13

Organic Compunds with Functional Group Containing Nitrogen

In this unit, we shall focus our attention on the chemistry of organic compounds with functional groups containing nitrogen. The important functional groups containing nitrogen are :–

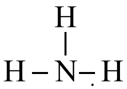
Functional group	**Structure**
Cyanide	$-C \equiv N$
Isocyanide	$-N \overset{\rightarrow}{=} C$
Nitro	
Nitrito	$-O-N=O$
Nitroso	$-N=O$
Primary amine	$-\underset{\substack{\vert \\ H}}{N}-H$
Secondary amine	$-\underset{\vert}{N}-H$
Tertiary amine	$-\underset{\vert}{N}-$
diazonium salt	$-N=N-X$

Part –A

13.1 Amine

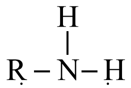
Amines may be regarded as the alkyl or aryl derivative of ammonia. They can be classified into primary, secondary, tertiary amines, depending upon whether one, two or three H atoms of ammonia have been replaced by alkyl groups.

$$NH_3 \xrightarrow[+R]{-H} RNH_2 \xrightarrow[+R]{-H} R_2NH \xrightarrow[+R]{-H} R_3N$$



$H-\overset{\substack{H \\ \vert}}{N}-H$

ammonia



$R-\overset{\substack{H \\ \vert}}{N}-H$

primary amine

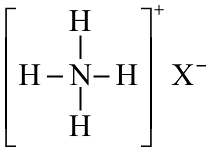
$R-\overset{\substack{R \\ \vert}}{N}-H$

secondary amine

$R-\overset{\substack{R \\ \vert}}{N}-R$

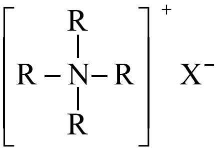
tertiary amine

Example



$\left[H-\overset{\substack{H \\ \vert}}{\underset{\substack{\vert \\ H}}{N}}-H\right]^+ X^-$

ammonium salt



$\left[R-\overset{\substack{R \\ \vert}}{\underset{\substack{\vert \\ R}}{N}}-R\right]^+ X^-$

tetra alkyl ammonium halide

$[(CH_3)_4N]^+Cl^-$
tetra methyl ammonium chloride

$[(C_2H_5)_4N]^+I^-$
tetra ethyl ammonium iodide

$[(C_6H_5)_4N]^+Br^-$
tetra phenyl ammonium bromide

Aliphatic and Aromatic amine

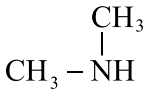
Amines may be classified into two categories:–

1. Aliphatic amine

Amines in which the nitrogen atom is directly bonded to one or more alkyl groups are called aliphatic amines.

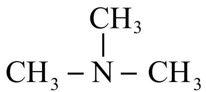
Example –

CH_3NH_2
methyl amine
(1°)



$CH_3-\overset{\substack{CH_3 \\ \vert}}{N}H$

dimethyl amine
(2°)



$CH_3-\overset{\substack{CH_3 \\ \vert}}{N}-CH_3$

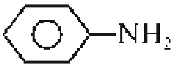
trimethyl amine
(3°)

2. Aromatic amine

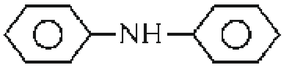
These are of two types–

(a) **Aryl amines–** Amines in which the nitrogen atom is directly bonded to one or more aromatic aryl groups are called aromatic amines

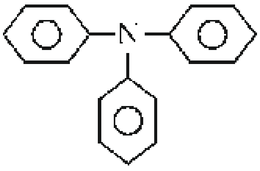
Example–



aniline (1°)



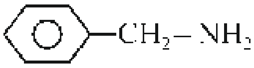
diphenyl amine (2°)



triphenyl amine (3°)

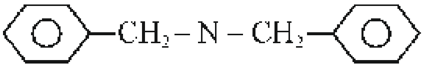
(b) **Aryl alkyl amine–** Amines in which the nitrogen atom is bonded to the side chain of the aromatic ring are called arylalkyl amines.

Example–

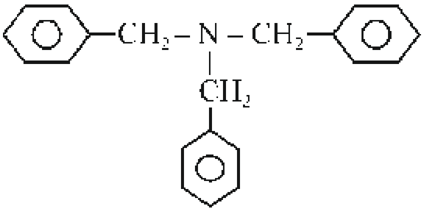


benzyl amine (1°)

II



di benzyl amine (2°)



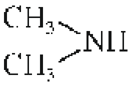
tri benzyl amine (3°)

13.1.1 Nomenclature of Amines-

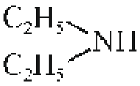
According to common system, amines are called alkyl amines by adding the suffix amine to the name of the corresponding alkyl groups.

Example–

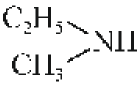
CH_3NH_2 methyl amine	$C_2H_5NH_2$ ethyl amine	$C_3H_7NH_2$ propyl amine



dimethyl amine



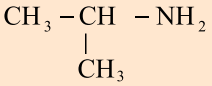
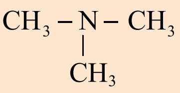
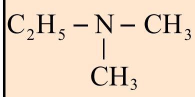
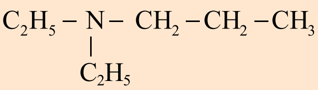
diethyl amine



ethylmethyl amine

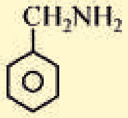
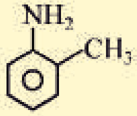
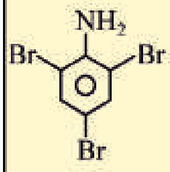
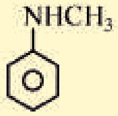
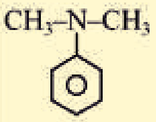
In the IUPAC system, the aliphatic amines are also called alkanamines. These names are written by replacing 'e' of parent alkane by suffix 'amine'.

The common and IUPAC names of a few aliphatic amines are given below:_

Amine	Common name	IUPAC name
CH_3NH_2	Methyl amine	Methanamine
$CH_3CH_2NH_2$	Ethyl amine	Ethanamine
$CH_3CH_2CH_2NH_2$	n-propyl amine	Propane–1–amine
 $\underset{\displaystyle CH_3}{CH_3-\underset{\vert}{CH}-NH_2}$	isopropyl amine	Propane–2–amine
$H_2N–(CH_2)_6–NH_2$	Hexa methylene di amine	Hexane–1, 6–diamine
$CH_3–NH–CH_3$	dimethyl amine	N–methyl methanamine
$CH_3CH_2NHCH_3$	ethyl methyl amine	N–methyl ethanamine
 $\underset{\displaystyle CH_3}{CH_3-\underset{\vert}{N}-CH_3}$	tri methyl amine	N,N–dimethyl methan amine
 $\underset{\displaystyle CH_3}{C_2H_5-\underset{\vert}{N}-CH_3}$	ethyl dimethyl ethane	N,N–dimethyl ethanamine
 $\underset{\displaystyle C_2H_5}{C_2H_5-\underset{\vert}{N}-CH_2-CH_2-CH_3}$	diethyl-n-propyl amine	N,N–diethyl propane-1-amine

In common system, aromatic amines are called aryl amines. The simplest amine is $C_6H_5NH_2$ and it is known as benzenamine or aniline. Other aromatic amines are named as derivatives of benzenamine and the position of other groups are indicated by numbers.

Example–

amine	common name	IUPAC name
	aniline	aniline or benzenamine
	benzyl amine	phenyl methanamine
	O-toludine	2-methyl benzenamine
	2,4,6-tribromo aniline	2,4,6-tri bromo benzenamine
	N-methyl aniline	N-methyl benzen amine
	N,N-di methyl aniline	N,N-di methyl benzenamine

13.1.2 Isomerism in Amines

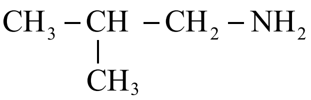
Amines exhibit the following types of isomerism–

(a) Chain isomerism– Aliphatic amines containing four or more carbon atoms exhibit chain isomerism.

$C_4H_{11}N$–

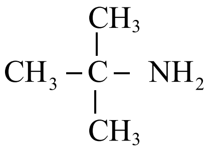
$CH_3CH_2CH_2CH_2NH_2$

butane–1–amine



$$CH_3-\underset{\substack{|\\CH_3}}{CH}-CH_2-NH_2$$

2-methyl propanamine
(isobutyl amine)



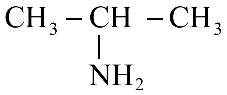
$$CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-NH_2$$

2–methyl propane–2–amine
(neo butyl amine)

(b) Position isomerism– Alkyl amines with three or more C-atoms can exhibit position isomerism.

C_3H_9N– $CH_3–CH_2–CH_2–NH_2$

propane-1-amine



$$CH_3-\underset{\substack{|\\NH_2}}{CH}-CH_3$$

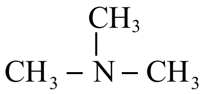
propane-2-amine

(c) Functional group isomerism– Primary, secondary, tertiary amines having same molecular formula are functional isomers of one another.

C_3H_9N –

$CH_3CH_2CH_2NH_2$ propane-1-amine (1°)

$CH_3CH_2NH\,CH_3$ N-methyl ethane amine (2°)



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

N,N-dimethyl methane amine (3°)

(d) Metamerism– Secondary and tertiary amines can exibit metamerism.

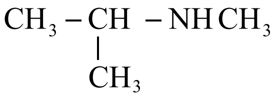
$C_4H_{11}N$ –

$CH_3CH_2CH_2-NH-CH_3$

N–methyl propane amine

$CH_3CH_2NH\,CH_2\,CH_3$

N–ethyl ethane amine



$$CH_3-\underset{\substack{|\\CH_3}}{CH}-NH\,CH_3$$

2–(N–methyl) propane amine

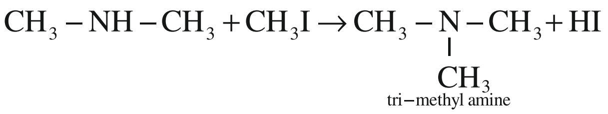
13.1.3 Preparation of amines

1. From alkyl halides

(a) By ammonolysis (Hoffmann's method)– When an aqueous or alcoholic solution of ammonia is heated with an alkyl halide at 373k in a sealed tube, all the types of amines are formed.

$$CH_3I + NH_3 \rightarrow \underset{\substack{\text{methyl amine}\\(1^\circ)}}{CH_3NH_2} + HI$$

$$CH_3-NH_2 + CH_3I \rightarrow \underset{\substack{\text{di methyl amine}\\(2^\circ)}}{CH_3NH-CH_3} + HI$$



$$CH_3-NH-CH_3 + CH_3I \rightarrow \underset{\text{tri−methyl amine}}{CH_3-\underset{\substack{|\\CH_3}}{N}-CH_3} + HI$$

Tertiary amines also combine with methyl iodide to form quaternary ammonium salts.

$$(CH_3)_3\ddot{N} + CH_3I \rightarrow \underset{\text{tetra methyl ammonium iodide}}{[(CH_3)_4N]^+I^-}$$

The order of reactivity of halides is–

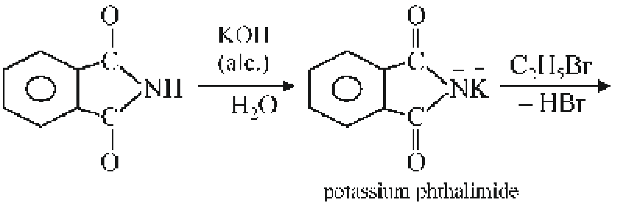
$$RI > RBr > RCl$$

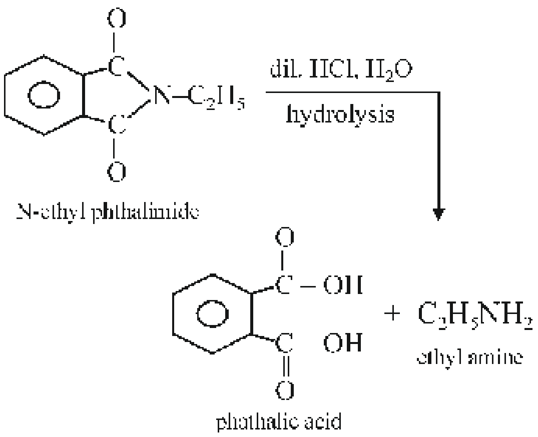
This reaction is an example of nucleophilic substitution reaction in which ammonia or amine molecules acts as a nucleophile due to the presence of lone pair on the nitrogen atom.

This method gives a mixture of amines and it is very difficult to separate the mixture in laboratory.

If ammonia is taken in large excess and the alkyl halide in small amount, then the primary amine is the main product.

(b) By Gabriel phathalimide synthesis– This method is used for preparing only primary amines. In this method, phthalimide is treated with alcoholic KOH to give potassium phthalimide, which is treated with alkyl halide to form N-alkyl phthalimide. The hydrolysis of N-alkyl phthalimide with 20% HCl under pressure gives primary amine.





2. Reduction of nitriles (cyanides) and isonitriles (iso cyandies)

Nitriles can be reduced to corresponding amines using H_2/raney Ni or $LiAlH_4$ or Na/C_2H_5OH.

$$\underset{\text{ethane nitrile}}{CH_3CN} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{ethane amine}}{CH_3CH_2NH_2}$$

The method of reduction of cyanide with Na and alcohol is called **Mandius reduction**.

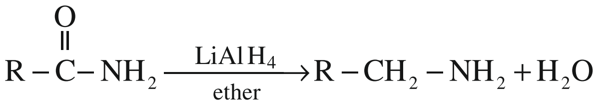
Reduction of isocyanides under similar conditions gives secondary amines.

$$\underset{\substack{\text{methane}\\\text{iso nitrile}}}{CH_3NC} + 4[H] \xrightarrow{LiAlH_4} \underset{\substack{\text{N−methyl}\\\text{methane amine}}}{CH_3NHCH_3}$$

3. From amides

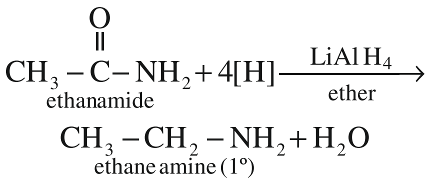
(a) Reduction of amides–

Amides are reduced to corresponding amines by $LiAlH_4$ or Na/C_2H_5OH.



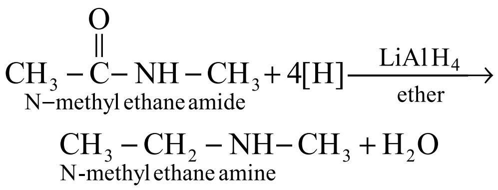
$$R-\overset{\substack{O\\\|}}{C}-NH_2 \xrightarrow[\text{ether}]{LiAlH_4} R-CH_2-NH_2 + H_2O$$

Example–



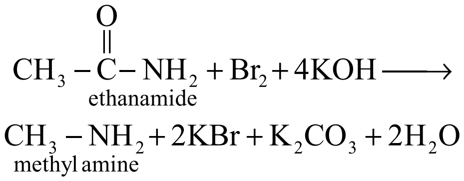
$$\underset{\text{ethanamide}}{CH_3-\overset{\substack{O\\\|}}{C}-NH_2} + 4[H] \xrightarrow[\text{ether}]{LiAlH_4}$$

$$\underset{\text{ethane amine }(1^\circ)}{CH_3-CH_2-NH_2} + H_2O$$



$$\underset{\text{N–methyl ethane amide}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH-CH_3}+4[H]\xrightarrow[\text{ether}]{LiAlH_4}\underset{\text{N-methyl ethane amine}}{CH_3-CH_2-NH-CH_3}+H_2O$$

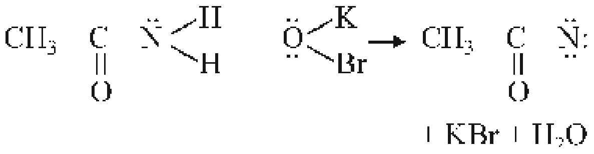
(b) **Hofmann bromamide reaction–** Primary amines are formed with one carbon atom less than the parent amide by the reaction of amide with bromine water and KOH.



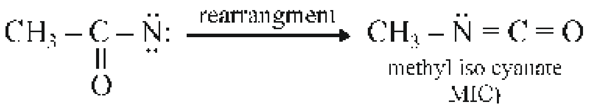
$$\underset{\text{ethanamide}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2}+Br_2+4KOH\longrightarrow\underset{\text{methyl amine}}{CH_3-NH_2}+2KBr+K_2CO_3+2H_2O$$

The reaction proceeds into following steps–

$$Br-Br+2KOH\rightarrow K-Br+\underset{\text{potassium hypobromite}}{K-\ddot{\underset{\cdot\cdot}{O}}-Br}+H_2O$$



$$CH_3\;\underset{\underset{\displaystyle O}{\|}}{C}\;\ddot{N}{<}^{H}_{H}\quad\ddot{\underset{\cdot\cdot}{O}}{<}^{K}_{Br}\rightarrow CH_3\;\underset{\underset{\displaystyle O}{\|}}{C}\;\ddot{\underset{\cdot\cdot}{N}}:\;+KBr+H_2O$$

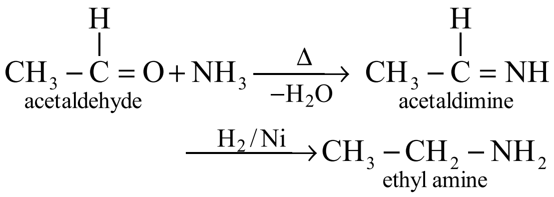


$$CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-\ddot{\underset{\cdot\cdot}{N}}:\xrightarrow{\text{rearrangment}}\underset{\text{methyl iso cyanate (MIC)}}{CH_3-\ddot{N}=C=O}$$

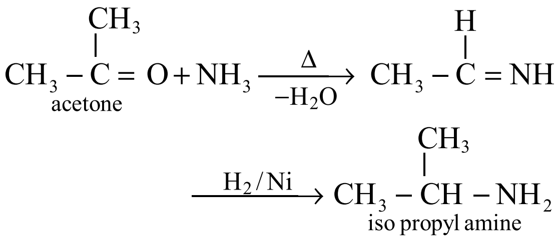
$$CH_3-\ddot{N}=C=O+2KOH\longrightarrow CH_3-\ddot{N}H_2+K_2CO_3+H_2O$$

4. Reductive amination of carbonyl compounds

Primary amines may be prepared by reaction of carbonyl compounds with ammonia to form imines which can be hydrogenated in presence of Ni.



$$\underset{\text{acetaldehyde}}{CH_3-\overset{\overset{\displaystyle H}{|}}{C}=O}+NH_3\xrightarrow[-H_2O]{\Delta}\underset{\text{acetaldimine}}{CH_3-\overset{\overset{\displaystyle H}{|}}{C}=NH}\xrightarrow{H_2/Ni}\underset{\text{ethyl amine}}{CH_3-CH_2-NH_2}$$



$$\underset{\text{acetone}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=O}+NH_3\xrightarrow[-H_2O]{\Delta}CH_3-\overset{\overset{\displaystyle H}{|}}{C}=NH\xrightarrow{H_2/Ni}\underset{\text{iso propyl amine}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-NH_2}$$

5. From Grignard reagent

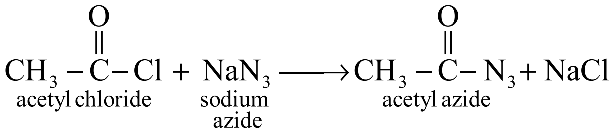
Primary amine can be obtained by the reaction of Grignard reagent with chloro amine.

$$R\,Mg\,X+Cl-NH_2\rightarrow RNH_2+Mg\,X\,Cl$$

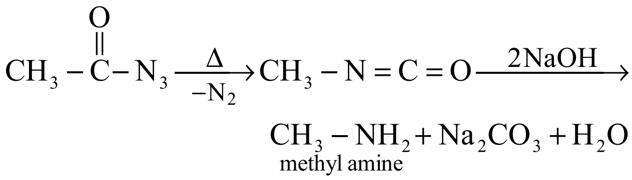
$$\underset{\text{methyl magnisium chloride}}{CH_3\,Mg\,Cl}+Cl-NH_2\rightarrow\underset{\text{methyl amine}}{CH_3NH_2}+Mg\,Cl_2$$

6. From acid chloride (Curtius rearrangement)

This method is used for the formation of primary amine from acid chloride.



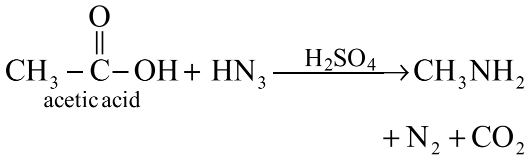
$$\underset{\text{acetyl chloride}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl}+\underset{\text{sodium azide}}{NaN_3}\longrightarrow\underset{\text{acetyl azide}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-N_3}+NaCl$$



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-N_3\xrightarrow[-N_2]{\Delta}CH_3-N=C=O\xrightarrow{2NaOH}\underset{\text{methyl amine}}{CH_3-NH_2}+Na_2CO_3+H_2O$$

7. From Carboxylic acid (Schmidt reaction)

Schmidt Reaction involves the reaction between the carboxylic acid and hydrazoic acid in the presence of sulfuric acid to form amines.

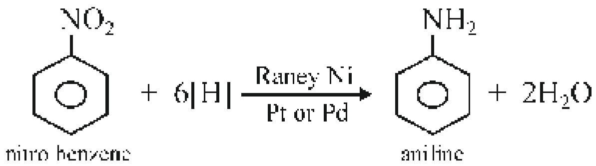


$$\underset{\text{acetic acid}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH}+HN_3\xrightarrow{H_2SO_4}CH_3NH_2+N_2+CO_2$$

8. From Nitro alkanes–

Aliphatic and aromatic amines can be easily prepared by the reduction of corresponding nitro compounds.

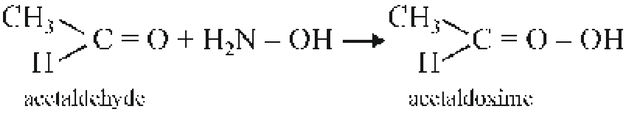
$$\underset{\text{nitro ethane}}{CH_3-CH_2-NO_2}+6[H]\xrightarrow[\text{Pt or Pd}]{\text{Raney Ni}}\underset{\text{ethyl amine}}{CH_3-CH_2-NH_2}+2H_2O$$



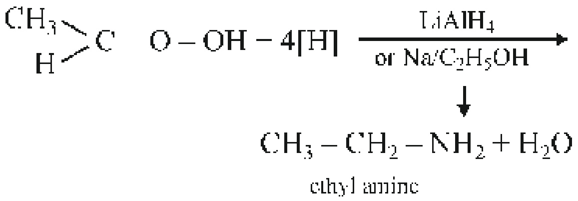
Nitro compounds can be reduced with active metals in acidic medium. Example– Fe + HCl, Zn + HCl or Sn + HCl

9. By reduction of oximes–

Primary amines can be prepared by the reduction of oximes with either Na/C_2H_5OH or by $LiAlH_4$. The oximes can be obtained by the reaction of carbonyl compound with hydroxyl amine.

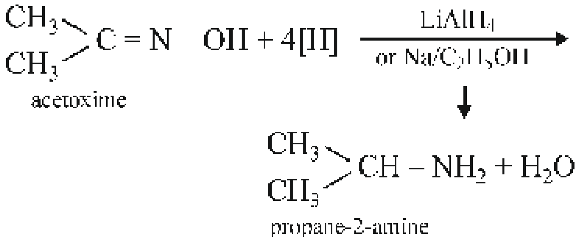


$$\underset{\text{acetaldehyde}}{\begin{matrix}CH_3\\H\end{matrix}\!\!>C=O}+H_2N-OH\longrightarrow\underset{\text{acetaldoxime}}{\begin{matrix}CH_3\\H\end{matrix}\!\!>C=O-OH}$$



$$\begin{matrix}CH_3\\H\end{matrix}\!\!>C\quad O-OH-4[H]\xrightarrow[\text{or }Na/C_2H_5OH]{LiAlH_4}\underset{\text{ethyl amine}}{CH_3-CH_2-NH_2+H_2O}$$

from acetoxime



$$\underset{\text{acetoxime}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=N\quad OH}+4[H]\xrightarrow[\text{or }Na/C_2H_5OH]{LiAlH_4}\underset{\text{propane-2-amine}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH-NH_2+H_2O}$$

13.1.4 Physical properties of amines

(1) Physical state and smell–

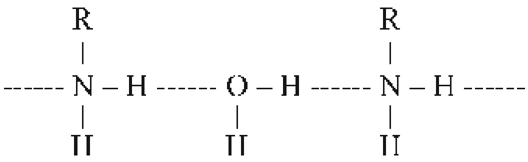
Among amines, lower members e.g. methane amine and ethane amine are gases. Primary amine of higher number of carbons are liquid or colourless solid substances.

Lower members have ammonia like smell but higher members have fishy smell.

Most of the aromatic amines are colourless in pure form. However they become coloured on keeping due to oxidation in air.

(2) Solubility and Boiling Points–

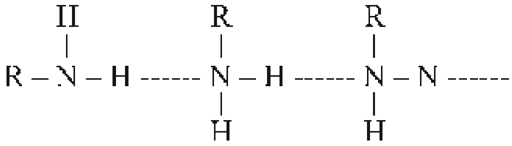
The lower amines are soluble in water because they are capable of forming hydrogen bond with water. However, higher amine containing six or more carbon atoms are insoluble.



$$\begin{array}{ccccc} & R & & & R \\ & | & & & | \\ \text{------}\,N-H\,\text{------} & & O-H\,\text{------} & & N-H\,\text{------} \\ & | & | & & | \\ & H & H & & H \end{array}$$

Aromatic amines are insoluble in water but soluble in organic solvents.

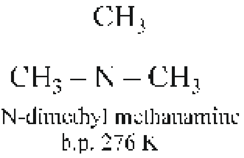
Among isomeric amines, the primary amines have highest boiling point due to their large tendency to form hydrogen bonds whereas tertiary amines have lowest boiling points because of their inability to form hydrogen bonds.



$$\begin{array}{ccc} H & R & R \\ | & | & | \\ R-N-H\,\text{------} & N-H\,\text{------} & N-N\,\text{------} \\ & | & | \\ & H & H \end{array}$$

Example –

$\underset{\substack{\text{propyl amine}\\ \text{b.p. 323 K}}}{CH_3\,CH_2\,CH_2\,NH_2}$ $\quad$ $\underset{\substack{\text{N-methyl ethanamine}\\ \text{b.p. 307 K}}}{CH_3-CH_2-NH-CH_3}$

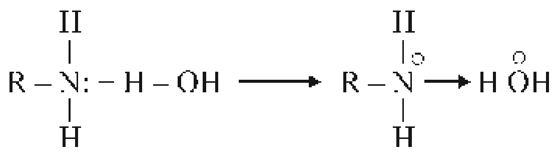


$$\underset{\substack{\text{N,N-dimethyl methanamine}\\ \text{b.p. 276 K}}}{\begin{array}{c}CH_3\\ CH_3-N-CH_3\end{array}}$$

13.1.5 Chemical properties of amines

1. Basic character of amines–

Due to the presence of lone pair on N-atom of the $-NH_2$ group, the aliphatic amines are generally basic in nature. As a result, these have tendency to donate this lone pair of electrons to different electron deficient compounds and therefore behave as bases. Like ammonia the amines react with water to form alkyl ammonium hydroxide.



$$R-\underset{H}{\overset{H}{N}}:-H-OH \longrightarrow R-\underset{H}{\overset{H}{\overset{\oplus}{N}}}\rightarrow H\overset{\ominus}{O}H$$

Alkyl amines are stronger bases than ammonia. This is due to the reason that alkyl groups are electron releasing (+I effect). As a result of electron releasing effect of alkyl group, it increases the electron density on the nitrogen atom and therefore they can donate electron pair more easily than ammonia.

Among primary, secondary and tertiary aliphatic amines, due to the number of alkyl groups, the order of basicity is-

tertiary amine > secondary amine > primary amine

but the above order is true only in gaseous phase and in non aqueous solvent e.g. chlorobenzene.

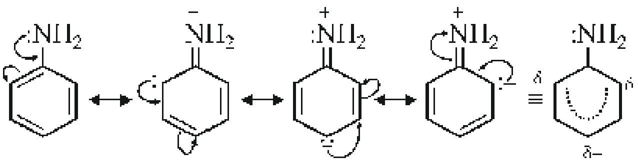
However from the K_b values of amines, it has been observed that tertiary amines are unexpectedly less basic than the others and in aqueous phase the correcct order of basicity is–

$$\underset{(2^\circ)}{(CH_3)_2NH} > \underset{(1^\circ)}{CH_3NH_2} > \underset{3^\circ}{(CH_3)_3N} > NH_3$$

$$(C_2H_5)_2NH > C_2H_5NH_2 > NH_3 > (C_2H_5)_3N$$

The size of alkyl group is more than that of hydrogen and therefore, it hinders the attack of acid on the amine and therefore, basic strength decreases. Now, crowding of alkyl groups increases from primary to tertiary amines. As a result, their basic strength decreases. This is called **steric hinderance.**

The less basic character of aniline i.e. aromatic amine can be explained on the basis of resonance.



It is quite evident from the above resonating structures that the lone pair of electrons on nitrogen is withdraw away from it and is being partially shared with benzene ring. Therefore in aniline, the electron donating capacity of nitrogen for protonation is considerably decreased as compared to that of ammonia and aliphatic amines. Hence, aniline is weaker base than aliphatic amines and ammonia.

The following reactions shows basicity of amines–

$$RNH_2 + HCl \longrightarrow \underset{\text{alkyl ammonium chloride}}{R\overset{+}{N}H_3\overset{-}{Cl}}$$

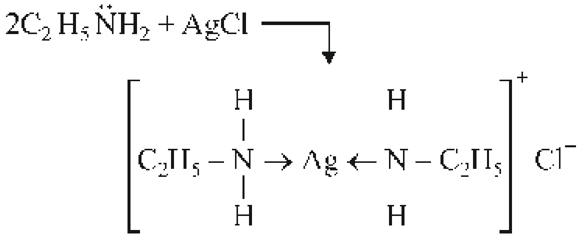
$$2RNH_2 + H_2SO_4 \longrightarrow \underset{\text{alkyl ammonium sulphate}}{(R\overset{+}{N}H_3)_2SO_4^{-2}}$$

$$2RNH_2 + \underset{\text{chloro platinic acid}}{H_2PtCl_6} \longrightarrow \underset{\text{alkyl ammonium chloro platinate}}{(R\overset{+}{N}H_3)_2PtCl_6^{-2}}$$

$$RNH_2 + \underset{\text{chloro auric acid}}{HAuCl_4} \longrightarrow \underset{\text{alkyl ammonium chloro aurate}}{(R\overset{+}{N}H_3)AuCl_4^-}$$

2. Reaction with metal ions–

Lower aliphatic amines form coordination complexes with metal ions like Ag^+ and Cu^{2+}.



$$2C_2H_5\ddot{N}H_2 + AgCl \longrightarrow \left[C_2H_5-\underset{H}{\overset{H}{N}}\rightarrow Ag \leftarrow \underset{H}{\overset{H}{N}}-C_2H_5\right]^+ Cl^-$$

Bis(ethylamine) silver (I) chloride (soluble)

$$4C_2H_5\ddot{N}H_2 - CuCl_2 \longrightarrow [Cu(C_2H_5NH_2)_4]^{2+}Cl_2$$

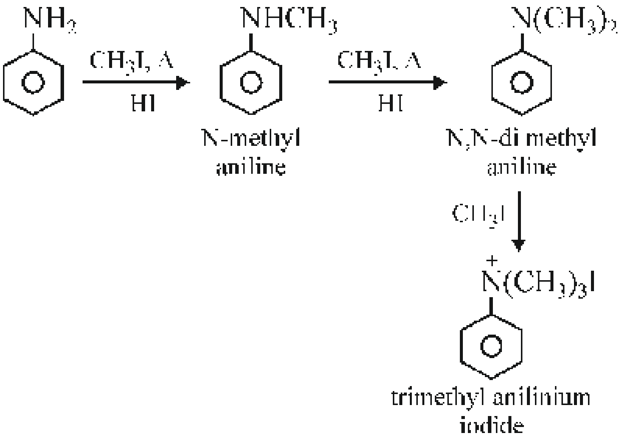
tetrakis (ethylamine) copper (II) chloride (deep blue solution)

3. Alkylation–

Amines react with alkyl halides to form amines of higher class.

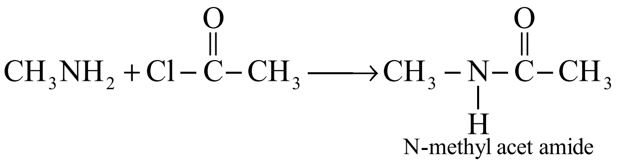
$$\underset{1^\circ}{RNH_2} \xrightarrow[-HI]{+RI} \underset{2^\circ}{R_2NH} \xrightarrow[-HI]{+RI} \underset{3^\circ}{R_3N} \xrightarrow{+RI} \underset{\text{tetra alkyl ammonium iodide}}{R_4\overset{+}{N}\overset{-}{I}}$$

Aromatic amines also undergo similar reaction. For example when aniline is treated with excess of methyl iodide under pressure, mixture of secondary, tertiary amines and quaternary salt are formed.

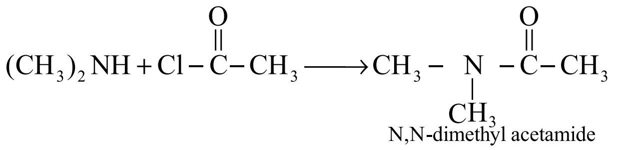


4. Acylation–

Primary and secondary amines react with acid chlorides or acid anhydrides to form substituted amides.



$$CH_3NH_2 + Cl-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \longrightarrow \underset{\text{N-methyl acet amide}}{CH_3-\underset{\underset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}$$



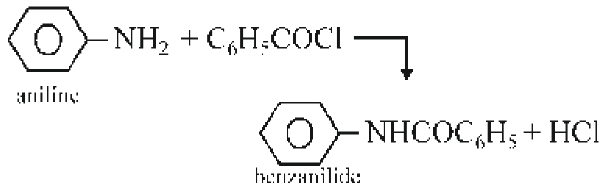
$$(CH_3)_2NH + Cl-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \longrightarrow \underset{\text{N,N-dimethyl acetamide}}{CH_3-\underset{\underset{\displaystyle CH_3}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}$$

Tertiary amine do not undergo this reaction because they do not have H atom on the nitrogen.

5. Benzoylation–

Benzoylation of compounds containing active hydrogen such as alcohols, phenols or amines with benzoyl chloride in the presence of dilute aqueous NaOH solution is called **Schotten-Baumann** reaction.

$$CH_3NH_2 + C_6H_5COCl \xrightarrow{\Delta} \underset{\text{N–methyl benzamide}}{CH_3NHCOC_6H_5} + HCl$$



6. Carbyl amine reaction–

Aliphatic and aromatic primary amines when heated with chloroform and alcoholic KOH gives isocyanide or carbylamine of foul smelling.

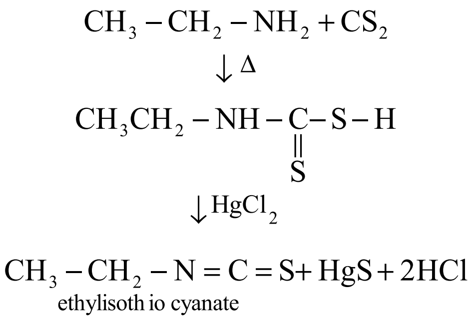
The carbyl amine test does not give a positive reaction with secondary and tertiary amines.

$$CH_3NH_2 + CHCl_3 + \underset{\text{(alcoholic)}}{3KOH} \xrightarrow{\Delta} \underset{\text{carbylamino methane}}{CH_3NC} + 3KCl + 3H_2O$$

7. Reaction with carbon disulphide–

Primary amines react with CS_2 in presence of $HgCl_2$ to give isothiocyanates.

This isothiocyanates have characteristic smell like mustard oil, the reaction is called **Hoffmann's mustard oil reaction**.



$$\begin{array}{c} CH_3-CH_2-NH_2+CS_2 \\ \downarrow \Delta \\ CH_3CH_2-NH-\underset{\underset{\displaystyle S}{\|}}{C}-S-H \\ \downarrow HgCl_2 \\ \underset{\text{ethylisoth io cyanate}}{CH_3-CH_2-N=C=S} + HgS + 2HCl \end{array}$$

8. Reaction with nitrous acid–

Amines of different classes react with nitrous acid to yield different products.

Example –

(i) Primary aliphatic amines react with nitrous acid to form alcohols and N_2 gas evolved.

$$CH_3-CH_2-NH_2 + HNO_2 \rightarrow CH_3-CH_2-OH + N_2 + H_2O$$

(ii) Seondary aliphatic amines react with nitrous acid to produce nitroso amines that are insoluble in the aqueous solution and separate out as a yellow oily layer.

$$(C_2H_5)_2NH + HNO_2 \rightarrow \underset{\text{N-nitroso diethyl amine}}{(C_2H_5)_2N-NO} + H_2O$$

(iii) Tertiary aliphatic amines on reaction with nitrous acid form nitrites.

$(C_2H_5)_3N + HNO_2 \rightarrow [(C_2H_5)_3NH]^+ NO_2^-$

tri ethyl ammonium nitrite

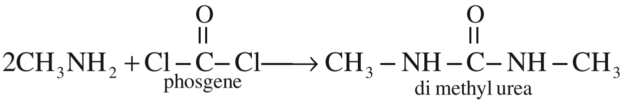
9. Reaction with nitrosyl chloride–

Nitrosyl chloride is also known as **Tilden's reagent**. Primary amine react with nitrosyl chloride to yield alkyl chloride.

$$CH_3NH_2 + NOCl \longrightarrow \underset{\text{choloro methane}}{CH_3-Cl} + N_2 + H_2O$$

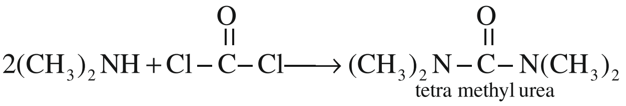
10. Reaction with phosgene–

Primary and secondary aliphatic amines react with phosgene to form substituted urea.



$$2CH_3NH_2 + \underset{\text{phosgene}}{Cl-\overset{\overset{O}{||}}{C}-Cl} \longrightarrow \underset{\text{di methyl urea}}{CH_3-NH-\overset{\overset{O}{||}}{C}-NH-CH_3}$$

$+2HCl$



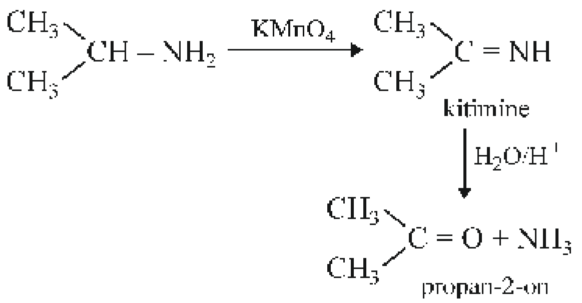
$$2(CH_3)_2NH + Cl-\overset{\overset{O}{||}}{C}-Cl \longrightarrow \underset{\text{tetra methyl urea}}{(CH_3)_2N-\overset{\overset{O}{||}}{C}-N(CH_3)_2}$$

$+2HCl$

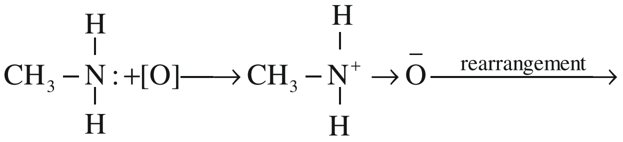
11. Oxidation–

(i) Aliphatic primary amine on oxidation with potassium permanganate followed by hydrolysis gives carbonyl compounds.

$$\underset{\text{ethan amine}}{CH_3-CH_2-NH_2} \xrightarrow{KMnO_4} \underset{\text{acet aldimine}}{CH_3-CH=NH} \xrightarrow{H_2O/H^+} \underset{\text{ethanal}}{CH_3CHO} + NH_3$$



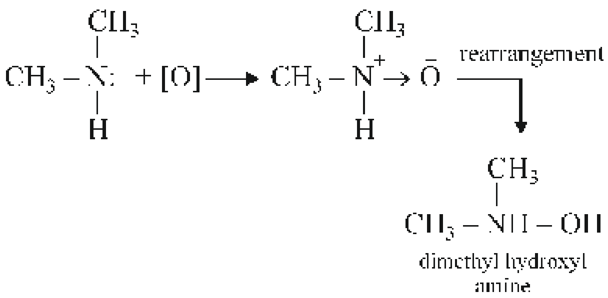
(ii) Aliphatic primary amines undergo oxidation by Hydrogen peroxide (H_2O_2) or per acid (H_2SO_5) and give amine oxide which yield N-alkyl hydroxyl amine on rearrangement.



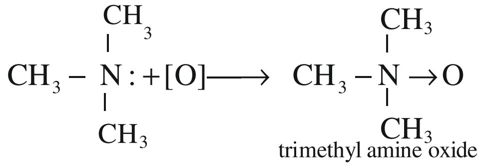
$$CH_3-\overset{H}{\underset{H}{N}}: + [O] \longrightarrow CH_3-\overset{H}{\underset{H}{N^+}} \rightarrow \bar{O} \xrightarrow{\text{rearrangement}}$$

$$\underset{\text{methyl hydroxyl amine}}{CH_3-NH-OH}$$

Secondary amine with H_2O_2 or per acid (H_2SO_5) give N,N-dialkyl hydroxyl amine.



Tertiary amines with H_2O_2 or per acid (H_2SO_5) gives corresponding amine N-oxide.



$$CH_3-\overset{CH_3}{\underset{CH_3}{N}}: + [O] \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{N}} \rightarrow O$$

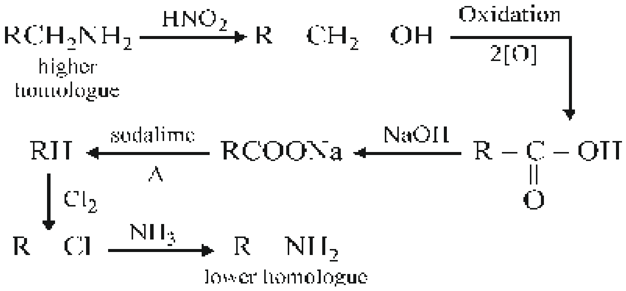
trimethyl amine oxide

13.1.6 Interconversion of primary amines

(A) Conversion of lower homologue into higher homologue

$$\underset{\text{lower homologue}}{R-NH_2} \xrightarrow[(NaNO_2+HCl)]{HNO_2} \underset{\text{alcohol}}{R-OH} \xrightarrow{PCl_5} R-Cl \xrightarrow{KCN} R-CN \xrightarrow[4[H]]{Na/C_2H_5OH} \underset{\text{higher homologue}}{RCH_2-NH_2}$$

(B) Conversion of higher homologue into lower homologue



13.1.7 Distinction between primary, secondary and tertiary amines

Test	1° amine	2° amine	3° amine
1. Isocyanide test	foul smell comes out	no reaction	no reaction
2. carbon di sulphide	gives mustard oil test reaction	di thio carbamic acid derivative formed	no reaction
3. Hinsberg reagent (benzene sulphonyl chloride)	mono alkyl sulphonamide is formed	dialkyl suphon-amide is formed	no reaction
4. Nitrous acid	N_2 gas evolved	nitrosa amine formed which gives Libermann's test	no reaction

13.1.8 Uses of amines

1. Lower aliphatic amines are used as reagents in the synthesis of organic compouds.
2. Aniline and other aromatic amine are used in the manufacture of dyes, drugs and indicators.
3. Methyl amine is used as refrigerant.
4. Amines are used in photographic developer.

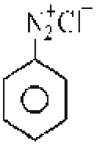
Part-B

13.2 Diazonium salt

The diazonium salts are represented by the general formula $ArN_2^+X^-$ where Ar is aryl group and X^- ion is Cl^-, HSO_4^-, BF_4^-, etc.

The N_2^+ group is called diazonium group.

Example –

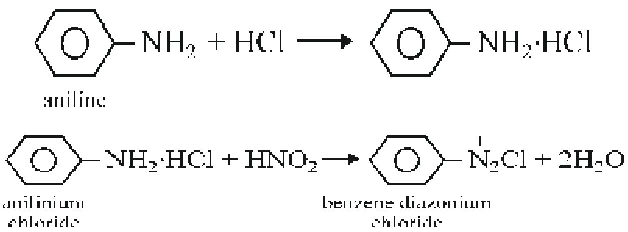


benzene diazonium chloride

13.2.1 Preparation method

Benzene diazonium chloride is obtained by the reaction of aniline and nitrous acid at low temperature i.e. 273-278 K.

$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$



In this reaction amino group is replaced by diazo group. So it is known as diazotisation.

13.2.2 Physical properties :

Diazonium salts are colourless and crystalline solids. These are readily soluble in water. They are unstable and explode in dry state. Therefore they are generally used in solution state.

13.2.3 Chemical properties :

The diazonium salts give the following types of reactions–

(A) Nitrogen substitution reactions– In substitution reactions, nitrogen of diazonium salts is lost as $-N_2^+Cl^-$ and different groups are introduced in its place. Some of the important reactions are:

1. Formation of aryl halides: When benzene diazonium chloride reacts with Cu_2Cl_2 and HCl, Cu_2Br_2 and HBr, then $-N_2Cl$ group is replaced by –Cl and –Br groups. These reactions are known as **Sandmeyer's reactions.**

$$\underset{\text{benzene diazonium chloride}}{C_6H_5N_2^+Cl^-} + HCl \xrightarrow{Cu_2Cl_2} \underset{\text{chloro benzene}}{C_6H_5-Cl} + N_2$$

$$C_6H_5N_2^+Cl^- + HBr \xrightarrow{Cu_2Br_2} \underset{\text{bromo benzene}}{C_6H_5-Br} + N_2$$

Gattermann reactions, When benzene diazonium chloride is warmed with copper powder and the corresponding halogen acid, the respective halogen is introduced. The reaction is a modified form of

Sandmeyer reaction.

$$C_6H_5N_2^+Cl^- \xrightarrow[\Delta]{Cu/HCl} \underset{\text{chloro benzene}}{C_6H_5Cl} + N_2$$

$$C_6H_5N_2^+Cl^- + HBr \xrightarrow[\Delta]{Cu/HBr} \underset{\text{bromo benzene}}{C_6H_5Br} + N_2$$

Fluoro benzene is obtained by the reaction of benzene diazonium chloride with fluoboric acid.

$$C_6H_5N_2^+Cl^- + HBF_4 \longrightarrow C_6H_5N_2^+BF_4 \xrightarrow{\Delta} \underset{\text{fluoro benzene}}{C_6H_5-F} + N_2 + BF_3$$

The reaction is called **Balz Schiemann** reaction.

Iodo benzene is obtained by warming the diazonium salt with KI.

$$C_6H_5N_2^+Cl^- + KI(aq.) \xrightarrow{\Delta} \underset{\text{iodo benzene}}{C_6H_5-I} + KCl + N_2$$

2. Formation of Nitro compounds– This is done by heating benzene diazonium chloride with sodium nitrite.

$$C_6H_5N_2^+Cl^- + NaNO_2(aq.) \xrightarrow{\Delta} \underset{\text{nitro benzene}}{C_6H_5-NO_2} + NaCl + N_2$$

3. Formation of Phenol– When benzene diazonium chloride is distilled with water vapour, phenol is produced.

$$C_6H_5N_2^+Cl^- + H-OH \rightarrow \underset{\text{phenol}}{C_6H_5-OH} + N_2 + HCl$$

4. Formation of cyano compound– Benzene diazonium chloride on reaction cuprous cyanide give cyano benzene.

$$C_6H_5N_2^+Cl^- \xrightarrow[KCN]{CuCN} C_6H_5-CN + N_2$$

5. Formation of Thiol– When benzene diazonium chloride is treated with potassium hydrosulphide, thiophenol is produced.

$$C_6H_5N_2^+Cl^- + KSH \longrightarrow \underset{\text{thiophenol}}{C_6H_5-SH} + N_2 + KCl$$

6. Oxidation– o-hypophosphorous acid or ethanol which are weak reducing agent, oxidise benzene diazonium chloride into benzene.

$$C_6H_5N_2^+Cl^- + H_3PO_2 + H_2O \rightarrow \underset{\text{benzene}}{C_6H_6} + N_2 + HCl + \underset{\text{phophorous acid}}{H_3PO_3}$$

$$C_6H_5N_2^+Cl^- + CH_3CH_2OH \longrightarrow C_6H_6 + N_2 + HCl + \underset{\text{ethanal}}{CH_3CHO}$$

7. Reduction– Reduction of benzene diazonium chloride with $SnCl_2/HCl$ gives phenyl hydrazine hydrochloride.

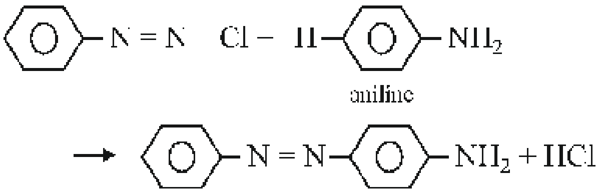
$$C_6H_5N_2^+Cl^- + 4[H] \xrightarrow[HCl]{SnCl_2} \underset{\text{phenyl hydrazine}}{C_6H_5NHNH_2} + HCl$$

8. Formation of diphenyl– It is obtained by the reaction of benzene diazonium chloride with benzene in alkaline medium.

$$C_6H_5N_2^+Cl^- + C_6H_6 \xrightarrow{NaOH} \underset{\text{diphenyl}}{C_6H_5-C_6H_5} + N_2 + HCl$$

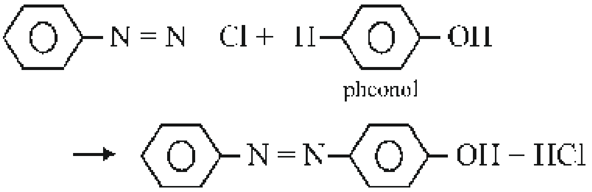
(B) Coupling reactions– Diazonium salts react with aromatic compounds to form azo compounds which are coloured and many of them are used as dyes and indicators.

(i) Reaction with aniline



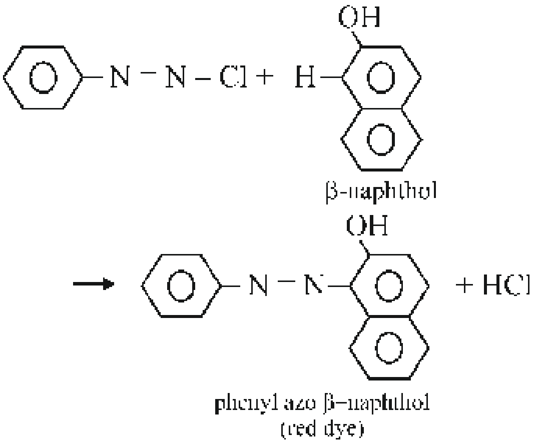
p-amino azobenzene (yellow dye)

(ii) Reaction with phenol

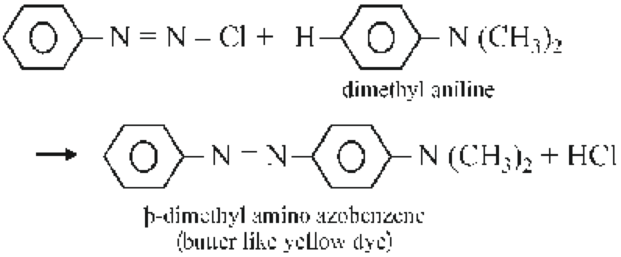


p-hydroxy azobenzene (dark red)

(iii) β-naphthol



(iv) Reaction with dimethyl aniline



13.2.4 Importance of Diazonium salts in the synthesis of Aromatic compounds

(i) It is clear from the reactions that diazonium salts are good intermediate for the bonding of halogens (F,Cl,Br,I), –CN, $-NO_2$, etc. with benzene.

(ii) Aryl fluoride and aryl iodide which are not easily prepared directly from benzene can easily prepared by diazonium salts.

(iii) Benzonitrile (C_6H_5CN) can not be prepared by SN reactions of chlorobenzene but it is easily prepared by benzene diazonium chloride.

Thus many substituted aromatic compounds are easily synthesized by diazonium salts.

Part C

13.3 Cyanides and Isocyanides

Cyanides and isocyanides are considered to be the derivatives of HCN in which H atom is replaced by alkyl or aryl group. There are two tautomers of HCN.

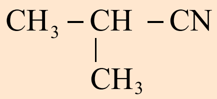
$$\underset{\text{hydrogen cyanide}}{H-C\equiv N} \rightleftharpoons \underset{\text{hydrogen isocyanide}}{H-N\overset{\rightarrow}{=}C}$$

Cyanides and isocyanides are derivatives of hydrogen cyanide.

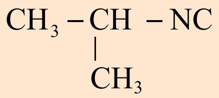
$$\underset{\text{Cyanides or nitriles}}{R-C\equiv N} \rightleftharpoons \underset{\text{isocyanides or isonitriles}}{R-N\overset{\rightarrow}{=}C}$$

13.3.1 Nomenclature of cyanides and icocyanides–

The common and IUPAC names of some cyanides are listed below:

Molecular formula	Common name	On the basis of Acid	IUPAC name
CH_3CN	methyl cyanide	aceto nitrile	ethane nitrile
CH_3CH_2CN	ethyl cyanide	propion nitrile	propane nitrile
$CH_3CH_2CH_2CN$	n-propyl cyanide	n-butyro nitrile	butane nitrile
 $CH_3-\underset{\underset{CH_3}{\mid}}{CH}-CN$	isopropyl cyanide	isobutyro nitrile	2-methyl propane nitrile

The common and IUPAC names of some isocyanides are listed below–

Molecular Formula	Common name	On the basis of acids	IUPAC name
CH_3NC	methyl isocyanide	aceto isonitrile	methyl carbyl amine
CH_3CH_2NC	ethyl isocyanide	propion isonitrile	ethyl carbyl amine
$CH_3CH_2CH_2NC$	n-propyl isocyanide	n-butyro isonitrile	n-propyl carbyl amine
 $CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-NC$	iso propyl isocyanide	isobutyro isonitrile	isopropyl carbyl amine

13.3.2 Preparations of cyanides and iso cyanides–

1. **From alkyl haides–** Alkyl haides on treatment with ethanolic solution of KCN give alkyl cyanides.

$$R-X+KCN \longrightarrow R-CN+KX$$

Example–

$$\underset{\text{ethyl bromide}}{C_2H_5Br} + KCN \longrightarrow \underset{\text{propane nitrile}}{C_2H_5CN} + KBr$$

Whe alkyl halides are heated with ethanolic solution of AgCN, alkyl iso cyanides are formed as major products.

$$C_2H_5Br + AgCN \longrightarrow \underset{\text{ethyl carbyl amine}}{C_2H_5NC} + AgBr$$

2. **From acid amide–** Alkyl cyanides are prepared by dehydration of acid amide with phosphorus penta oxide (P_2O_5) or thionyl chloride ($SOCl_2$).

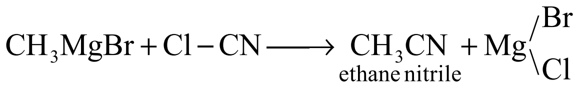
$$CH_3CONH_2 \xrightarrow{P_2O_5} \underset{\text{ethane nitrile}}{CH_3CN} + H_2O$$

and $CH_3CONH_2 + SOCl_2 \longrightarrow CH_3CN + SO_2\uparrow + HCl$

3. **From aldoxime–** Aldoxime are functional group isomers of amide which on dehydration with phosphorous penta oxide (P_2O_5) gives alkyl cyanides.

$$\underset{\text{acet aldoxime}}{CH_3CH=NOH} \xrightarrow{P_2O_5} \underset{\text{ethane nitrile}}{CH_3CN} + H_2O$$

4. **From Grignard reagent–** Alkyl cyanides are obtained by the treatment of the Grignard reagent with cyanogen chloride.



$$CH_3MgBr + Cl-CN \longrightarrow \underset{\text{ethane nitrile}}{CH_3CN} + Mg\begin{matrix}/Br\\ \backslash Cl\end{matrix}$$

5. **Carbyl amine reaction–** Isocyanides are obtained by treating primary amines with chloroform, in the presence of KOH. The aryl isocyanides have untolerable smell.

$$\underset{\text{aniline}}{C_6H_5NH_2} + CHCl_3 + 3KOH \longrightarrow \underset{\substack{\text{phenyl carbyl}\\ \text{amine}}}{C_6H_5NC}$$
$$+ 3KCl + 3H_2O$$

6. **From carboxylic acid–** Alkyl cyanides can be commercially obtained by heating carboxylic acid and ammonia mixture at 500°C in presence of alumina.

$$\underset{\text{acetic acid}}{CH_3COOH} + NH_3 \longrightarrow \underset{\text{ammonium acetate}}{CH_3COONH_4} \xrightarrow[Al_2O_3]{\Delta}$$
$$\underset{\text{acetamide}}{CH_3CONH_2} \xrightarrow{\Delta} \underset{\text{methyl cyanide}}{CH_3CN} + H_2O$$

13.3.3 Physical porpoerties of cyanide and Iso cyanide

1. **Physical state–** The lower members of the family are colourless liquids while the higher members are crysalltine solids. Alkyl cyanides have fairly pleasant odour while the corresponding isocyanides have untolerable smell.

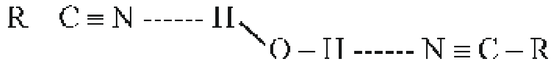
2. **Boiling points–** Both the cyanides and isocyanides are highly polar. Therefore, both have high dipole moments resulting in strong intermolecular attraction between their molecules. Thus they have relatively high boiling points. Alkyl

cyanides have relatively high boiling points than the corresponding isomeric isocyanides.

Example– CH_3CN (b.p.) =355 K

CH_3NC (b.p.) =332 K

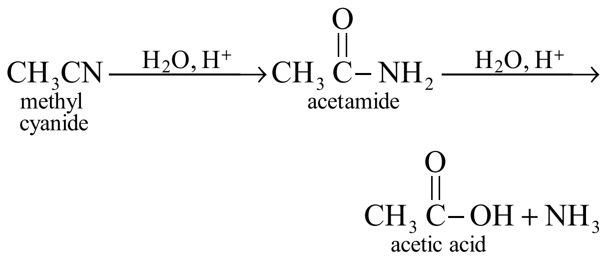
3. **Solubility–** Alkyl cyanides are more soluble in water than alkyl isocyanides. The solubility of cyanides in water is due to their tendency to form hydrogen bonds with water molecules.



In general, the solubility of cyanides decreases with increasing molecular mass.

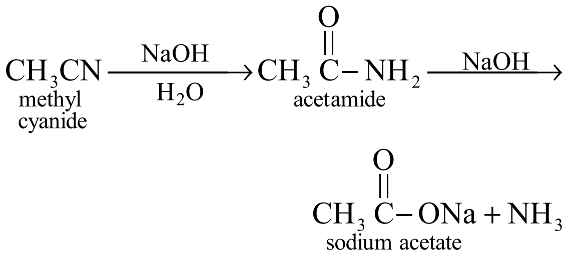
13.3.4 Chemical properties of cyanides and iso cyanides

1. **Hydrolysis–** Alkyl cyanides can be hydrolysed under acidic and basic conditions to give amides. The further hydrolysis of amides give carboxylic acid in acidic medium and carboxylic acid salt in basic medium.



$$\underset{\text{methyl cyanide}}{CH_3CN} \xrightarrow{H_2O, H^+} \underset{\text{acetamide}}{CH_3\overset{\overset{O}{||}}{C}-NH_2} \xrightarrow{H_2O, H^+} \underset{\text{acetic acid}}{CH_3\overset{\overset{O}{||}}{C}-OH} + NH_3$$

and



$$\underset{\text{methyl cyanide}}{CH_3CN} \xrightarrow[H_2O]{NaOH} \underset{\text{acetamide}}{CH_3\overset{\overset{O}{||}}{C}-NH_2} \xrightarrow{NaOH} \underset{\text{sodium acetate}}{CH_3\overset{\overset{O}{||}}{C}-ONa} + NH_3$$

Alkyl isocyanides can be hydrolysed by dilute acids to form primary amines and formic acid.

$$CH_3NC \xrightarrow{2H_2O, H^+} \underset{\text{methyl amine}}{CH_3-NH_2} + \underset{\text{formic acid}}{HCOOH}$$

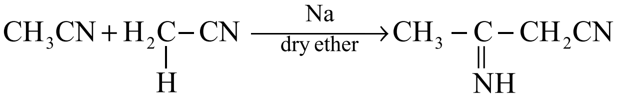
2. **Reduction–** The chemical reduction of alkyl cyanide by using $LiAlH_4$ or Na/ethanol is called Mendius reaction.

$$\underset{\text{methyl cyanide}}{CH_3CN} + 4[H] \xrightarrow[Na/C_2H_5OH]{LiAlH_4 \text{ or}} \underset{\text{ethyl amine}}{CH_3CH_2NH_2}$$

On the other hand in presence of Pt or Ni on hydrogenation, isocyanides give secondary amines.

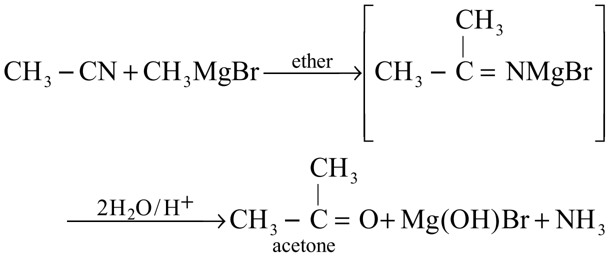
$$\underset{\text{methyl iso cyanide}}{CH_3NC} + 2H_2 \xrightarrow[Ni]{Pt \text{ or}} \underset{\text{di methyl amine}}{CH_3NHCH_3}$$

3. **Thorpe reaction–** It is a chemical reaction described as self condensation of aliphatic nitriles catalyzed by base to form enamines.



$$CH_3CN + H_2\underset{\underset{H}{|}}{C}-CN \xrightarrow[\text{dry ether}]{Na} CH_3-\underset{\underset{NH}{||}}{C}-CH_2CN$$

4. **Reaction with Grignard reageents–** Grignard reagents add to the alkyl nitriles forming intermediate imino salt which on subsequent hydrolysis give ketones.



$$CH_3-CN + CH_3MgBr \xrightarrow{ether} \left[CH_3-\overset{\overset{CH_3}{|}}{C}=NMgBr\right] \xrightarrow{2H_2O/H^+} \underset{\text{acetone}}{CH_3-\overset{\overset{CH_3}{|}}{C}=O} + Mg(OH)Br + NH_3$$

5. **Addition reactions–** Alkyl isocyanides react with halogens, sulphur, ozones, mercuric oxide to give addition compounds.

Example–

$$CH_3NC + Cl_2 \longrightarrow \underset{\text{methyl imino carbonyl chloride}}{CH_3-N=CCl_2}$$

$$CH_3NC + S \longrightarrow \underset{\text{methyl iso thio cyanate}}{CH_3-N=C=S}$$

$$CH_3NC + O_3 \longrightarrow \underset{\text{(MIC)}}{CH_3-N=C=O} + O_2$$

$$CH_3NC + 2HgO \longrightarrow \underset{\text{methyl isocyanate}}{CH_3-N=C=O} + Hg_2O$$

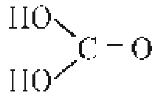
6. **Isomerism–** Alkyl isocyanides on heating for a long time rearrange to more stable alkyl cyanides.

$$\underset{\text{methyl iso cyanide}}{CH_3-N\equiv C}\xrightarrow{\Delta}\underset{\text{methyl cyanide}}{CH_3-C\equiv N}$$

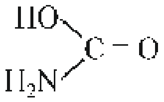
Part (D)

13.4 Urea

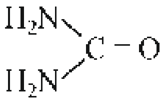
Urea is the most important derivative of carbonic acid. This amide has two -NH_2 groups joined by a carbonyl functional group.



carbonic acid or hydroxy methanoic acid



carbamic acid or hydroxy methan amide



urea or amino methan amide

It is the first organic compound synthesized in the laboratory by Wohler in 1828.

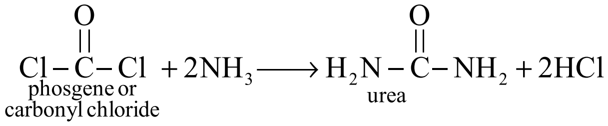
13.4.1 Preparation method–

1. **Wohler's Transformation –** Urea is obtained when a aqueous solution containing ammonium sulphate and potassium cyanate is evaporated.

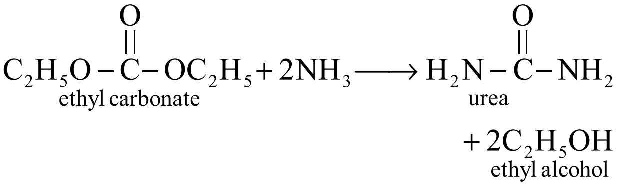
$$(NH_4)_2SO_4+2KCNO\longrightarrow 2NH_4CNO+K_2SO_4$$

$$NH_4CNO\xrightarrow{\Delta}\underset{\text{urea}}{NH_2CONH_2}$$

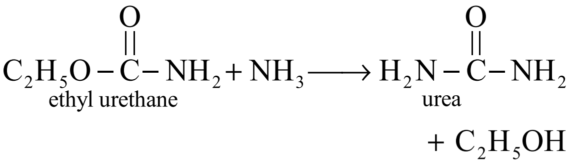
2. **Laboratory preparation–** In laboratory, urea is readily obtained by the action of ammonia on carbonyl chloride, ethyl carbonate or urethane.



$$\underset{\substack{\text{phosgene or}\\\text{carbonyl chloride}}}{Cl-\overset{\overset{O}{\|}}{C}-Cl}+2NH_3\longrightarrow \underset{\text{urea}}{H_2N-\overset{\overset{O}{\|}}{C}-NH_2}+2HCl$$

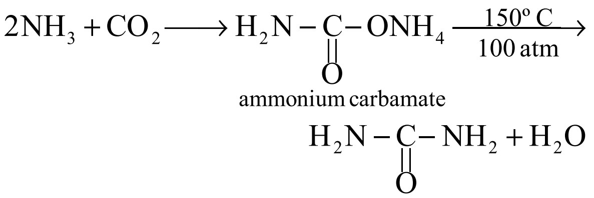


$$\underset{\text{ethyl carbonate}}{C_2H_5O-\overset{\overset{O}{\|}}{C}-OC_2H_5}+2NH_3\longrightarrow \underset{\text{urea}}{H_2N-\overset{\overset{O}{\|}}{C}-NH_2}+\underset{\text{ethyl alcohol}}{2C_2H_5OH}$$



$$\underset{\text{ethyl urethane}}{C_2H_5O-\overset{\overset{O}{\|}}{C}-NH_2}+NH_3\longrightarrow \underset{\text{urea}}{H_2N-\overset{\overset{O}{\|}}{C}-NH_2}+C_2H_5OH$$

3. **Industrial preparation–** Treatment of liquid carbon dioxide with liquid ammonia affords ammonium carbamate which upon heating at high pressure gives urea.

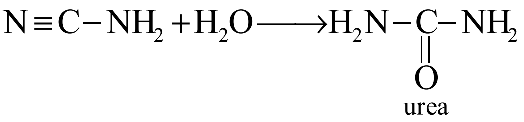


$$2NH_3+CO_2\longrightarrow \underset{\text{ammonium carbamate}}{H_2N-\underset{\underset{O}{\|}}{C}-ONH_4}\xrightarrow[100\text{ atm}]{150^{\circ}C} H_2N-\underset{\underset{O}{\|}}{C}-NH_2+H_2O$$

4. **From cyanamide–** Cyanamide is obtained by the reaction of calcium carbide and nitrogen. This on hydrolysis gives urea.

$$\underset{\text{calcium carbide}}{CaC_2+N_2}\xrightarrow{400^{\circ}C}\underset{\text{calcium cyanamide}}{CaNCN+C}$$

$$CaNCN+H_2SO_4\longrightarrow CaSO_4+\underset{\text{cyanamide}}{N\equiv C-NH_2}$$



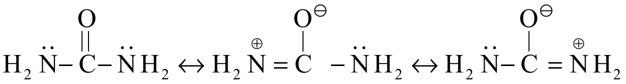
$$N\equiv C-NH_2+H_2O\longrightarrow \underset{\text{urea}}{H_2N-\underset{\underset{O}{\|}}{C}-NH_2}$$

13.4.2 Physical properties–

Urea is a colourless crystalline solid. m.p. 132°C. It is readily soluble in water and insoluble in organic solvents.

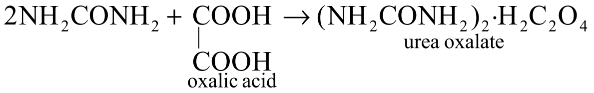
13.4.3 Chemical properties :

1. **Basic nature–** Urea behaves as a monoacid base towards strong acids. It is due to hybrid of the following contributing forms:



$$H_2\ddot{N}-\overset{\overset{O}{\|}}{C}-\ddot{N}H_2\leftrightarrow H_2\overset{\oplus}{N}=\overset{\overset{O^{\ominus}}{|}}{C}-\ddot{N}H_2\leftrightarrow H_2\ddot{N}-\overset{\overset{O^{\ominus}}{|}}{C}=\overset{\oplus}{N}H_2$$

$$\underset{\text{urea}}{NH_2CONH_2}+\underset{\text{nitric acid}}{HNO_3}\longrightarrow \underset{\text{urea nitrate}}{NH_2CONH_2.HNO_3}$$



$$2NH_2CONH_2+\underset{\text{oxalic acid}}{\begin{matrix}COOH\\|\\COOH\end{matrix}}\rightarrow \underset{\text{urea oxalate}}{(NH_2CONH_2)_2{\cdot}H_2C_2O_4}$$

2. **Hydrolysis–** Urea can be hydrolysed on heating with acids or alkali or in the presence of enzyme urease.

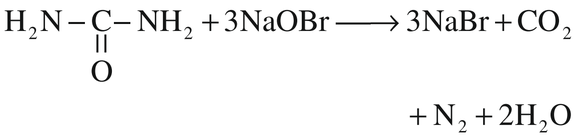
$$NH_2CONH_2+2HCl+HOH\rightarrow 2NH_4Cl+CO_2$$

$$NH_2CONH_2+2NaOH+2HOH\rightarrow 2NH_4OH+Na_2CO_3$$

$$NH_2CONH_2+2HOH\xrightarrow{\Delta}(NH_4)_2CO_3$$

3. **With nitrous acid–** Urea when treated with nitrous acid, it decomposes into nitrogen and carbon dioxide.

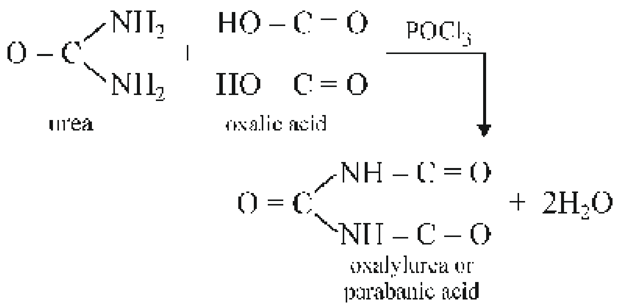
4. **Action of Sodium hypobromite–** Urea is decomposed with the evolution of nitrogen when it is treated with an excess of alkaline hypobromite solution (NaOBr).

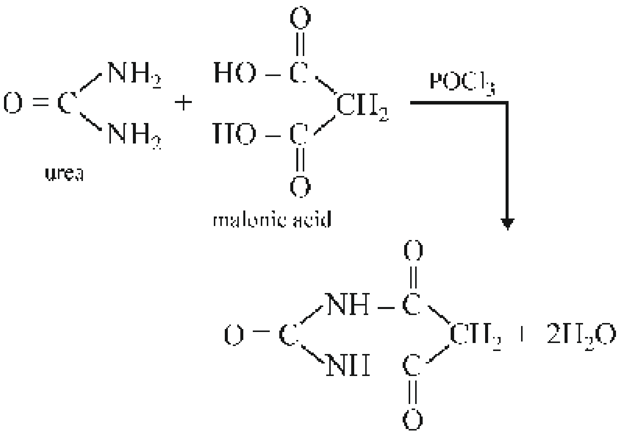


$$H_2N-\underset{\underset{O}{||}}{C}-NH_2 + 3NaOBr \longrightarrow 3NaBr + CO_2 + N_2 + 2H_2O$$

The reaction is quantitative and is often used for the estimation of urea.

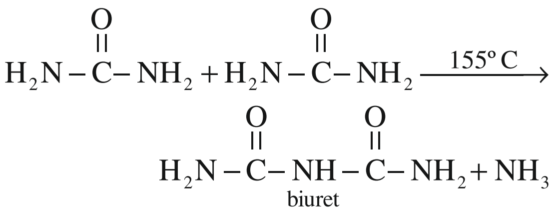
5. **With dicaroboxylic acid–** Dicarboxylic acids condense with urea forming cyclic ureides.





malonyl urea or barbituric acid
(central nervous system depressant)

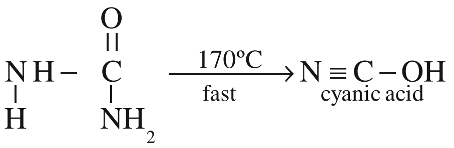
6. **Action of heat–** (i) When heated gently, at little above its melting point (155°C), urea loses a molecule of ammonia forming biuret.



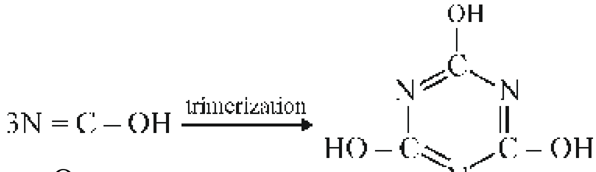
$$H_2N-\overset{\overset{O}{||}}{C}-NH_2 + H_2N-\overset{\overset{O}{||}}{C}-NH_2 \xrightarrow{155°\,C} \underset{\text{biuret}}{H_2N-\overset{\overset{O}{||}}{C}-NH-\overset{\overset{O}{||}}{C}-NH_2} + NH_3$$

This reaction forms the basis of the well known biuret test, detecting urea. An aqueous solution of biuret gives violet colour with aqueous copper sulphate in presence of little alkali.

(ii) However, when urea is heated rapidly at 170°C, it forms cyanic acid which readily trimerizes to cyanuric acid.



$$\underset{\underset{H}{|}}{NH}-\overset{\overset{O}{||}}{\underset{\underset{NH_2}{|}}{C}} \xrightarrow[\text{fast}]{170°C} \underset{\text{cyanic acid}}{N\equiv C-OH}$$

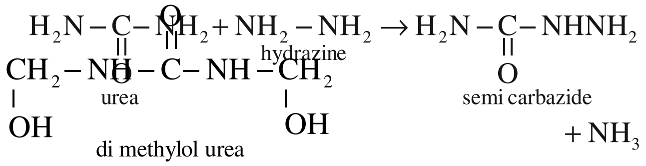


cyanuric acid

$$H_2N-\underset{\underset{O}{||}}{C}-NH_2 + 2HNO_2 \rightarrow CO_2 + 3N_2 + 3H_2O$$

$$\underset{\text{urea}}{H_2N-\underset{\underset{O}{||}}{C}-NH_2} + \underset{\text{formaldehyde}}{2HCHO} \downarrow$$

7. **Reaction with hydrazine–** Urea condenses with hydrazine forming semi carbazide.



$$\underset{\text{urea}}{H_2N-\underset{\underset{O}{||}}{C}-NH_2} + \underset{\text{hydrazine}}{NH_2-NH_2} \rightarrow \underset{\text{semi carbazide}}{H_2N-\underset{\underset{O}{||}}{C}-NHNH_2} + NH_3$$

$$\underset{\text{di methylol urea}}{\underset{\underset{OH}{|}}{CH_2}-NH-\overset{\overset{O}{||}}{C}-NH-\underset{\underset{OH}{|}}{CH_2}}$$

8. **With formaldehyde–** In presence of acid or alkali, dimethylol urea is formed by the reaction of one mole of urea with two moles of formaldehyde.

13.4.4 Uses of urea

(i) For the preparation of barbiturate which is used as a central nervous system depresant.

(ii) Urea is most commonly used as nitrogen fertilizer.

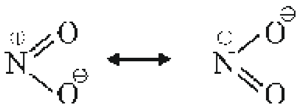
(iii) It is a raw material for the manufacture of urea-formaldehyde plastic.

(iv) In the formation of semicarbazide.

Part (E)

13.5 Nitro compounds

Nitro compounds are obtained by replacement of hydrogen in aliphatic or aromatic hydrocarbons.

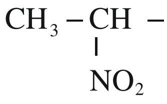


13.5.1 Nomenclature– These are named by prefixing nitro to the parent alkane and the position of the nitro group of the carbon chain is indicated by a number.

Nitroalkanes may further be classified as primary (1°), secondary (2°) or tertiary (3°) depending upon whether the nitro group is attached to primary, secondary or tertiary carbon atom.

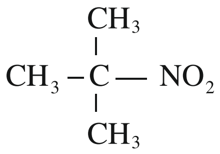
Example–

1° $CH_3–NO_2$ nitro methane, $CH_3–CH_2–NO_2$ nitro ethane

2° 

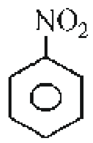
$$CH_3-\underset{\displaystyle NO_2}{\underset{|}{CH}}-CH_3$$

2–nitro propane

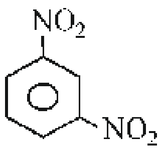
3° 

$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-NO_2$$

2–methyl–2–nitro propane



nitrobenzene



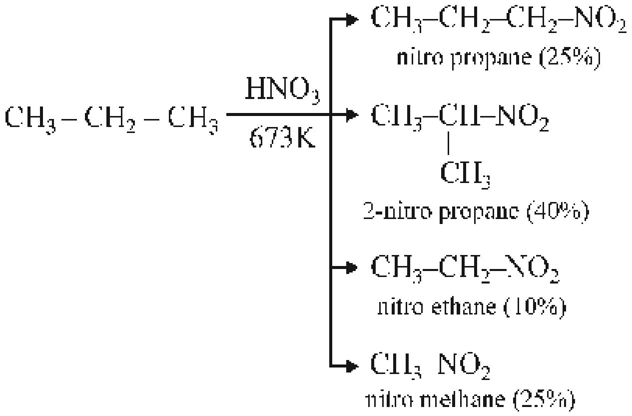
m-dinitrobenzene

13.5.2 Preparation method of nitro compounds

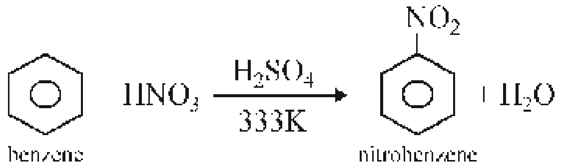
1. **From hydrocarbons–** Nitro compounds are prepared by the vapour phase nitration of hydrocarbons with nitric acid at about 673K. However, it gives a mixture of nitro alkanes.

$$\underset{\text{methane}}{CH_4} + HNO_3 \xrightarrow{673\text{ K}} \underset{\text{nitro methane}}{CH_3-NO_2} + H_2O$$

$$\underset{\text{ethane}}{CH_3-CH_3} \xrightarrow[673\text{ K}]{HNO_3} \underset{\substack{\text{nitro ethane}\\(80\%)}}{CH_3-CH_2-NO_2} + \underset{\substack{\text{nitro methane}\\(20\%)}}{CH_3NO_2}$$



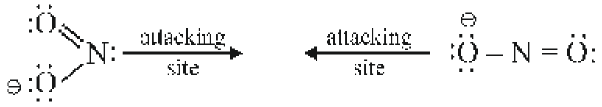
Nitrobenzene is produced when benzene is allowed to react with a mixture of concentrated HNO_3 and concentrated H_2SO_4 (also called nitrating mixture.



2. **From alkyl halides–** Alkyl halides (especially bromides or iodides) when treated with $AgNO_2$ in alcoholic solution give nitro compounds.

$$R-X + AgNO_2 \rightarrow \underset{\substack{\text{nitro alkane}\\\text{(major product)}}}{R-NO_2} + \underset{\substack{\text{alkyl nitrite}\\\text{(minor product)}}}{R-ONO} + AgX$$

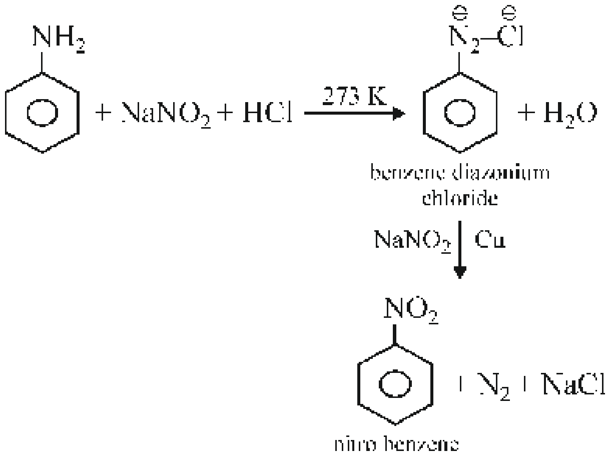
In the above reaction a small amount of alkyl nitrite is also formed because nitrite ion is an ambident nucleophile, having two attacking sites, N and O atoms.



Silver nitrite is a covalent compound and therefore only N is available for attack. As a result, silver nitrite gives mainly nitroalkanes.

The above method cannot be used for the preparation of aromatic nitro compounds because of less reactivity of aryl halides towards nucleophilic substitution.

3. **From aniline–** Nitrobenzene is obtained by the reaction of benzene diazonium chloride which is obtained from aniline by the reaction with $NaNO_2$ and HCl.



13.5.3 Physical Properties

1. Nitro alkanes are colourless liquids with pleasant smell.
2. Nitrobenzene is a pale yellow liquid having a smell of bitter almond.
3. Nitro alkanes are sparingly soluble in water while aromatic nitro compounds are insoluble in water.
4. The nitro compounds are highly polar with the dipole moments ranging approximately between 3 to 3D. Due to strong dipole-dipole interactions they have high boiling points in comparison to the hydrocarbons of comparable molecular masses.

13.5.4 Chemical prpoerties

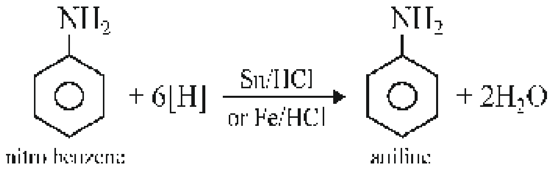
1. **Reduction–** The various reduction stages of nitro group are given below:

$$\underset{\text{nitro alkane}}{R-NO_2} \xrightarrow[-H_2O]{+2[H]} \underset{\text{nitroso alkane}}{R-N=O} \xrightarrow{+2[H]}$$

$$\underset{\text{alkyl hydroxyl amine}}{R-NH-OH} \xrightarrow[-H_2O]{+2[H]} \underset{\text{primary amine}}{R-NH_2}$$

The final product, however, depend upon the nature of reducing agent as well as the pH of medium as described below:

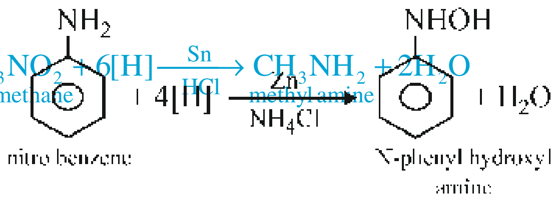
(a) Acidic medium



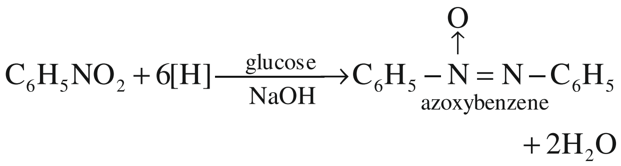
(b) Natural medium

$$\underset{\text{nitro methane}}{CH_3-NO_2} + 4[H] \xrightarrow[NH_4Cl]{Zn} \underset{\text{N–methyl hydroxyl amine}}{CH_3NHOH + H_2O}$$

$$\underset{\text{nitro methane}}{CH_3NO_2} + 6[H] \xrightarrow[HCl]{Sn} \underset{\text{methyl amine}}{CH_3NH_2} + 2H_2O$$



(c) Alkaline medium



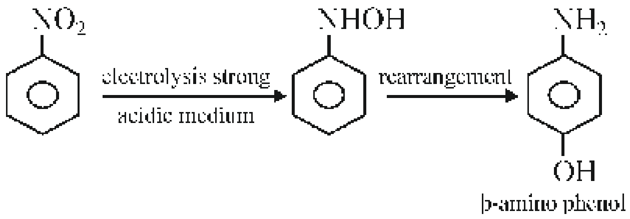
$$C_6H_5NO_2 + 6[H] \xrightarrow[NaOH]{glucose} \underset{\text{azoxybenzene}}{C_6H_5-\overset{\overset{O}{\uparrow}}{N}=N-C_6H_5} + 2H_2O$$

$$2C_6H_5NO_2 + 8[H] \xrightarrow[\text{NaOH (alchol)}]{Zn} \underset{\text{azobenzene}}{C_6H_5-N=N-C_6H_5} + 4H_2O$$

$$2C_6H_5NO_2 + 10[H] \xrightarrow[\text{NaOH (aq.)}]{Zn} \underset{\text{hydrazobenzene}}{C_6H_5NH-NHC_6H_5} + 4H_2O$$

(d) Electrolytic reduction– Electrolytic reduction of nitro benzen in weakly acidic medium give aniline whereas, if the reduction is carried out in strongly acidic medium, p-amino phenol is formed.

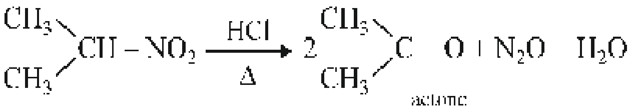
$$C_6H_5NO_2 \xrightarrow[\text{acidic medium}]{\text{electrolys is}} C_6H_5NH_2$$



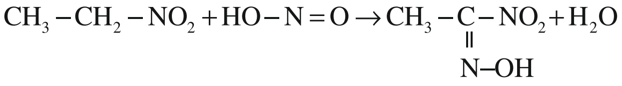
2. **Hydrolysis–** Primary nitroalkanes can be hydrolysed by boiling with concentrated solution of HCl or 85% H_2SO_4 to give carboxylic acid and hydroxyl amine.

$$\underset{\text{nitro ethane}}{CH_3CH_2NO_2} + H_2O \xrightarrow[H_2SO_4]{\text{HCl or}} \underset{\text{acetic acid}}{CH_3COOH} + NH_2OH$$

Secondary nitro alkanes gives ketones with HCl at high temperature.

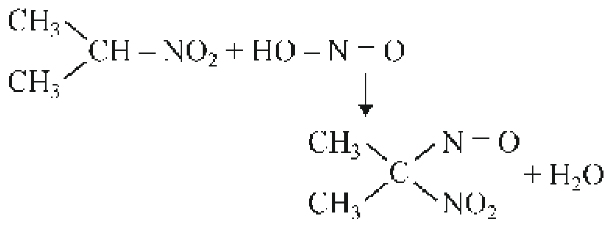


3. **Reaction with nitrous acid–** Primary nitro alkanes react with nitrous acid to form nitrolic acid which gives red colouration with alkali.



$$CH_3-CH_2-NO_2+HO-N=O \rightarrow CH_3-\underset{\underset{\text{N–OH}}{\|}}{C}-NO_2+H_2O$$

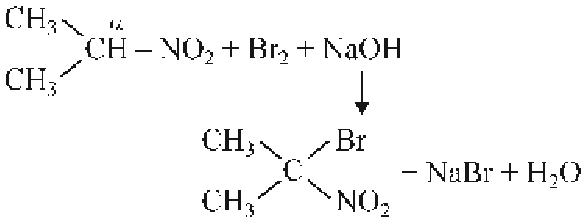
Secondary nitroalkanes react with nitrous acid to give blue coloured, pseudo nitroles. These are insoluble in water as well as in alkali.



Tertiary nitroalkanes do not react with nitrous acid because these is no α–H atom on the carbon.

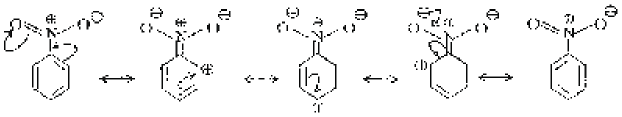
4. **Halogenation–** Primary and secondary nitro alkanes on treatment with halogen in presence of NaOH give halo nitroalkanes. The α–H atoms of nitroalkanes are successively replaced by halogen atoms.

$$\underset{\text{nitro methane}}{\overset{\alpha}{C}H_3\,NO_2} + 3Cl_2 + 3NaOH \rightarrow \underset{\text{chhoro picrin}}{CCl_3NO_2}$$
$$+ 3NaCl + 3H_2O$$



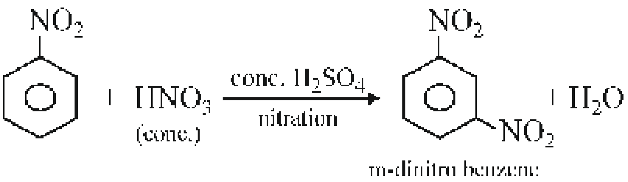
13.5.5 Ring substitution reaction

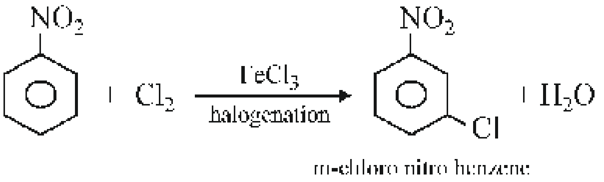
(a) **Electrophilic substitution reactions–** Nitrobenzene may be represented by the following resonating structures.

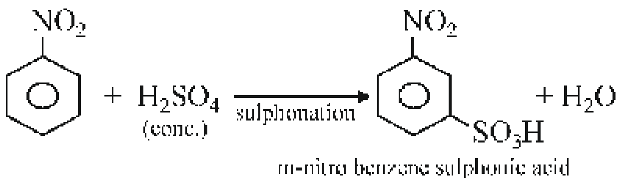


It is clear from the above structures that because of electron withdrawing nature of NO_2 group, the electron density is reduced at ortho- and para-positions. Therefore electron density is comparatively more at meta-position and consequently nitro group is meta directing group. Moreover, $-NO_2$ is electrong withdrawing group and it deactivate the benzene ring. Thus nitrobenzene is less reactive towards electrophilic substitution reactions and it undergoes reaction only under drastic conditions.

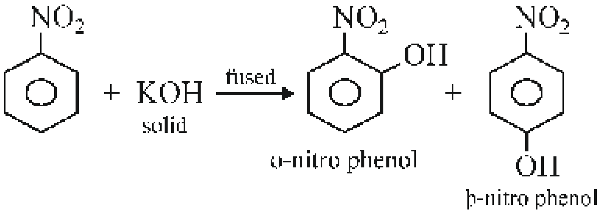
Example–







(b) **Nucleophilic substitution reactions–** From the above resonating structures, it is clear that electron density is reduced at o– and p– positions so nucleophile in presence of strong base (solid KOH) is substituted at o– and p–positions in nitro benzene.



EXERCISE QUESTIONS

Multiple Choice Questions

1. Which one of the following is most basic
   (a) CH_3NH_2 (b) $(CH_3)_2NH$
   (c) $(CH_3)_3N$ (d) $C_6H_5NH_2$

2. Hinsberg reagent is–
   (a) Benzene sulphonyl chloride
   (b) Benzene sulphonic acid
   (c) Benzene sulphone amide
   (d) Phenyl isocyonide

3. C_3H_9N does not form–
   (a) Primary amine (b) Quaternary salt
   (c) Tertiary amine (d) Secondary amine

4. Hybridization state of N in alkyl amine is–
   (a) sp^2 (b) sp^3
   (c) sp (d) sp^3d

5. Formula of compound which has mustard oil smell is–
   (a) RCN (b) RNS
   (c) RNCO (d) RNCS

6. Formula of chloropicrin is–
   (a) $C(NO_2)Cl_3$ (b) $CCl(NO_2)_3$
   (c) $C(NO_2)_2Cl_2$ (d) none of above

7. Nitrobenzene obtained from benzene where HNO_3 and H_2SO_4 takes part in the reaction. What is behaviour of HNO_3 like–
   (a) base (b) acid
   (c) redcuing agent (d) catalyst

8. A dye obtained by the reaction of reactant X with benzene diazonium chloride. The reactant X is–
   (a) C_2H_5OH (b) C_6H_6
   (c) $C_6H_5NH_2$ (d) H_2O

9. The formula of acetonitrile is-
   (a) CH_3CN (b) CH_3COCN
   (c) CH_3CH_2CN (d) $CN–CH_2–COOH$

10. The main product formed by the reaction of methane amine with Tilden reagent is–
    (a) CH_3OH (b) CH_3CHO
    (c) CH_3Cl (d) CH_3COOH

Very Short Answer Questions

1. Explain why aromatic diazonium salt is more stable than aliphatic.
2. Explain why alkane amine is strong base than ammonia.
3. Identify X and Y in the following reaction.

$$R-CONH_2 \xrightarrow{Br_2/NaOH} X$$
$$\xrightarrow{CHCl_3/KOH\ alcohol} Y$$

4. Identify A and B in the following reaction.

$$C_6H_5N_2Cl \xrightarrow[\Delta]{HOH} A \xrightarrow{Br_2} B$$

5. Dimethyl amine is strong base than methyl amine. give reasons.
6. Write the structural formula and IUPAC name of vinyl cyanide.
7. Write the equation of Mendius reduction.

8. How will you convert aniline into phenyl iso cyanide.

9. Write the equation for getting ethanol from ethanamine.

10. Write the structural formula and IUPAC name of urea.

11. Write the reduction equation of nitro benzene in presence of Zn + HCl

12. Complet the following reaction.

$$NH_4CNO \xrightarrow{\Delta} ?$$

13. Write an equation which shows the basic nature of ethane amine.

14. Explain why boiling point of primary amine is higher than tertiary amine.

Short Answer Type Questions

1. Write a note on biuret test. Gives chemical equation.

2. Gives the reactions of urea with the following compounds–

   (a) Formaldehyde (b) Hydrazine

   (c) Malonic acid

3. Complete the following reactions.

$$R - X + KCN \longrightarrow ? + ?$$
$$R - X + AgCN \longrightarrow ? + ?$$

4. Give balanced chemical equation of reduction of nitrobenzene in.

   (a) Basic medium

   (b) Neutral medium

5. Arrange aliphatic amines in increasing order of basicity and comment briefly on basicity.

6. Write notes on

   (a) Hoffmann bromamide reaction

   (b) Mono basic nature of urea

7. Identify A, B and C in the following reactions.

(a) $C_6H_5N_2Cl \xrightarrow[HCN]{CuCN} A \xrightarrow{H_2O/H^+} B$

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

$\xrightarrow{NaNO_2/HCl} C$

(c) $CH_3Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow{HNO_2} C$

8. Write hydrolysis reactions of urea in various medium.

Answers (Multiple Choice Questions)

1. (b), 2. (a), 3. (b), 4. (b),
5. (d), 6. (a), 7. (a), 8. (c),
9. (a), 10. (c),

❑❑❑