH_2$ is called hydrazine

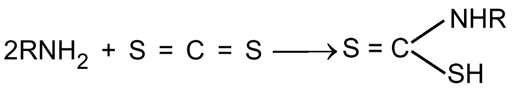
**(ii)** $NH_2\text{-}OH$ is called Hydroxylamine

**5.8 Reaction with Aldehydes and Ketone:**

$$RNH_2 + CH_3CHO \longrightarrow RN = CHCH_3 + H_2O$$

(schiff's base or anil's base)

**5.9 Mustard oil reaction:** A 1° amine reacts with $CS_2$ and then with $HgCl_2$ to form iso thiocyanate having pungent smell of mustard oil.



$$2RNH_2 + S = C = S \longrightarrow S = C\begin{matrix} \diagup NHR \\ \diagdown SH \end{matrix}$$

$$\xrightarrow{HgCl_2} R - N = C = S + RNH_2 + HgS + 2HCl$$

alkyl isothiocyanate

**5.10 Reaction with Grignard reagent :** Since primary and secondary amines have active hydrogen, they on reaction with Grignard reagent give alkanes

$$RNH_2 + CH_3MgBr \xrightarrow{ether} CH_4 + RNH.MgBr$$

$$R_2NH + CH_3MgBr \xrightarrow{ether} CH_4 + R_2N.Mg\ Br$$

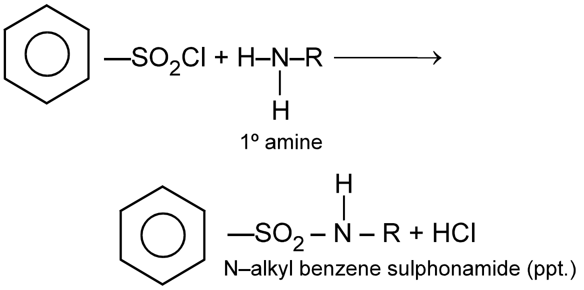
**Note :** Tertiary do not react because of absence of active hydrogen.

**5.11 Reaction with Hinsberg reagent :** This is a method for seperation of 1° , 2° and 3° amines Hinsberg Reagent is

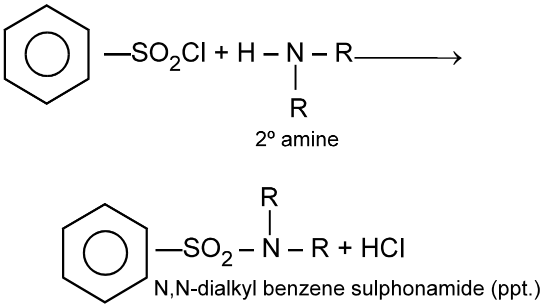
$C_6H_5\text{-}SO_2\text{-}Cl$. (Benzene sulphonyl chloride)

$$RNH_2 + Cl - SO_2\text{-}C_6H_5 \longrightarrow R\text{-}NH\text{-}SO_2\text{-}C_6H_5 + HCl$$

**(a)** Primary amines form N—Alkyl benzene sulphonamide



**(b)** Secondary amines form N, N-dialkyl benzene sulphonamide



**(c)** Tertiary amines do not react because they do not possess a replacable Hydrogen atom.

**5.12 Reaction with Nitrosyl chloride (TILDEN'S REAGENT) :**

$$R\text{-} NH_2 + NOCl \longrightarrow R\text{-}Cl + N_2 + H_2O$$

**5.13 Reaction with $HAuCl_4$ (Chloroauric Acid) and $H_2\ PtCl_6$ (Chloroplatinic Acid) :**

$$R\text{-}NH_2 + HAuCl_4 \longrightarrow [R\text{-}NH^+{}_3]\ AuCl_4^-$$

alkylamine chloraurate

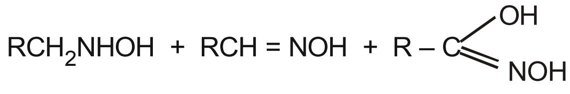
$$2R\text{-}NH_2 + H_2PtCl_6 \longrightarrow [R\text{-}N^+H_3]_2\ PtCl_6^-$$

alkyl amine chloroplatinate

**5.14 Reaction with Caro's acid [$H_2SO_5$] :**

With caro's acid, the oxidation products of primary amine are also dependent on the nature of the alkyl group present in the amine.

$$RCH_2NH_2 \xrightarrow[\text{by } H_2SO_5]{[O]}$$



$$RCH_2NHOH + RCH = NOH + R - C\begin{matrix} \diagup OH \\ \diagdown\!\!\diagdown NOH \end{matrix}$$

(N–alkyl hydroxyl amine) (aldoxime) (hydroxamic acid)

$$R_2CHNH_2 \xrightarrow[\text{by } H_2SO_5]{[O]} R_2C = NOH \text{ (ketoxime)}$$

$$R_3CNH_2 \xrightarrow[\text{by } H_2SO_5]{[O]} R_3CNO \text{ (nitrosoalkane)}$$

### Examples based on Chemical reaction

**Ex.6** The smell of mustard oil is given by the compounds -

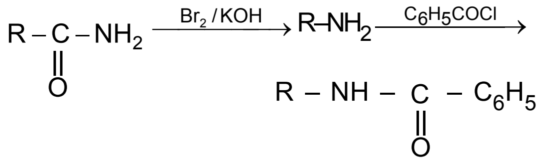
(A) Carbylaminoalkane (B) RNCS

(C) RCNO (D) RCNS

**(Ans. B)**

**Sol.** Alkyl isothiocyanate gives the smell of mustard oil.

**Ex.7**



$$R-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow{Br_2/KOH} R-NH_2 \xrightarrow{C_6H_5COCl} R-NH-\underset{\underset{O}{\|}}{C}-C_6H_5$$

The reactions involved in the above reaction sequence are -

(A) Stephen and Schotten Boumann

(B) Hofmann and Schotten Boumann

(C) Hofmann and Cannizaro

(D) Gabriel and Schotten Boumann

**(Ans. B)**

**Ex.8** When 1-propane amine is treated with $NaNO_2$ and HCl the products will be -

(A) 1-propanol, 2-propanol

(B) Propene

(C) 2-Chloropropane, 1-chloropropane

(D) All of these **(Ans. D)**

**Sol.** The products formed in the reaction between $CH_3CH_2CH_2NH_2$ and $HNO_2$ are

1- Propanol, 2 propanol, propene,

1-Chloropropane and 2-chloropropane

## 6. SEPERATION OF MIXTURES OF AMINES

### 6.1 Fractional distillation :

The mixture of primary, secondary and tertiary amines, may be separated by fractional distillation because their B.P's. are quite different . This method is extensively used in industry.

### 6.2 Hofmann method :

This involves the treatment of the mixture with diethyl oxalate.

**(a)** The primary amine forms a dialkyloxamide, which is a solid

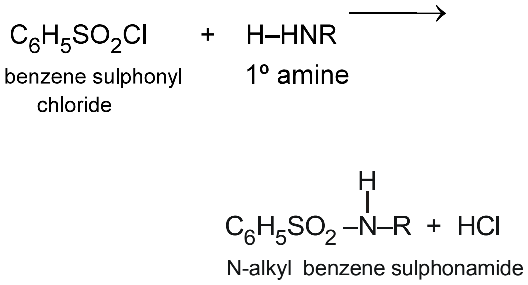
**(b)** The secondary amine forms a dialkyl oxamic ester, which is an oily liquid.

**(c)** The tertiary amine does not react at all.

### 6.3 Hinsberg method :

This involves the treatment of the mixture with benzene sulphonyl chloride (Hinsberg Reagent) and KOH.

**(a)** The primary amine forms N - alkyl benzene sulphonamide which forms a salt with KOH, which is soluble in water.



$$\underset{\text{benzene sulphonyl chloride}}{C_6H_5SO_2Cl} + \underset{1^{o}\text{ amine}}{H-HNR} \longrightarrow \underset{\text{N-alkyl benzene sulphonamide}}{C_6H_5SO_2-\overset{\overset{H}{|}}{N}-R} + HCl$$

**(b)** The secondary amine gives N, N- dialkyl benzene sulphonamide which is insoluble in KOH solution

**(c)** The tertiary amine does not react at all.

## 7. CYANIDES, ISOCYANIDES, ALKYL NITRITES AND NITRO ALKANES

### 7.1 Introduction

Hydrogen cyanide is known to exist as a tautomeric mixture.

$$H-C\equiv N \rightleftharpoons H-N \equiv C$$

Hence, it forms two types of alkyl derivatives which are known as alkyl cyanides and alkyl isocyanides.

| $R-C\equiv N$ | $R-N\equiv C$ |
|---|---|
| Alkyl cyanide | Alkyl isocyanide |

Compounds having the formula RCN are called alkyl cyanides or as nitriles of the acid which they produce on hydrolysis. According to IUPAC system, cyanides are named as alkane nitriles, i.e., in the name of parent hydrocarbon 'nitrile' is suffixed. In naming the hydrocarbon part, carbon of the — CN group is also counted.

| Formula | As cyanide | IUPAC name |
|---|---|---|
| $CH_3CN$<br>(Acetonitrile) | Methyl cyanide | Ethane nitrile |
| $C_2H_5CN$<br>(Propiononitrile) | Ethyl cyanide | Propane nitrile |
| $C_3H_7CN$ | Propyl cyanide | Butane nitrile |
| $C_4H_9CN$ | Butyl cyanide | Pentane nitrile |

The compounds having the formula RNC are called isocyanide or isonitriles. The nomenclature of isocyanides is similar to cyanides.

| Formula | As isocyanides<br>(Comman name) | IUPAC names |
|---|---|---|
| $CH_3NC$ | Methyl isocyanide<br>(Methyl isonitrile) | Methylcarbylamine<br>(Carbylamino methane) |
| $C_2H_5NC$ | Ethyl isocyanide<br>(Ethyl isonitrile) | Ethyl carbylamine<br>(Carbylamino ethane) |
| $C_3H_7NC$ | Propyl isocyanide<br>(Propyl isonitrile) | Propyl carbylamine<br>(Carbylamino propane) |

Isocyanides are also named as alkane isonitrile.

| | |
|---|---|
| $CH_3NC$ | Methane isonitrile |
| $C_2H_5NC$ | Ethane isonitrile |
| $C_3H_7NC$ | Propane isonitrile |

## 7.2 Alkyl cyanides

### 7.2.1 Methods of Preparation

(i) **From alkyl halides :** The alkyl cyanides are prepared by refluxing an alcoholic solution of an alkyl halide with potassium cyanide. The disadvantage of this method is that a mixture of nitrile and isonitrile is formed.

$$RX + KCN \text{ (or NaCN)} \rightarrow \underset{\text{(Major product)}}{\underset{\text{Nitrile}}{RCN}} + \underset{\text{(Minor product)}}{\underset{\text{Isonitrile}}{RNC}}$$

Alkyl halide

(ii) **From acid amides** : Pure nitriles are obtained by dehydration of acid amides with phosphoruspentoxide. Amides are distilled with phosphorus pentoxide, $P_2O_5$.

$$RCONH_2 \xrightarrow[-H_2O]{P_2O_5} RCN$$

$$CH_3CONH_2 \xrightarrow{P_2O_5} CH_3CN + H_2O$$

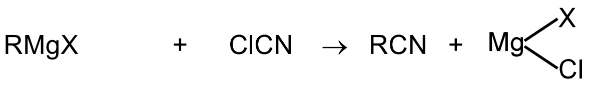
Acetamide Methyl cyanide

Industrially, alkyl cyanides are prepared by passing a mixture of carboxylic acid and ammonia over alumina at 500°C.

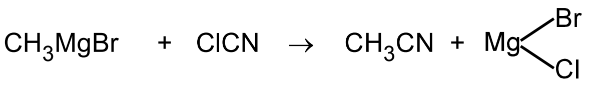
$$\underset{\text{Acid}}{RCOOH} + NH_3 \longrightarrow \underset{\text{Ammonium Salt}}{RCOO\overset{+}{N}H_4}$$

$$\xrightarrow[-H_2O]{Al_2O_3, 500°C} \underset{\text{Amide}}{RCONH_2} \xrightarrow[-H_2O]{Al_2O_3} \underset{\text{Alkyl Cyanide}}{RCN}$$

(iii) **From Grignard reagent :** Grignard reagent reacts with cyanogen chloride to form alkyl cyanides.



$$\underset{\text{Grignard reagent}}{RMgX} + ClCN \rightarrow \underset{\text{Alkyl Cyanide}}{RCN} + Mg\begin{matrix}X\\Cl\end{matrix}$$



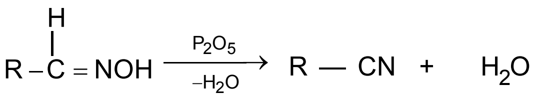
$$\underset{\text{Methyl magnisium bromide}}{CH_3MgBr} + \underset{\text{Cyanogen chloride}}{ClCN} \rightarrow \underset{\text{Methylcyanide}}{CH_3CN} + Mg\begin{matrix}Br\\Cl\end{matrix}$$

(iv) **From primary amines :** Primary amines are dehydrogenated when passed over copper or nickel at high temperature to form alkyl cyanides. This is also a commercial method.

$$\underset{\text{Primary amine}}{RCH_2NH_2} \xrightarrow[500°C]{\text{Cu or Ni}} RCN + 2H_2$$

$$\underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow[500°C]{\text{Cu or Ni}} \underset{\text{Methyl cyanide}}{CH_3CN} + 2H_2$$

(v) **From oximes :** Aldoximes are converted into alkyl cyanides when distilled with phosphorus pentoxide or acetic anhydride. The dehydration of aldoximes occurs.



$$\underset{\text{Aldoxime}}{R-\overset{\overset{H}{|}}{C}=NOH} \xrightarrow[-H_2O]{P_2O_5} \underset{\text{Alkyl cyanide}}{R-CN} + H_2O$$

## 7.3 Physical properties :

(i) Alkyl cyanides are neutral substances with pleasant odour, similar to bitter almonds.

(ii) Lower members containing upto 15 carbon atoms are liquids, while higher members of carbon atoms in the molecule.

(iii) They are soluble in water. The solubility decreases with the increase in number of carbon atoms in the molecule.

(iv) They are soluble in organic solvents.

(v) They are poisonous but less poisonous than HCN.

## 7.4 Chemical properties :

(i) **Hydrolysis :** Alkyl cyanides are hydrolysed by both acid and alkalies. On partial hydrolysis amides are formed while on complete hydrolysis acids are obtained.

$$\underset{\text{Alkyl cyanide}}{RCN} \xrightarrow[H^+]{H_2O} \underset{\text{Amide}}{RCONH_2} \xrightarrow[H^+]{H_2O} \underset{\text{Acid}}{RCOOH} + NH_3$$

$$\underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow[H^+]{H_2O} \underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[H^+]{H_2O} \underset{\text{Acetic acid}}{CH_3COOH} + NH_3$$

(ii) **Reduction :** When reduced with hydrogen in presence of Pt or Ni, or $LiAlH_4$ (Lithium aluminium hydride) or sodium and alcohol, alkyl cyanides yield primary amines.

$$\underset{\text{Alkyl cyanide}}{RCN} \xrightarrow{4H} \underset{\text{Primary amine}}{RCH_2NH_2}$$

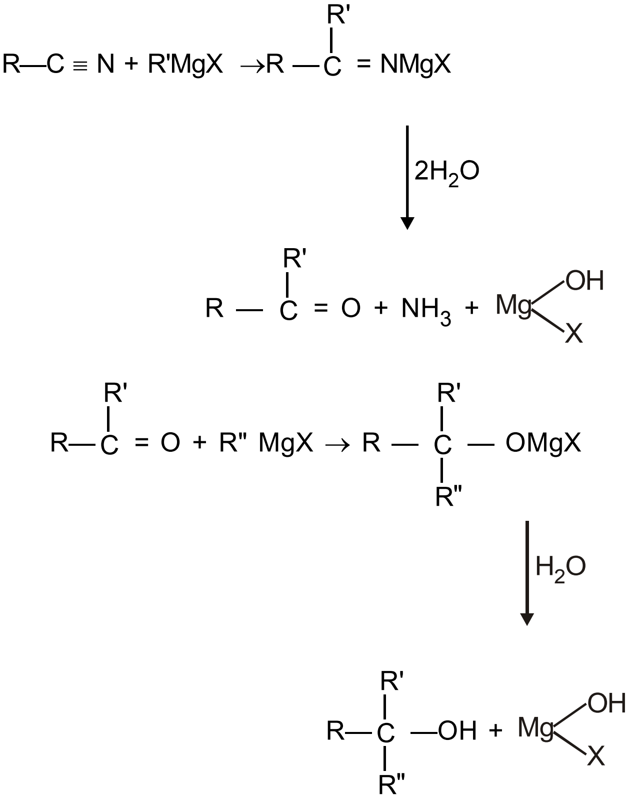
However, when a solution of alkyl cyanides in ether is reduced with stannous chloride and hydrochloric acid and then steam distilled, an aldehyde is formed (**Stephen's reaction**).

$$R-C\equiv N \xrightarrow[{[2H]}]{SnCl_2/HCl} \underset{\text{Imine hydrochloride}}{RCH = NH.HCl}$$

$$\downarrow H_2O$$

$$\underset{\text{Aldehyde}}{RCHO} + NH_4Cl$$

(iii) **Reaction with Grignard reagent :** With Grignard's reagent, an alkyl cyanide forms a ketone which further reacts to form a tertiary alcohol.

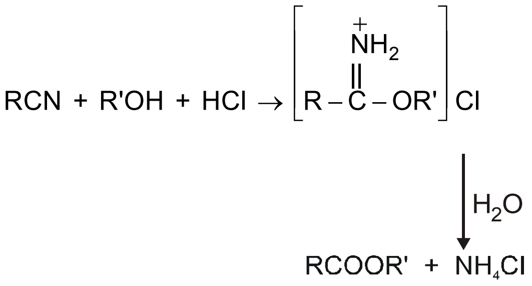


$$R-C\equiv N + R'MgX \rightarrow R-\overset{\overset{R'}{|}}{C}=NMgX \xrightarrow{2H_2O} R-\overset{\overset{R'}{|}}{C}=O + NH_3 + Mg\langle^{OH}_{X}$$

$$R-\overset{\overset{R'}{|}}{C}=O + R''MgX \rightarrow R-\underset{\underset{R''}{|}}{\overset{\overset{R'}{|}}{C}}-OMgX \xrightarrow{H_2O} R-\underset{\underset{R''}{|}}{\overset{\overset{R'}{|}}{C}}-OH + Mg\langle^{OH}_{X}$$

Tertiary alcohol

(iv) **Alcoholysis :** When an alkyl cyanide is refluxed with an anhydrous alcohol in presence of dryHCl, an imido ester is formed, which on hydrolysis with water forms ester.



$$RCN + R'OH + HCl \rightarrow \left[R-\overset{\overset{\overset{+}{N}H_2}{||}}{C}-OR'\right]Cl \xrightarrow{H_2O} \underset{\text{Ester}}{RCOOR'} + NH_4Cl$$

**Uses :** Alkyl cyanides are important intermediates in the laboratory synthesis of a large number of compounds like acids, amides, ester, amines, etc.

## 7.5 Alkyl isocyanides

### 7.5.1 Methods of Preparation

**(i) From alkyl halides :** The isocyanides are prepared by refluxing an alkyl halide solution in alcohol with silver cyanide. The isonitrile is the main product but small amount of nitrile is also formed.

$$R-X + AgCN \longrightarrow RNC + RCN$$

Alkyl halide Isocyanide Cyanide
(Isonitrile) (Nitrile)
Main product Minor product

$CH_3Cl + AgCN \longrightarrow CH_3NC + CH_3CN$

Methyl chloride Methyl isocyanide
(Main product)

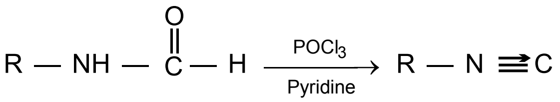
This method is, thus, suitable for preparing isocyanides.

**(ii) From Primary Amines : (Carbylamine reaction) :** Alkyl isocyanides may be prepared by heating primary amines with chloroform and alcoholic potash.

$RNH_2 + CHCl_3 + 3KOH \rightarrow RNC + 3KCl + 3H_2O$

Primary amine Chloroform Isocyanide

**(iii) From N-alkyl formamides** : N-alkyl formamides when dehydrated with $POCl_3$ in presence of pyridine give isocyanides.



$$R-NH-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow[\text{Pyridine}]{POCl_3} R-N \rightleftarrows C$$

N-alkyl formamide Isocyanide

### 7.5.2 Physical properties :

(i) Alkyl isocyanides are colourless, unpleasant smelling liquids.

(ii) The boiling points of isonitiriles are lower than corresponding alkyl cyanides.

(iii) They are insoluble in water but freely soluble in organic solvents.

(iv) Isonitriles are much more poisonous than isomeric cyanides.

### 7.5.3 Chemical properties :

(i) **Hydrolysis** : Alkyl isocyanides are hydrolysed by dilute mineral acids (but not by alkalies ) to form primary amines.

$RN \rightleftarrows C + 2H_2O \xrightarrow{H^+} RNH_2 + HCOOH$

Alkyl isocyanide Primary amine Formic acid

(ii) **Reduction :** When reduced with nascent hydrogen or hydrogen in presence of nickel, isocyanides form secondary amines containing methyl as one of the alkyl groups.

$R-N \rightleftarrows C + 4H \longrightarrow RNHCH_3$

Alkyl isocyanide Secondary amine

(iii) **Action of heat :** When heated for sometime at 250°C, a small amount of isonitrile changes into isomeric nitrile.

$RNC \xrightarrow{heat} RCN$

(iv) **Addition reaction :** Alkyl isocyanide give addition reactions due to presence of unshared electron pair on carbon atom.

$R : N :::C : \text{ or } R - \overset{+}{N} \equiv \overset{-}{C}$

The following are some of the addition reactions shown by alkyl isocyanides.

$RNC + \underset{\text{(Halogen)}}{X_2} \longrightarrow RNCX_2$ Alkyl iminocarbonyl halide

$RNC + S \longrightarrow RNCS$ Alkyl isothiocyanate

$RNC + HgO \longrightarrow RNCO + Hg$
(Alkyl isocyanate)

### 7.6 Distinction between Ethyl Cyanide and Ethyl Isocyanide

| Test | Ethyl Cyanide ($C_2H_5CN$) | Ethyl isocyanide ($C_2H_5NC$) |
|---|---|---|
| 1. Odour | Not unpleasant | Extremely unpleasant |
| 2. Solublity in water | Soluble | Insoluble |
| 3. Hydrolysis | Yields propionic aci | Produces ethyl amine |
| 4.Reduction | Gives propylamine | Gives ethylmethylamine |
| | (Primary amine) | (Secondary amine) |
| 5.Heating at 250°C | No effect | Changes to ethyl cyanide |

## Examples based on Cynides & Isocynides

**Ex.9** Alkyl halide reacts with AgCN to form –
(A) Alcohol (B) Cyanide
(C) Isocyanide (D) Both B & C

**(Ans.D)**

**Sol.** In the above reaction major product is Isocyanide and minor product is Cyanide.

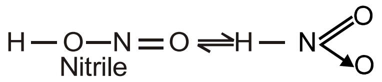
**Ex.10** Amide on heating with $P_2O_5$ gives –
(A) Alkane nitrile (B) Alkyl halide
(C) Amine (D) None

**(Ans.A)**

**Sol.** See text.

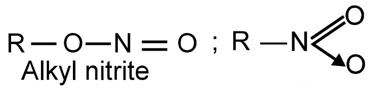
## 7.7. Alkyl nitrites and nitro alkanes

Nitrous acid exists in two tautomeric forms.



Nitro form

Corresponding to these two forms, nitrous acid gives two types of derivatives , i.e., alkyl nitrites and nitro alkanes.



Nitro alkane

The most important alkyl nitrite is ethyl nitrite.

### 7.7.1 Ethyl nitrite $C_2H_5O–N=O$

(i) It is prepared by adding concentrated hydrochloric acid or sulphuric acid to aqueous solution of sodium nitrite and ethyl alcohol at very low temperature (0°C).

$NaNO_2 + HCl \rightarrow NaCl + HNO_2$

$C_2H_5I + KONO \rightarrow C_2H_5ONO + KI$

Ethyl nitrite

(ii) **From Ethyl iodide :**

| $C_2H_5I$ + | KONO → | $C_2H_5ONO$ + | KI |
|---|---|---|---|
| Ethyl iodide | Pot. nitrite | Ethyl nitrite | |

(iii) It is also prepared by the action of nitrogen trioxide, $N_2O_3$ on ethyl alcohol.

$2C_2H_5OH + N_2O_3 \rightarrow 2C_2H_5ONO + H_2O$

**7.7.2 Properties :** Ethyl nitrite is a gas at ordinary conditions. It has a characteristic smell of apples. It is insoluble in water.

It is hydrolysed by aqueous alkalies or acids into ethyl alcohol.

$$C_2H_5ONO + H_2O \xrightarrow{NaOH} C_2H_5OH + HNO_2$$

When reduced with tin and HCl, it produces ethyl alcohol and ammonia.

$$C_2H_5ONO + 6H \xrightarrow[HCl]{Sn} C_2H_5OH + NH_3 + H_2O$$

Small amount of hydroxylamine is also formed.

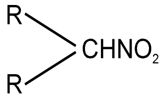
$$C_2H_5ONO + 4H \rightarrow C_2H_5OH + NH_2OH$$

It accelerates pulse rate and lowers blood pressure and reduces hypertension and severe pain of angina pictoris so it is used as a medicine for the treatment of asthama and heart diseases. Its 4% solution (alcoholic) commonly known as "sweet spirit of nitre" used as diuretic.

### 7.7.3 Nitro alkanes

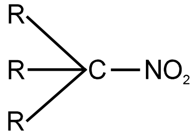
Nitro alkanes are the derivatices of alkanes. They are isomeric to nitrites (esters). They are classified as primary, secondary and tertiary depending on the nature of carbon atom to which nitro group is linked.

$RCH_2NO_2$
Primary nitro alkane ;



;

Secondary nitro alkane



Tertiary nitro alkane

### (a) General Methods of Preparation

(i) **From alkyl halides :** They are prepared by heating an alkyl halide with aqueous ethanolic solution of silver nitrite.

$R — X + AgNO_2 \rightarrow R — NO_2 + AgX$

Some quantity of alkyl nitrite is also formed in the reaction. It can be removed by fractional distillation since alkyl nitrites have much lower boiling points as compared to nitro alkanes.

(ii) **Nitration :** Paraffins (alkanes) after hexane can be nitrated directly with concentrated nitric acid. The nitration is carried out in liquid phase or in vapour phase at about 400°C.

(iii) By boiling aqueous solution of sodium nitrite with α-halogen acids α-nitro substituted acids are first formed which lose $CO_2$ to form nitro alkanes.

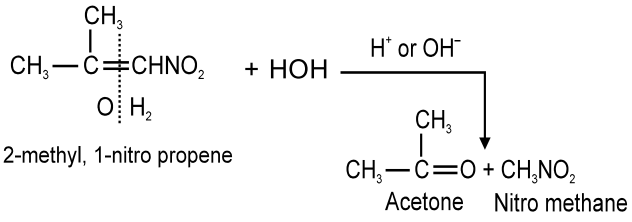
$$CH_2ClCOOH \xrightarrow[-NaCl]{NaNO_2} CH_2NO_2COOH$$

α-Chloro acetic acid α-Nitro acetic acid

$CH_3NO_2 + CO_2$

Nitro methane

(iv) A recent method is by the hydrolysis of α-nitro alkene with water or acid or alkali.



**7.7.4 Physical properties :** Nitro alkanes are colourless pleasant smelling liquids. Their boiling points are much higher than isomeric alkyl nitrites. They are less soluble in water but readily soluble in organic solvents.

### 7.7.5 Chemical properties :

(i) **Reduction :** Nitro alkanes are reduced to corresponding primary amines with Sn and HCl or Iron and HCl or catalytic hydrogenation using nickel as catalyst.

$$RNO_2 + 6H \rightarrow RNH_2 + 2H_2O$$

However, when reduced with a neutral reducing agent (zinc dust + $NH_4Cl$), nitro alkanes fromhydroxylamines.

$$R-NO_2 + 4H \xrightarrow{Zn+NH_4Cl} R-NHOH + H_2O$$

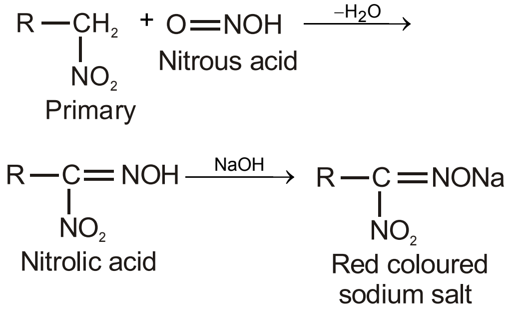
(ii) **Hydrolysis :** Primary nitro alkanes on hydrolysis with HCl or 80% $H_2SO_4$ produce hydroxylamine and carboxylic acid.

$$RCH_2NO_2 + H_2O \rightarrow RCOOH + NH_2OH$$

Secondary nitro alkanes on hydrolysis form ketones

$$2R_2CHNO_2 \xrightarrow{HCl} \underset{\text{Ketone}}{2R_2CO} + N_2O + H_2O$$

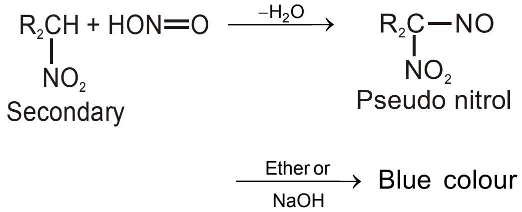
(iii) **Action of nitrous acid :** Nitrous acid reacts with primary secondary and tertiary nitroalkanes differently, Primary nitro compound forms nitrolic acid which dissolves in alkali to give red solution.



$$\underset{\text{Primary}}{R-\underset{NO_2}{\underset{|}{CH_2}}} + \underset{\text{Nitrous acid}}{O{=}NOH} \xrightarrow{-H_2O}$$

$$\underset{\text{Nitrolic acid}}{R-\underset{NO_2}{\underset{|}{C}}{=}NOH} \xrightarrow{NaOH} \underset{\text{Red coloured sodium salt}}{R-\underset{NO_2}{\underset{|}{C}}{=}NONa}$$

Secondary nitro compounds give pseudo nitrols which are colourless solids but dissolvesin ether or NaOH giving blue colouration.



$$\underset{\text{Secondary}}{R_2\underset{NO_2}{\underset{|}{CH}}} + HON{=}O \xrightarrow{-H_2O} \underset{\text{Pseudo nitrol}}{R_2\underset{NO_2}{\underset{|}{C}}-NO}$$

$$\xrightarrow[NaOH]{Ether\ or} \text{Blue colour}$$

Tertiary nitro alkanes do not react with nitrous acid.

The different behaviour of nitrous acid with p., sec., and tert. nitro alkanes forms the basis of the **Victor Meyer's Test** for the distinction of p., sec. and tert. alcohols.

(vi) **Thermal decomposition :** Upon rapid heating, nitro alkanes decompose with great voilence.Advantage is taken of this reaction in the commercial use of nitro alkanes as explosives.

(v) **Halogenation :** Primary and secondary nitro alkanes are readily halogenated in the $\alpha$-positin by treatment with chlorine or bromine, Chloropicrin is formed when nitro methane reacts with $Cl_2$ in presence of NaOH. Chloropicrin is an improtant insecticide.

$$CH_3 - NO \xrightarrow[NaOH]{Cl_2} CCl_3NO_2$$

Chloropicrin

### 7.7.6 Uses : Nitro alkanes are used :

(i) As solvents for polar substances such as cellulose acetate, synthetic rubber, etc.

(ii) As explosives.

(iii) For the preparation of amines, hdroxylamines, etc.

# SOLVED EXAMPLES

**Ex.1** An example of a primary amine is -

(A) n-Propylamine

(B) Isopropylamine

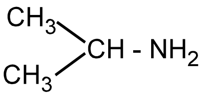
(C) t-Butyl amine

(D) All of above **(Ans.D)**

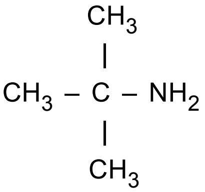
**Sol.** All the compounds given above are examples of primary amine.

$CH_3\,CH_2\,CH_2 - NH_2$

n-propyl amine



Iso propyl amine



t-butyl amine

**Ex.2** For the elimination of $\overset{O}{\overset{\|}{-C-}}$ group of amide following reaction is used -

(A) Hoffmann hypobromite reaction

(B) Kolbe reaction

(C) Hunsdiecker reaction

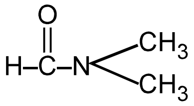
(D) Liebermann's reaction **(Ans.A)**

Sol. For the formation of $RNH_2$ from $RCONH_2$, NaOH and $Br_2$ are used as reagent. It is called Hofmann hypobromite reaction.

**Ex.3** Which of the following is hydrolysed to give secondary amine -

(A) Alkyl cyanide

(B)

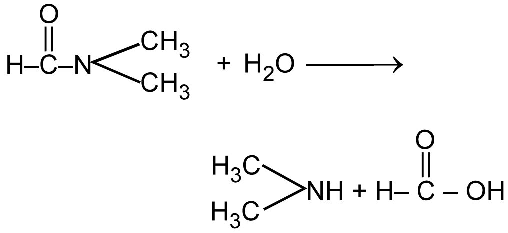


(C) Nitro paraffins

(D) Acid amide

**(Ans.B)**

**Sol.** The compound H-CO - N $(CH_3)_2$ on hydrolysis produces secondary amine .



dimethyl amine Formic acid

**Ex.4** The structure of intermediate acetyl nitrene is -

(A) $CH_3 - CO - \overset{+}{N}:$

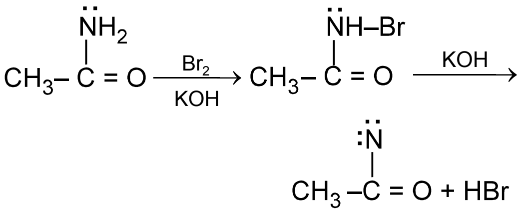
(B) $CH_3-CO-\overset{-}{N}:$

(C) $CH_3-CO-\underset{\cdot\cdot}{N}:$

(D) $CH_3 - CO= N:$

**(Ans.C)**

**Sol.** The structure of intermediate acetyl nitrene is $CH_3$–CO–N. It is formed by the following reaction



**Ex.5** In hypobromite reaction of amide, carbonyl carbon atom is lost as -

(A) CO

(B) $CO_2$

(C) $CO_3^{-2}$

(D) None of above **(Ans.C)**

**Sol.** In hypobromite reaction of amide, carbonyl carbon atom is lost as $CO_3^{-2}$ ion. The reaction takes place as follows:

$$CH_3CONH_2 + Br_2 + 4KOH \longrightarrow CH_3NH_2 + 2KBr + K_2CO_3 + H_2O$$

$K_2CO_3$ is an ionic compound and ionizes as $K^+$ and $CO_3^{-2}$ ions.

**Ex.6** Which one of the following will give primary amine on hydrolysis-

(A) Nitroparaffins

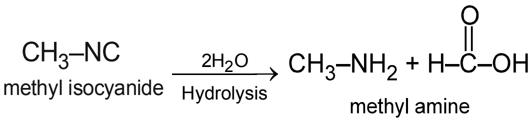
(B) Alkyl cyanide

(C) Amide

(D) Alkyl isocyanide

**(Ans.D)**

**Sol.** Alkyl isocyanide on hydrolysis produces a primary amine. The reaction takes place as follows.



$$\underset{\text{methyl isocyanide}}{CH_3–NC} \xrightarrow[\text{Hydrolysis}]{2H_2O} \underset{\text{methyl amine}}{CH_3–NH_2} + H–\overset{O}{\overset{\|}{C}}–OH$$

**Ex.7** The correct set of the products obtained in the following reactions-

(1) $RCN \xrightarrow{\text{reduction}}$

(2) $RCN \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CH_3MgBr}$

(3) $RNC \xrightarrow{\text{hydrolysis}}$

(4) $RNH_2 \xrightarrow{HNO_2}$

The answer is-

|  | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| (A) | 2° Amine | Methyl ketone | 1° Amine | Alcohol |
| (B) | 1° Amine | Methyl ketone | 1° Amine | Alcohol |
| (C) | 2° Amine | Methyl ketone | 2° Amine | Acid |
| (D) | 2° Amine | Methyl ketone | 2° Amine | Aldehyde |

**(Ans.B)**

**Sol.** The products of the reaction 1, 2, 3 and 4 respectively are : 1° amine, methyl ketone, 1° amine and alcohol.

**Ex.8** The reaction of an alkyl cyanide with sodium and alcohol to form an alkyl amine is known by the name of -

(A) Mendius reaction

(B) Hofmann's reaction

(C) Gabriel reaction

(D) Ammonolysis **(Ans.A)**

**Sol.** Cyanoalkanes are reduced to primary amines in the presence of Na and ethanol. It is called Mendius reacion

$$R\text{-}C \equiv N + 4[H] \xrightarrow{Na/C_2H_5OH} RCH_2\text{–}NH_2$$

alkyl amine

**Ex.9** Formaldoxime on reaction with Na/EtOH gives –

(A) 1° Amine (B) 2° Amine

(C) 3° Amine (D) All above

**(Ans.A)**

**Sol.** Formaldoxime on reaction with Na/EtOH gives 1° amine. The reaction is representated as follows :

$$H\text{–}CH\text{=}N\text{–}OH \xrightarrow[4H]{Na/EtOH} CH_3NH_2 + H_2O$$

formaldoxime methyl amine

This method is used for the preparation of primary amines.

**Ex.10** Which of the following compounds on reduction gives an amine -

(A) Alkyl cyanide (B) Aldoxime

(C) Alkyl isocyanide (D) All above

**(Ans.D)**

**Sol.** All the given compounds like alkyl cyanide, aldoxime, alkyl isocyanide on reduction gives an amine

$$CH_3\text{–}C{\equiv}N \xrightarrow[Sn/HCl]{4H} CH_3\ CH_2NH_2$$

acetonitrile ethyl amine

$$CH_3\text{–}CH\text{=}NOH \xrightarrow[H_2O]{4H} CH_3\text{–}CH_2\text{–}NH_2 + H_2$$

acetaldoxime ethyl amine

$$CH_3\text{–}NC \xrightarrow[Sn/HCl]{4H} CH_3\text{–}NH\text{–}CH_3$$

methyl isocyanide dimethyl amine

(2° amine)

**Ex.11** An alkyl amine is prepared by the following reaction -

$$RCOOH + N_3H \xrightarrow{Conc.\ H_2SO_4} RNH_2 + CO_2 + N_2$$

Name of the above reaction is :

(A) Schmidt reaction

(B) Stephan's reaction

(C) Schotton-Baumann reaction

(D) Reimer- tiemann reaction **(Ans.A)**

**Sol.** The given reaction is represented as :

$$RCOOH + N_3H \xrightarrow{Conc.\ H_2SO_4}$$

alkanoic acid hydrazoic acid

$$RNH_2 + CO_2 + N_2$$

alkylamine

The above reaction is known as Schmidt reaction. This is an important method of preparing primary amines.

**Ex.12** N-Ethyl pthalimide on hydrolysis gives -

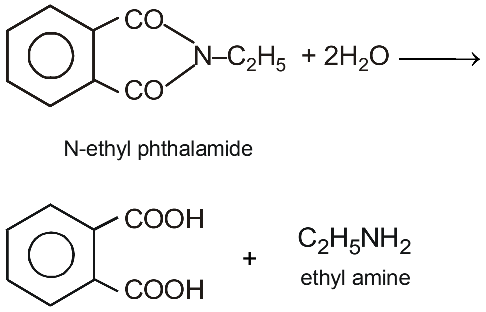
(A) Methyl alcohol

(B) Ethyl amine

(C) Dimethyl amine

(D) Diethyl amine **(Ans.B)**

**Sol.** N- ethyl pthalimide on hydrolysis forms ethylamine. It is called Gabriel phthalimide reaction. It is an important method of preparing primary amines.



N-ethyl phthalamide

ethyl amine

phthalic acid

**Ex.13** Gabriel phthalimide reaction is used to prepare -

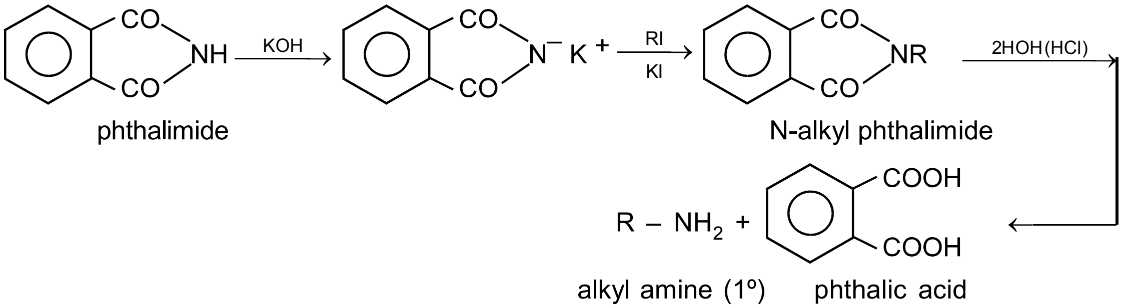
(A) Primary amine

(B) Secondry amine

(C) Tertiary amine

(D) All of above **(Ans.A)**

**Sol.** Gabriel phthalimide reaction is used to prepare primary amine.



**Ex.14** Assign number 1 for least to 4 for most to indicate the relative base strength of the following-

| I | II | III | IV |
|---|---|---|---|
| $C_6H_5NH_2$ | $p–NO_2C_6H_4NH_2$ | $m–NO_2C_6H_4NH_2$ | $p–CH_3OC_6H_4NH_2$ |

| | I | II | III | IV |
|---|---|---|---|---|
| (A) | 2 | 3 | 1 | 4 |
| (B) | 1 | 2 | 3 | 4 |
| (C) | 2 | 3 | 4 | 1 |
| (D) | 4 | 1 | 2 | 3 |

**(Ans.A)**

**Sol.** $p–NO_2C_6H_4NH_2$ is the least basic due to electron withdrawing group at the p–position (in conjugation with $NH_2$ group) $p–CH_3OC_6H_4NH_2$ is the most basic due to interaction of lone pair of electron on oxygen atom of $–OCH_3$ group with the benzene ring. As such lone pair of electron on $–NH_2$ group is more available.

**Ex.15** Which compound is soluble in water-

(A) $[(CH_3)_2NH_2]^+ Cl^-$
(B) $[CH_3NH_3]^+ Cl^-$
(C) $[(CH_3)_3NH]^+ Cl^-$
(D) All the above **(Ans.D)**

**Sol.** Amines salt are soluble in water.

**Ex.16** Which compound will liberate $CO_2$ from $NaHCO_3$ solution-

(A) $CH_3CO\ NH_2$ (B) $CH_3NH_2$
(C) $(CH_3)_4\ N^+OH^-$ (D) $CH_3N^+H_3Cl^-$
**(Ans.D)**

**Sol.** The compound which will liberate $CO_2$ from $NaHCO_3$ solution is $CH_3N^+\ H_3Cl^-$. The reaction takes place as follows:

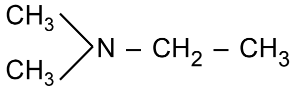
$CH_3N^+H_3Cl^- + NaHCO_3 \longrightarrow$
methyl amine
hydrogen chloride
$CH_3–NH_2 + NaCl + H_2O + CO_2\uparrow$
methyl amine

**Ex.17** Which amine will not react with nitrous acid -

(A) Methyl amine
(B) Ethyl amine
(C) Dimethyl amine
(D) N, N Dimethyl ethane amine **(Ans.D)**

**Sol.** Primary and secondary amines react with $HNO_2$, while tertiary amines do not react with $HNO_2$.

Since N, N dimethyl ethane amine


$(CH_3)_2N – CH_2 – CH_3$ is a tertiary amine,

hence it will not react with $HNO_2$.

**Ex.18** Which gas will be evolved out when $[CH_3CH_2NH_2 + (CH_3)_2CHNH_2]$ is treated with sodium nitrite and HCl -

(A) Chlorine (B) Ammonia
(C) Nitrogen (D) $NO_2$
**(Ans.C)**

**Sol.** Primary amine and $HNO_2$ produces nitrogen gas.

$RNH_2 + HNO_2 \longrightarrow ROH + N_2 + H_2O$

**Ex.19** Which of the following compound cannot be produced if 1-propane amine is treated with $NaNO_2$ and HCl -

(A) Propane -1-ol
(B) Propane-2-ol
(C) 2-Chloropropane
(D) 2-Propaneamine **(Ans.D)**

**Sol.** In the reaction,
$CH_3–CH_2–{}^{\oplus}CH_2$ and $CH_3–{}^{\oplus}CH–CH_3$, carbonium ions are formed.

As such 1-propanol, 2-propanol, 2-chloropropane, 1-chloropropane and propene are the products while 2-propaneamine is not obtained.

**Ex.20** In the following sequence of reactions the product B, will be

$$C_2H_5MgBr \xrightarrow{ClNH_2} A \xrightarrow[HCl]{NaNO_2} B$$

(A) $C_2H_5OH$ (B) $C_2H_5NO_2$
(C) $C_2H_2$ (D) All of the above **(Ans.A)**

**Sol.** In the given sequence of reactions, the product B, will be ethanol. The reaction takes place as

$$C_2H_5MgBr \xrightarrow[MgBrCl]{ClNH_2} C_2H_5NH_2 \xrightarrow[NaNO_2/HCl]{HONO} \underset{\text{'B'}}{C_2H_5OH} + N_2 + H_2O$$

**Ex.21** Which set of the following compounds on reaction with an alkyl amine gives schiff's base :

(A) HCHO, $C_6H_5CHO$, $CH_3CHO$
(B) HCHO, $NH_2OH$, $NH_2 - NH_2$
(C) $CH_3CHO$, $NH_2OH$, $NH_2\text{-}NH_2$
(D) $CH_3COCH_3$, $C_2H_5OH$ **(Ans.A)**

**Sol.** The aldehydes e.g. HCHO, $C_6H_5CHO$ and $CH_3CHO$ on reaction with alkylamine gives schiff's base

$$\underset{\text{benzaldehyde}}{C_6H_5CHO} + \underset{\text{methylamine}}{H_2NCH_3} \longrightarrow \underset{\text{schiff's base}}{C_6H_5CH = N - CH_3} + H_2O$$

**Ex.22** Which of the following does not give a sulphur compound with a 1° amine -

(A) Hinsberg reaction
(B) Mustard oil reaction
(C) Schotton - Baumann reaction
(D) Con. $H_2SO_4$ **(Ans.C)**

**Sol.** In Schotton - Baumann reaction a sulphur compound is not produced with a 1° amine

$$\underset{\text{alkyl amine}}{R – NH_2} + \underset{\text{benzoyl chloride}}{Cl – CO – C_6H_5} \xrightarrow{NaOH} \underset{\text{N-alkyl benzamide}}{R– NHCOC_6H_5} + HCl$$

**Ex.23** Ethylamine on oxidation with acidified $KMnO_4$ gives-

(A) Acetaldehyde
(B) Ethylamine oxide
(C) Ethanol
(D) Acetamide **(Ans.A)**

**Sol.** Oxidation of ethylamine gives acetaldehyde.

**Ex.24** Mustard oil reaction is given by -

(A) Primary amine (B) Urea
(C) Secondary amine (D) Acid amide
**(Ans.A)**

**Sol.** Mustard oil reaction is given by primary amine. It is known as Hoffmann's mustard oil reaction

$$R – NH_2 + S = C = S + HgCl_2 \longrightarrow \underset{\text{alkyl isothiocyanate}}{R – N = C = S} + HgS\downarrow + 2HCl$$

This compound alkyl isothiocyanate has a smell resembling that of mustard oil.

**Ex.25** Which of the following compounds has a smell of mustard oil

(A) Alkyl cyanate
(B) Alkyl thiocyanate
(C) Alkyl isothiocyanate
(D) alkyl isocyanate **(Ans.C)**

**Sol.** A primary amine condenses with $CS_2$ in the presence of $HgCl_2$ to form an alkyl isothiocyanate. This compound has a smell resembling that of mustard oil. It is called as Hofmann's mustard oil reaction

$$\underset{\text{alkyl amine}}{R – NH_2} + S = C = S + HgCl_2 \longrightarrow \underset{\text{alkyl isothiocyanate}}{R – N = C = S} + HgS\downarrow + 2HCl$$

**Ex.26** Which of the following amine does not react with Hinsberg reagent -

(A) Neopentyl amine
(B) Isopropyl amine
(C) Triethyl amine
(D) Ethyl methyl amine **(Ans.C)**

**Sol.** Triethyl amine is tertiary amine. It does not react with Hinsberg reagent.

**Ex.27** In which of the following sequence of reaction the end product does not exhibit tautomerism-

(A) $CH_3CH_2NH_2 \xrightarrow{NOCl} \xrightarrow{AgNO_2}$

(B) $(CH_3)_2CHNH_2 \xrightarrow{NOCl} \xrightarrow{AgNO_2}$

(C) $(CH_3)_3CNH_2 \xrightarrow{NOCl} \xrightarrow{AgNO_2}$

(D) $CH_3CH(NH_2)C_2H_5 \xrightarrow{NOCl} \xrightarrow{AgNO_2}$

**(Ans.C)**

**Sol.** In the 3rd reaction sequence the end product is a 3° nitro compound.

$(CH_3)_3CNO_2$ It does not have $\alpha$-hydrogen as such tautomerism is not possible.

**Ex.28** The acid used for the determination of molecular weights of amines is -

(A) $H_2PtCl_6$ (B) Picric acid
(C) $HAuCl_4$ (D) $H_2SO_4$

**(Ans.A)**

**Sol.** The acid used is $H_2PtCl_6$. It is a solution of platinic chloride, Pt $Cl_4$ in con.HCl

$$2R\text{-}NH_2 + H_2\,[PtCl_6] \longrightarrow [R\,NH_3]_2^+\,[PtCl_6]^{-2}$$

alkylamine platinichloride

Chloroplatinates on ignition leave a residue of metallic Pt. This reaction is employed in determining molecular weight of amines.

**Ex.29** Methyl amine on reaction with chlorine in the presence of NaOH gives-

(A) Chloroform
(B) Methyl chloride
(C) N-Methyl chloramine
(D) Chloramine

**(Ans.C)**

**Sol.** Methyl amine reacts with $Cl_2$ in the presence of NaOH undergoes a substitution of a H-atom of amino group by a Cl group and N-methyl chloramine is formed.

$$CH_3NH_2 + Cl_2 \xrightarrow[NaCl,\ H_2O]{NaOH} CH_3\text{–}NHCl$$

N-methyl chloramine