13

Amines

Alkyl Amine :

[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 posses $-NH_2$ (amino) group.

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

[d] If all hydrogen atoms of NH_2 are replaced than it is called tert. amine and has nitrilo N group.

[e] Aliphatic amine was discovered by 'Wurtz'.

[f] Aliphatic and aromatic amine shows chain, position, function and metamerism.

[g] $-NH_2$ group is called Amino group.

[h] –NH–group is called Imino group.

[i] –N– group is called Nitrilo group.

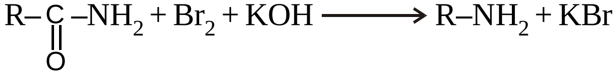
[j] N is in sp^3 hybridisation and tetrahedral geometry.

[k] Bond angle increases from ammonia to 3° amines.

NH_3 (107°) $< RNH_2 < R_2NH < R_3N$

Methods of Preparation :

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'.

2. From Alkylchloride :

$$R{-}Cl + H{-}NH_2 \xrightarrow[200^{\circ}C]{Cu_2O} R{-}NH_2 + HCl$$

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.

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)

$$RNO_2 \xrightarrow{\text{reduction}} RNH_2 + 3H_2O$$

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.

$$RNO_2 \xrightarrow[NH_4Cl]{Zn+} RNHOH + 2H_2O$$

N-alkylhydroxyl amine

[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.

$$RCH_2NO_2 \xrightarrow[\text{conc.HCl}]{SnCl_2+} RCH_2NHOH + RCH{=}NOH$$

4. **From Alcohol :**

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

5. **From Grignard reagent :**

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

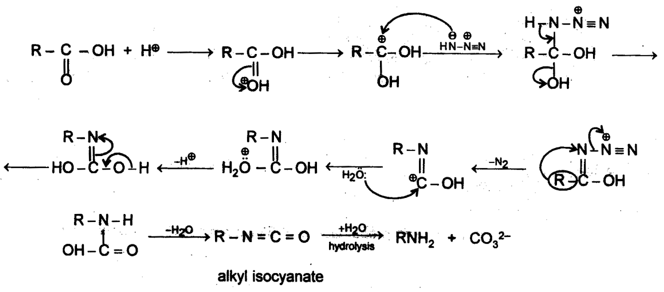
6. **From Alkyl isocyanate (Alkaline Hydrolysis) :**

$$R-N{=}C{=}O + 2KOH \longrightarrow R-NH_2 + K_2CO_3$$

7. **From Alkanoic acid (Schimdt Reaction);**

$$R-\underset{O}{\underset{\|}{C}}-O-H + N_3H \longrightarrow RNH_2 + N_2 + CO_2$$

Mechanism :



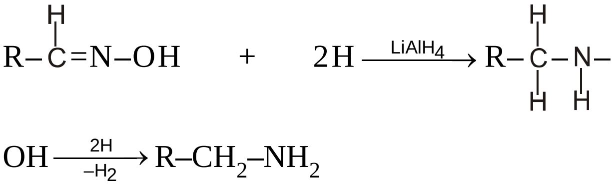
Note : Alkyl isocyanate can also be produced by heating the mixture of acyl halide and sodium azide, alklisocynate, once it is formed, can easily be hydrolysed into primary amine and CO_3^{2-}.

8. **By Alkyl cyanide (By reaction) :**

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

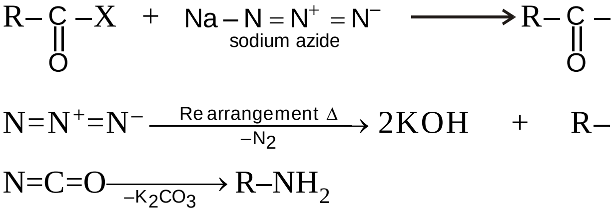
Note : When (Na + EtOH) is used as reducing agent then reaction is called '**Mandius Reaction**'.

9. **From Aldoxime (By Reduction) :**



$$R-\overset{H}{\overset{|}{C}}{=}N-OH \quad + \quad 2H \xrightarrow{LiAlH_4} R-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-\underset{H}{\underset{|}{N}}-OH \xrightarrow[-H_2]{2H} R-CH_2-NH_2$$

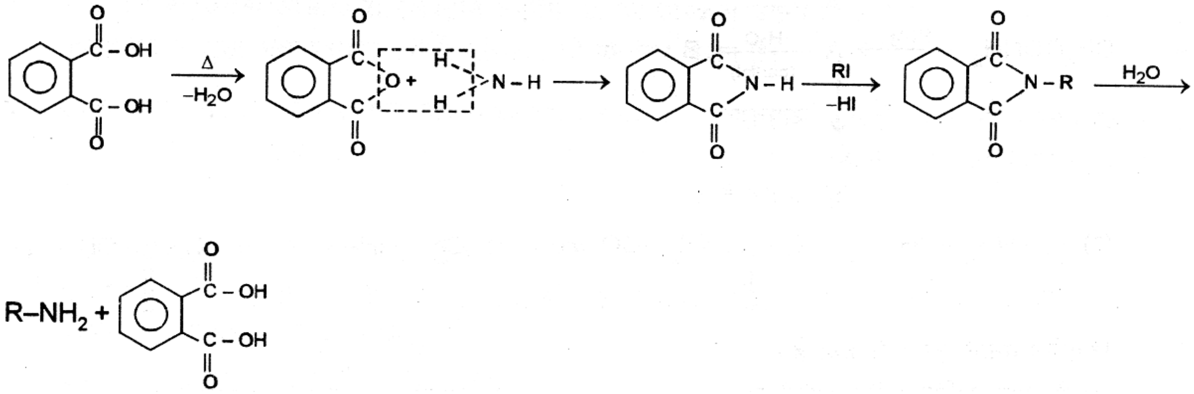
10. **From Acyl halide :**



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

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

11. **From Phthalic acid :**



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

12. By Aldehyde or ketone (reaction wtih H_2 and NH_3 in presence of catalyst) :

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

$$R_1R_2C{=}O + NH_3 \longrightarrow R_1R_2CHNH_2$$

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

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 or primary amine on hydrolysis yields primary amine and formate ions.

$$>C{=}O \;+\; \underset{\text{(ammonium formate)}}{2HCO_2NH_4} \longrightarrow\; >CH–$$

$$NHCHO + 2H_2O + NH_3 + CO_2$$

$$>C{=}O \;+\; 2HCONH_2 \longrightarrow\; >CH – NH–$$

$$CHO + CO_2 + NH_3$$

$$>CH–NH–CHO \xrightarrow[\text{in alkaline medium}]{2H_2O}\; >CH–NH_2$$

$$+ HCOO^-$$

Physical Properties :

[a] Unlike other 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 intermolcular 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.

[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

Chemical Properties :

[a] Almost all chemical properties and reaction of amines are governed by basicity of amines. So we should understand it clearly. A lone pair of electron on nitrogen atoms 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 nitrogen 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 except the order of basicity of ammonia.

1º, 2º and 3º amines to be

3º > 2º > 1º ammonia

[e] Some order factors like steric effect, Solvation or hydration and mainly crowding on nitrogen atom by three bulky alkyl groups, decreases the basicity of 3º 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 3º amine to form H–bonds with water which stabilizes R_2N^+H on because it has only one H–atom.

Chemical Reaction :

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.

Ex. $C_2H_5NH_3Cl \xrightarrow[\Delta]{} C_2H_5Cl + NH_3$

2. Reaction with water : Amine gives alkyl ammonium hydroxides which dissociate into ions :

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

3 Reaction with HNO_2 : This reaction distinguishes 1º, 2º and 3º alcohols.

[a] Primary Amine : 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)

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

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 2º amines.

[c] Tertiary Amine : These are inert to HNO_2 but being basic in nature forms salts with it.

$(CH_3)_3N + HNO_2 \longrightarrow (CH_3)_3N\text{–}HONO$

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 amines test or isocyanide test**.

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

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

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

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

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

5. Acylation : 1º and 2º amines react with acetyl chloride or acetic anhydride to form acetyl derivatives.

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

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

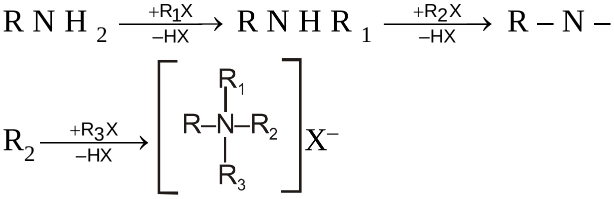
$(CH_3)_2NH + CH_3COCl \longrightarrow (CH_3)_2N\text{–}COCH_3 + HCl$

Note :

[a] Tertiary amines donot undergo this reaction because of absence of replaceable H–atom.

[b] When Benzoyl chloride is used in place of acetyl chloride reaction is called '**Schotten–Baumann**' reaction.

6. Alkylation :



$$RNH_2 \xrightarrow[-HX]{+R_1X} RNHR_1 \xrightarrow[-HX]{+R_2X} R\text{–}N\text{–}R_2 \xrightarrow[-HX]{+R_3X} \left[\begin{array}{c} R_1 \\ | \\ R\text{–}N\text{–}R_2 \\ | \\ R_3 \end{array}\right] X^-$$

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

[a] Primary Amine : Oxidised to aldehydes and ketones.

$RCH_2NH_2 \xrightarrow[KMnO_4]{[O]} \underset{\text{aldimine}}{R\text{–}CH{=}NH} \xrightarrow{H_2O} \underset{\text{aldehyde}}{R\text{–}CHO} + NH_3$

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

[b] Secondary Amine :

$2R_2NH \xrightarrow[KMnO_4]{[O]} \underset{\text{(tetra–alkyl hydrazine)}}{R_2N\text{–}NR_2}$

$R_2NH \xrightarrow{\text{caro's acid}} \underset{\text{(dialkyl hydroxylamine)}}{R_2N\text{–}OH}$

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

Note :

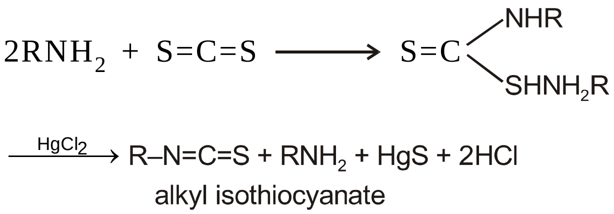
[i] $NH_2\text{–}NH_2$ is called hydrazine

[ii] $NH_2\text{–}OH$ is called Hydroxylamine

8. **Reaction with Aldehydes and Ketone :**

$RNH_2 + CH_3CHO \longrightarrow RN{=}CHCH_3 + H_2O$ (schiff's base or anil's base)

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.



$$2RNH_2 + S{=}C{=}S \longrightarrow S{=}C(NHR)(SHNH_2R)$$

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

alkyl isothiocyanate

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

$RNH_2 + CH_3MgBr \longrightarrow CH_4 + RNH.MgBr$

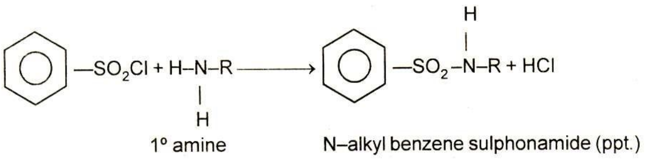
$R_2NH + CH_3MgBr \longrightarrow CH_4 + R_2N.MgBr$

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

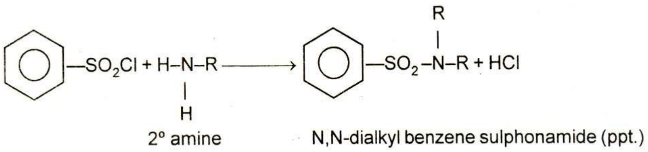
11. **Reaction with Hinsberg reagent :** This is a method for separation of 1°, 2° and 3° amines Hinsberg Reagent is $C_6H_5{-}SO_2{-}Cl$ (Benzene sulphonyl chloride)

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

[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.

12. **Reaction with Nitrosyl chloride (TILDEN'S REAGNET) :**

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

13. **Reaction with $HAuCl_4$ (Chloroauric Acid) and H_2PtCl_6 (Chloroplatinic Acid) :**

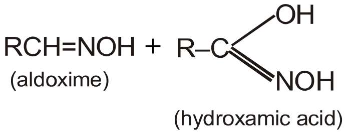
$R{-}NH_2 + HAuCl_4 \longrightarrow [R{-}NH^+{}_3]\,AuCl_4^-$ alkylamine chloraurate

$2R{-}NH_2 + H_2PtCl_6 \longrightarrow [R{-}N^+H_3]_2\,PtCl_6^-$ alkyl amine chloroplatinate

14. **Reaction with Caro's acids $[H_2SO_5]$:**

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

$RCH_2NH_2 \xrightarrow[\text{by } H_2SO_5]{[O]} RCH_2NHOH$ + (N–alkyl hydroxyl amine)



$RCH{=}NOH + R{-}C(OH){=}NOH$

(aldoxime) (hydroxamic acid)

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

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

Seperation of Mixtures of Amines :

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.

2. **Hofmann method :**

This involves the treatment of the mixture with diethyl oxalate

[a] The primary amines forms a dialkyloxaminde, 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.

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.

$$C_6H_5SO_2Cl + H{-}\overset{R}{\overset{|}{H}}NR \longrightarrow C_6H_5SO_2{-}N{-}H + HCl$$

benzene sulphonyl chloride	1° amine	N–alkyl benzene sulphonamide

[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.

Cyanides, Isocyanides, Alkyl Nitrites and Nitro Alkanes :

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 (Acetonitrile)	Methyl cyanide	Ethane nitrile
C_2H_5CN (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 (Comman name)	IUPAC names
CH_3NC	Methyl isocyanide (Methyl isonitrile)	Methylcarbylamine (Carbylamino methane)
C_2H_5NC	Ethyl isocyanide (Ethyl isonitrile)	Ethyl carbylamine (Carbylamino ethane)
C_3H_7NC	Propyl isocyanide (Propyl isonitrile)	(Propyl carbylamine (Carbylamino propane)

Isocyanides are also named as alkane isonitrile.

CH_3NC	Methane isonitrile
C_2H_5NC	Ethane isonitrile
C_3H_7NC	Propane isonitrile

2. Alkyl cyanides :

2.1 Methods of Preparation :

[i] **From alkyl haldies :** 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.

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

[ii] **From acid amides :** Pure nitriles are obtained by dehydration of acid amides with phosphrous pentaoxide. Amides are distilled with phosphorus pentaoxide, 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 500ºC.

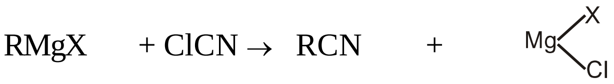
$$RCOOH + NH_3 \longrightarrow RCOONH_4$$

Acid　　　　Ammonium Salt

$$\xrightarrow[-H_2O]{Al_2O_3,\ 500°C} RCONH_2 \xrightarrow[-H_2O]{Al_2O_3} RCN$$

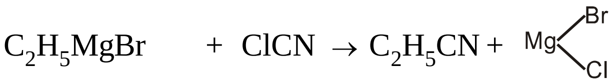
Amide　　　　Alkyl Cyanide

[iii] From Grignard reagent : Grignard reagent reacts with cyanogen chloride to from alkyl cyanides.



$$RMgX + ClCN \rightarrow RCN + Mg\begin{matrix} X \\ Cl \end{matrix}$$

Grignard reagent　　Alkyl Cyanide



$$C_2H_5MgBr + ClCN \rightarrow C_2H_5CN + Mg\begin{matrix} Br \\ Cl \end{matrix}$$

Methyl magnisium bromide　　Cyanogen chloride　　Methylcyanide

[iv] From Primary amines : Primary amines are dehydrogenated when passes over copper or nickel at high temperature to form alkyl cyanides. This is also a commerical method.

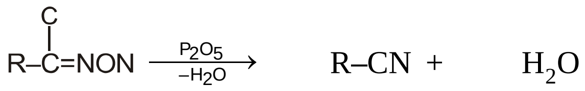
$$RCH_2NH_2 \xrightarrow[500°C]{Cu\ or\ Ni} RCN + 2H_2$$

Primary amine

$$CH_3CH_2NH_2 \xrightarrow[500°C]{Cu\ or\ Ni} CH_3CN + 2H_2$$

Ethylamine　　Methyl cyanide

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



$$R\overset{C}{\overset{|}{C}}=NON \xrightarrow[-H_2O]{P_2O_5} R–CN + H_2O$$

Aldoxime　　Alkyl cyanide

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 increases in number of carbon atoms in the molecule.

[iv] They are soluble in organic solvents.

[v] They are poisonous but less poisonous than HCN.

4. Chemical properties :

[i] **Hydrolysis :** Alkyl cyanides are hydrolysed by both acid and alkalines. On partial hydrolysis amides are formed while on complete hydrolysis acids are obtained.

$$RCN \xrightarrow[H^+]{H_2O} RCONH_2 \xrightarrow[H^+]{H_2O} RCOOH + NH_3$$

Alkyl cyanide	Amide	Acid
CH_3CN	CH_3CONH_2	$CH_3COOH+NH_3$
Methyl cyanide	Acetamide	Acetic acid

[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.

$$RCN \xrightarrow{4H} RCH_2NH_2$$

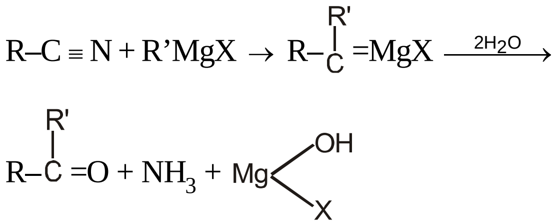
Alkyl cyanide　　Primary amine

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**).

$$R–C{\equiv}N \xrightarrow[2[H]]{SnCl_2\ /HCl} RCH=NH.HCl \xrightarrow{H_2O}$$

$$RCHO + NH_4Cl$$

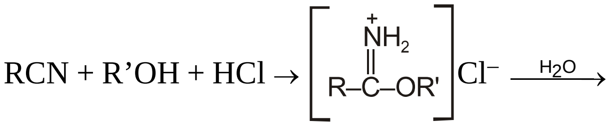
[iii] **Reaction with Grignard reagent :** With Grignard's reagent, an alkyl cyanide forms a ketone which further reacts to form a tertiary alcohol.



$$R–C \equiv N + R'MgX \rightarrow R–\overset{R'}{\overset{|}{C}}=MgX \xrightarrow{2H_2O}$$

$$R–\overset{R'}{\overset{|}{C}}=O + NH_3 + Mg\begin{matrix} OH \\ X \end{matrix}$$

[iv] **Alcholyis :** When an alkyl cyanide is refluxed with an anhydrous alcohol in presence of dry HCl, an imido ester is formed, which on hydrolysis with water forms ester.



$$RCN + R'OH + HCl \rightarrow \left[\begin{array}{c}\overset{+}{N}H_2 \\ \| \\ R\text{–}C\text{–}OR'\end{array}\right]Cl^- \xrightarrow{H_2O}$$

$RCOOR'$(Ester) + NH_4C

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

5. Alkyl isocyanides :

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.

$R\text{–}X + AgCN \rightarrow RNC + RCN$

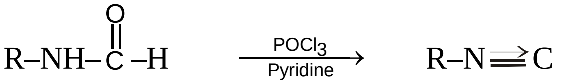
This method is, thus, not suitable for preparing isocyanides.

[ii] **From Primary Amines : (Carbylamine reaction):** Alkyl isocyanides may be prepared by heating primary amines with chloroform and alcholic 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 presnece of pyridine give isocyanides.



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

N–alkyl formamide → Isocyanide

5.2 Physical Properties :

[i] Alkyl isocyanides are colourless, unpleasant smelling liquids.

[ii] The boiling points of isonitriles 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.

5.3 Chemical Properties :

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

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

Alkyl isocyanide, Primary amine, Formic acid

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

$$R\text{—}N \equiv C + 4H \longrightarrow RNHCH_3$$

Alkyl isocyanide → Secondary amine

[iii] **Action of heat :** When heated for sometime at 250ºC, a small amount of isonitrile changes into isomeric nitrile.

$$RNC \xrightarrow{\text{heat}} RCN$$

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

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

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

$RNC + X_2$ (Halogen) $\longrightarrow RNCX_2$ Alkyl iminocarbonyl halide

$RNC + S \longrightarrow RNCS$ Alkyl isothiocyanate

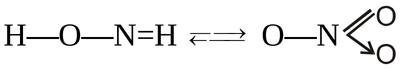
$RNC + HgO \longrightarrow RNCO + Hg$ (Alkyl isocyanate)

6. Distinction between Ethyl Cyanide and Ethyl Isocyanide :

Test	Ethyl Cyanide (C_2H_5CN)	Ethyl isocyanide (C_2H_5NC)
1. Odour	No unpleasant	Extremely unpleasant
2. Solubility in water	Soluble	Insoluble
3. Hydrolysis	Yields propionoic acid	Produces ethyl amine
4. Reduction	Gives propylamine (Primary amine)	Gives ethylmethylamine (Secondary amine)
5. Heating at 250° C	No effect	Changes to ethyl cyanid

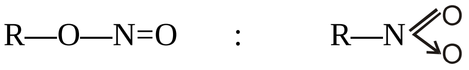
7. Alkyl nitriltes and nitro alkanes :

Nitrous acid exists in two tautomeric forms



Nitrile form Nitro form

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



Alkyl nitrite Nitro alkane

The most important alkyl nitrite is ethyl nitrite.

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).

$NaNO_2 + HCl \rightarrow NaCl + HNO_2$

$C_2H_5I + KONO \rightarrow C_2H_5ONO + H_2O$
Ethyl nitrite

[ii] **From Ethyl iodide :**

$C_2H_5I + KONO \rightarrow C_2H_5ONO + KI$
Ethyl iodide Pot. nitrite Ethyl nitrite

[iii] It is also prepared by the action of nitrogen trioxide, N_2O_3 on ethyl alcohol.

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

7.2 Properties :

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 aclohol.

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

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.

$C_2H_5ONO + 4H \rightarrow C_2H_5OH + NH_2OH$

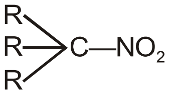
It accelerates pulse rate and lowers blood pressure and reduces hypertension and severe pain of angiana pictoris so it is used as a medicine for the treatement of asthama and heart diseases. Its 4% solution (alcoholic) commonly known as "sweet spirit of nitre" used as diuretic.

7.3 Nitro alkanes :

Nitro alkanes are the derivatives 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 aquous 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 nitrities have much lower boiling points as compared to nitro alkanes.

[ii] **Nitration :** Paraffins (alkanes) after hexane can be nitrated directly with concentrated nitric acid.

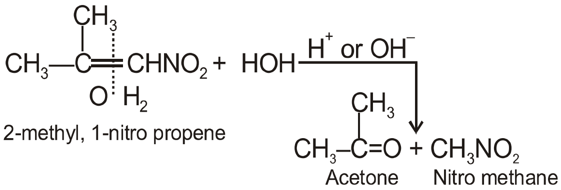
The nitration is carried out in liquid phase or in vapour phase at about 400ºC.

[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.

$$CH_2ClCOOH \xrightarrow[-NaCl]{NaNO_2} CH_2NO_2COOH \xrightarrow{heat} CH_3NO_2 + CO_2$$

α-Chloro acetic acid α-Nitro acetic acid Nitro methane

[iv] A recent method is by the hydrolysis of α–nitro alkene with water or acid or alkali.



$$CH_3\text{—}C(CH_3)\text{=}CHNO_2 + HOH \xrightarrow{H^+ \text{ or } OH^-} CH_3\text{–}C(CH_3)\text{=}O + CH_3NO_2$$

2-methyl, 1-nitro propene

Acetone Nitro methane

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.

7.5 Chemical properties :

[i] **Reduction :** Nitro alkanes are reudced 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 form hydroxylamines.

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

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

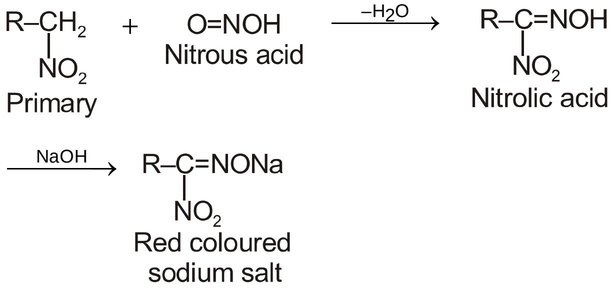
$$RCH_2NO_2 + H_2O \rightarrow RCOOH + NH_2OH$$

Secondary nitro alkanes on hydrolysis form ketones

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

Ketone

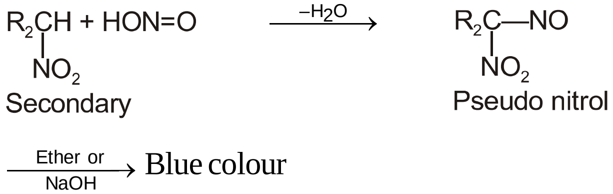
[iii] **Action of nitrous acid :** Nitrous acid reacts with primary, seondary and tertiary nitroalkanes differently, Primary nitro compound forms nitrolic acid which dissolves in alkali to give red solution.



$$R\text{–}CH_2(NO_2) + O\text{=}NOH \xrightarrow{-H_2O} R\text{–}C(NO_2)\text{=}NOH \xrightarrow{NaOH} R\text{–}C(NO_2)\text{=}NONa$$

Primary Nitrous acid Nitrolic acid Red coloured sodium salt

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



$$R_2CH(NO_2) + HON\text{=}O \xrightarrow{-H_2O} R_2C(NO_2)\text{—}NO \xrightarrow[NaOH]{Ether\ or} \text{Blue colour}$$

Secondary Pseudo nitrol

Teriary nitro alkanes do not react with nitrous acid. The different behaviour of nitrous acid with p., sec., and tert. nitro alkanes forms the bases of the **Victor Meyer's Test** for the distinction of p., sec. and tert. alcohols.

[iv] **Thermal decomposition :** Upon rapid heating, nitro alkanes decomposes with great violence. Advantage is taken of this reaction in the commercial use of nitro alkanes as explosives.

[v] **Halogenation :** Primary and secondary nitro alkanes are redialy halogenated in the α–position by treatment with chlorine or bromine, Chloropicirin is formed when nitro methane reacts with Cl_2 in presence of NaOH. Chloropicrin is an important insecticide.

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

Chloropicrin

7.6 Uses : Nitro alkanes are used :

[i] As solvents for substances such as cellulose acetate, synthetic rubber, etc.

[ii] As explosives.

[iii] For the preparation of amines, hydroxylamines, etc.

Urea

Introduction :

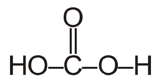
[a] IUPAC name of urea is **'Amino Methanamide'**.

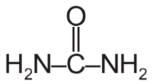
[b] It is also called **CARBAMIDE**.

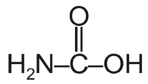
[c] It was first discovered in 1773 in urine.

[d] Wohler, a scientist first synthesied it in laboratory.

[e] Urea is diamide of carbonic acid and monoamide of carbamic acid.


(carbonic acid)


(urea)


(carbamic acid)

[f] Carbon in urea is sp^2 hybridised and N is sp^3 hybridisation state.

Method of Preparation :

1. **Extraction from Urine :** This completes in the following steps.

[a] First urine is concentrated by vapourisation.

[b] Oxalic acid is mixed to form crystals of urea oxalate which are very less stable.

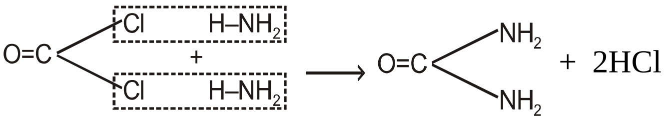
[c] These crystals are heated with $CaCO_3$.

$(NH_2CONH_2)_2H_2C_2O_4 + CaCO_3 \longrightarrow 2NH_2CONH_2 + CaC_2O_4 + CO_2 + H_2O$

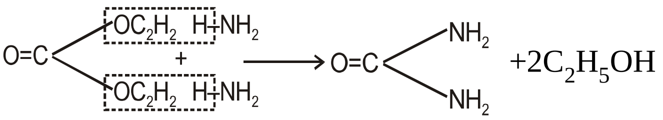
2. **Wohler's method :**

$KNCO + (NH_4)_2SO_4 \longrightarrow 2NH_4NCO + K_2SO_4 \xrightarrow{\Delta} NH_2CONH_2$

3. **From Phosgene gas :**

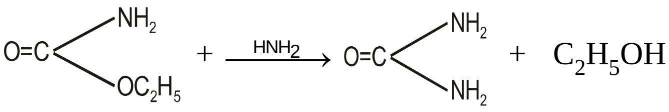


4. **From Ethyl carbonate :**



ethyl carbonate urea

5. **From Ethyl carbonate or urethane :**



urethane urea

6. **Hydrolysis of Cyanamide :**

$CaCN_2 + 3H_2O \longrightarrow Ca(OH)_2 + H_2N{-}CN$

calcium

cyanamide

$H_2N{-}CN + H_2O \longrightarrow NH_2CONH_2$

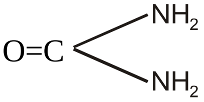
7. **From Carbondioxide :**

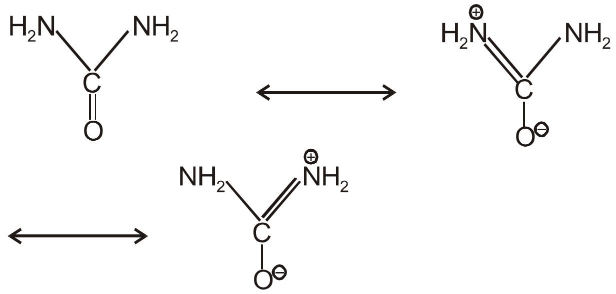
$O{=}C{=}O + 2NH_3 \longrightarrow NH_2COONH_4$

(liq.) (liq.)

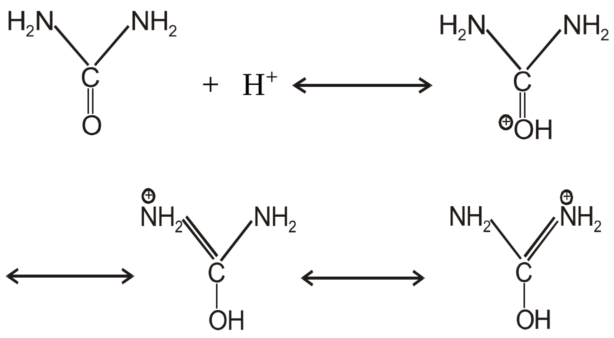
$\xrightarrow[100\text{ atm.}]{150^\circ} NH_2{-}CO{-}NH_2 + H_2O$

Physical Properties :

[a] **Structure of Urea :** The urea is represented by the diamide structure  This structure, however do not appear to explain all the reactions of urea and so give rise to a great deal of urea controversy. The physical methods of structure determination have now shown that the diamide structure is correct in the solid state. Crystal structure studies have shown that in the solid urea both nitrogen atoms are indentical. Both length measurement of urea give the C–N distance as 1.37Å, whereas the C–N distance in aliphatic amine is 1.47 Å. This indicate that the C–N bond in urea has some double bond character (about 28%), this can be explained by reasonance.



[b] Urea has been considered to be monoacidic base, becuase negatively charged oxygen atom can coordinate with one proton. Thus conjugate acid of urea can be formulated as the resonance hybrid of the following structure.



[c] This is colourless, ouderless, cystalline solid.

[d] It's boiling point is 132ºC.

[e] It is highly soluble in water, less soluble in alcohol and almost insoluble in ether.

[f] Urea is used chiefly as a fertiliser. It can also be used for manufacturing urea formaldehyde resins and stabiliser for explosives (nirocellulose).

Chemical Reactions :

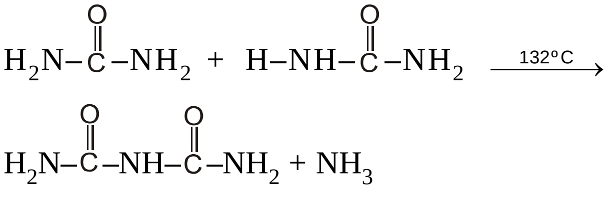
1. **Hydrolysis :**

$H_2N–CO–NH_2 + 2H_2O \longrightarrow (NH_4)_2CO_3$ (ammonium carbonate)

$H_2N–CO–NH_2 + 2NaOH \longrightarrow Na_2CO_3 + 2NH_3$

$H_2N–CO–NH_2 + 2HCl + H_2O \longrightarrow 2NH_4Cl + CO_2$

2. **Effect of heat :**



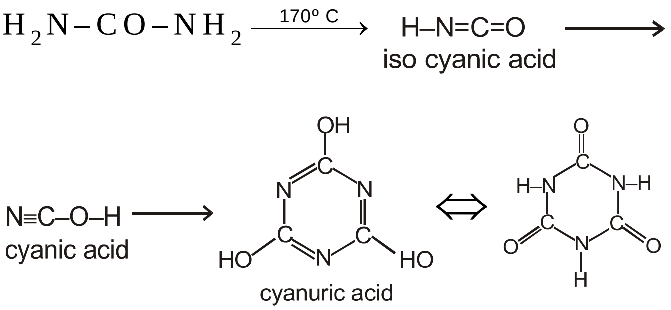
$$H_2N–\overset{O}{\overset{\|}{C}}–NH_2 + H–NH–\overset{O}{\overset{\|}{C}}–NH_2 \xrightarrow{132°C} H_2N–\overset{O}{\overset{\|}{C}}–NH–\overset{O}{\overset{\|}{C}}–NH_2 + NH_3$$

(biuret)

Note :

[a] When an aqueous solution of biuret is heated with sodium hydroxide solution and a drop of copper sulphate solution, a violet colour is produced which is characteristic of all compounds containing –CO–NH–group. This test is called **BIURET TEST**.

[b] If heated strongly first cyanide acid is formed which polymerises to trimer called cyanuric acid.



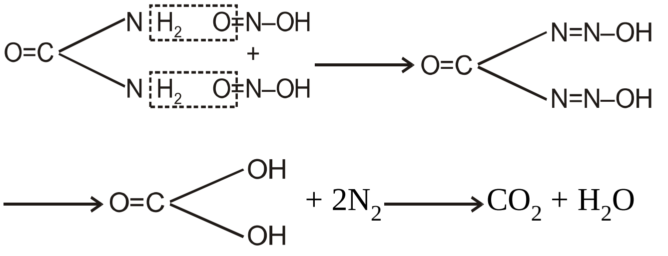
3. **Salt Formation :** If forms salts due to it's weak basic nature. Urea is a feeble monoacid base ($K_b = 1.5 \times 10^{-14}$). It reacts with cold conc. nitric acid and oxalic acid to forms salts.

$H_2N–CO–NH_2 + HNO_3 \longrightarrow [H_2N–CO–NH_2]. HNO_3$
urea Nitrate

$2H_2N–CO–NH_2 + (COOH)_2 \longrightarrow [H_2N–CO–NH_2]_2.(COOH)_2$
(Urea oxalate)

Note : The above salt contains oxygen–protonated cation, which is resonance stabilized.

4. **Reaction with Nitrous acid :**



Thus, the total reaction is :

$CO(NH_2)_2 + 2HNO_2 \longrightarrow 2N_2 + 3H_2O + CO_2$

5. **Reaction with Hypobromite solution :**

$H_2NCONH_2 + 3NaOBr \longrightarrow 3NaBr + CO_2 + H_2O + N_2$

6. **Acetylation :** From Aceyl urea

$CH_3COCl + H_2NCONH_2 \longrightarrow CH_3CONHCONH_2 + HCl$

$NH_2CONH_2 + (CH_3CO)_2O \longrightarrow CH_3CONHCONH_2 + CH_3COOH$

acetyl urea

7. **Reaction with Hydrazine (NH_2–NH_2) :** Give semicarbazide :

$H_2N–CO–NH_2 + NH_2–NH_2 \longrightarrow H_2N–NH–CO–NH_2 + NH_3\uparrow$

semi–carbazide

8. **Condensation with Formaldehyde :** Gives methylol urea then dimethylol urea which condeness to give Resins.

$H_2N–CO–NH_2 + CH_2{=}O \longrightarrow H_2N–CO–$

methylol urea

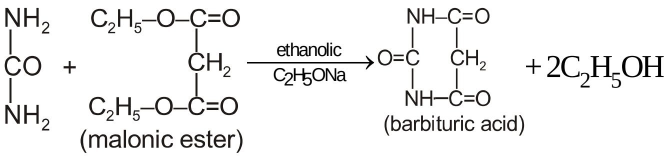
$NH–CH_2–OH \xrightarrow{CH_2=O} OH–CH_2–NH–CO–NH–CH_2–OH$

dimethylol urea

9. **Reaction with $SOCl_2$:**

$NH_2CONH_2 + SOCl_2 \rightarrow H_2NCN + 2HCl + SO_2$

10. **Reaction with Malonic ester :**



Note : Barbituric acid is used as sedatives and hypnotics.

11. Reaction with fuming H_2SO_4 :

$NH_2CONH_2 + H_2SO_4 + SO_3 \longrightarrow 2NH_2SO_3 + CO_2$

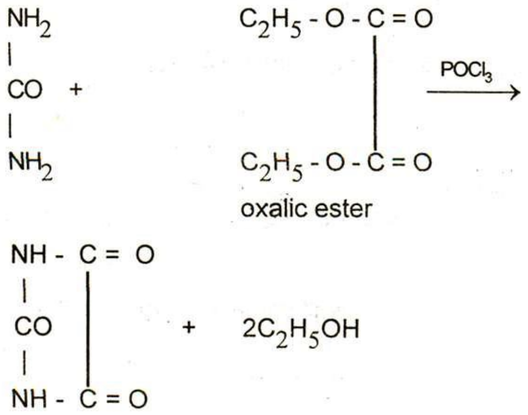
sulphamic acid

Sulphamic acid forms two things.

[a] Ammonium sulphamate used as flame proffing agent

[b] Sodium cyclohexyl sulphamate (50 times sweeter than sugar)

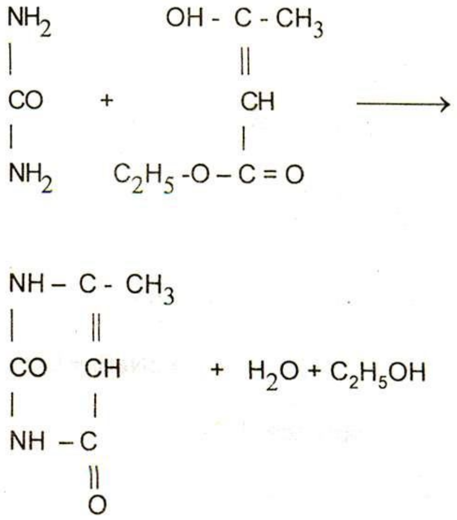
12. **Reaction with oxalic ester :**



oxalyl urea (parabanic acid)

Note : Parabanic acid (Oxalyl urea) can also be produced when urea reacts with oxalic acid in presence of $POCl_3$.

13. **Reaction with Acetoacetic ester :**



14. **Reaction with NaOCl :**

$NH_2CONH_2 + NaOCl \longrightarrow NaCl + CO_2 + NH_2–NH_2$

hydrazine

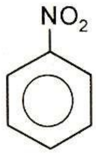
Nitro Benzene

Introduction :

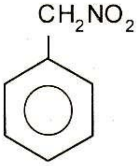
[a] Aromatic nitro compounds are obtained when hydrogen atom or atoms are of aromatic compound replaced by $-NO_2$ (nitro) group.

[b] Aromatic nitro compound are of two types.

- [i] Those compounds in which nitro group is attached directly to the benzene ring eg. nitrobenzene.
- [ii] Those compounds, in which nitro group is attached to a side chain which is directly attached to the benzne ring.



I
(nitro benzene)



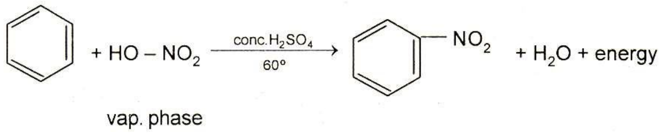
II
(phenyl nitromethane)

[c] Nitrobenzene is also called as 'oil of mirbane' or 'artifical oil of bitter almond's.

[d] If has a smell similar to benzaldehyde.

Methods of Preparation :

1. From Benzene (Nitration) :



Note :

- [i] The reaction species is $^+NO_2$ (nitronium ion)
- [ii] The above reaction is lab method of nitrobenzene preparation.

Physical Properties :

[a] It is yellowish, oily liquid, insoluble in water and soluble in organic solvents.

[b] It has odour like bitter almonds.

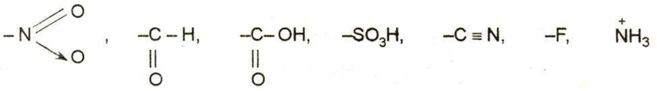
[c] It is steam volatile and poisonous in nature.

[d] Its boiling point is 211ºC.

Resonance in nitrobenzene :

[a] The groups which can attract the electron from benzene ring or deactivate the benzene ring or make electron dificient to the benzene ring or shows –I effect or shows –M effect or –R effect are called as meta directing groups. They do not show Friedel Craft reaction.

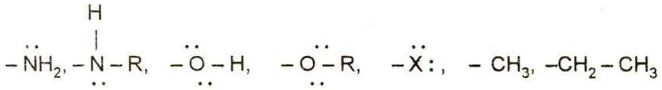
eg.



$-NO_2$, $-\underset{\underset{O}{\|}}{C}-H$, $-\underset{\underset{O}{\|}}{C}-OH$, $-SO_3H$, $-C\equiv N$, $-F$, $\overset{+}{N}H_3$

[b] The group which can donate the electron to the benzene ring or activate the benzene ring or make electron efficient to the benzene ring or shows + I effect of + M or +R effect are always ortho and para directing groups.

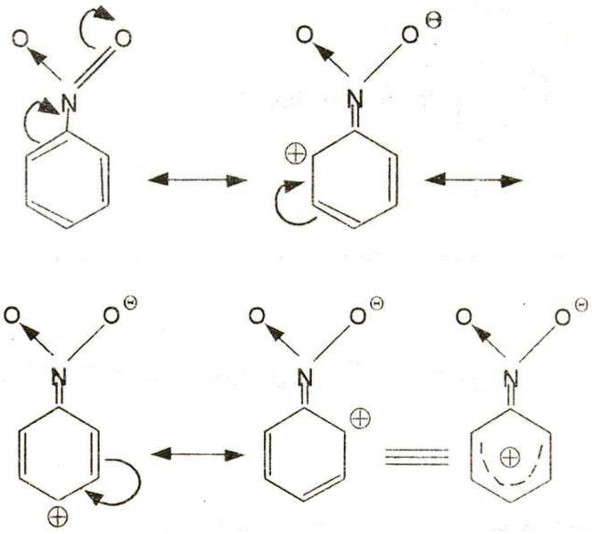
eg.



$-\ddot{N}H_2$, $-\underset{\cdot\cdot}{\overset{\overset{H}{|}}{N}}-R$, $-\ddot{\underset{\cdot\cdot}{O}}-H$, $-\ddot{\underset{\cdot\cdot}{O}}-R$, $-\ddot{X}:$, $-CH_3$, $-CH_2-CH_3$

etc.

[c] Resonating structures of nitrobenzene.



It is evident from the above structures that ortho and para positions are electron deficient and attacking electrophilie is also electron deficient, so it does not attack on ortho and para positions but attacks at meta position.

Chemical Reactions :

Chemical reaction of nitrobenzene are classified in three groups as follows :

1. Reaction of $-NO_2$ group
2. Reaction of Benzene ring
3. Other reactions

1. Reaction of $-NO_2$ group :

1.1 Readuction :

[a] Acidic medium :

Reagents : Sn/HCl or $SnCl_2$/HCl or Zn/CH_3COOH etc.

$$C_6H_5NO_2 \xrightarrow{+6H} \underset{\text{aniline}}{C_6H_5NH_2} + 2H_2O$$

Propbale intermediate steps :

$$C_6H_5-NO_2 \xrightarrow[-H_2O]{+2H} \underset{\text{nitrosobenzene}}{C_6H_5NO} \xrightarrow{+2H}$$

$$\underset{\text{phenyl hydroxylamine}}{C_6H_5NHOH} \xrightarrow[-H_2O]{+2H} \underset{\text{aniline}}{C_6H_5NH_2}$$

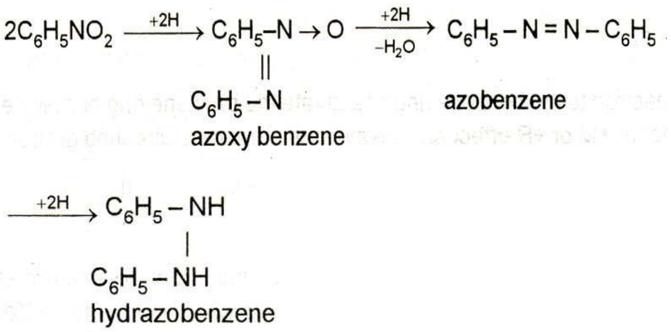
[b] Neutral Medium :

Reagents : Zn/NH_4Cl or Zn/$CaCl_2$ or Al–Hg/NH_4Cl etc.

$$C_6H_5NO_2 \xrightarrow{+4H} \underset{\text{Phenyl hydroxylamine}}{C_6H_5NHOH} + H_2O$$

[c] Alkaline Medium :

Reagents : Zn/NaOH or $SnCl_2$/NaOH, or Glucose/ NaOH etc.

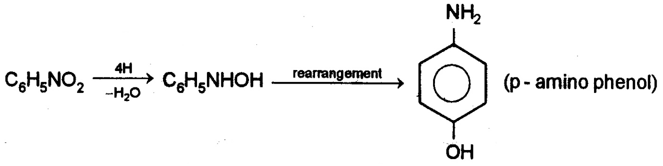


$$2C_6H_5NO_2 \xrightarrow{+2H} \underset{\text{azoxy benzene}}{\begin{matrix} C_6H_5-N \rightarrow O \\ \| \\ C_6H_5-N \end{matrix}} \xrightarrow[-H_2O]{+2H} \underset{\text{azobenzene}}{C_6H_5-N=N-C_6H_5}$$

$$\xrightarrow{+2H} \underset{\text{hydrazobenzene}}{\begin{matrix} C_6H_5-NH \\ | \\ C_6H_5-NH \end{matrix}}$$

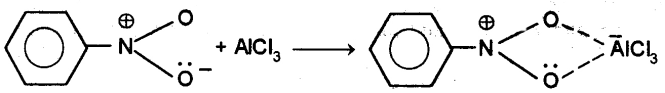
[d] Electrolytic reduction :

[Medium : conc, H_2SO_4]



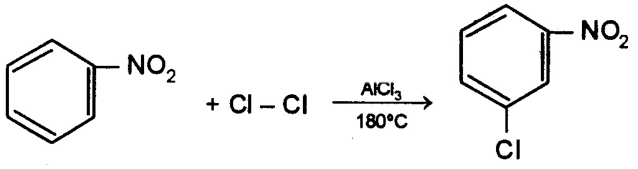
1.2 Reaction with $AlCl_3$:

Nitrobenzene behaves as weak base and makes a complex compound with aluminium chloride.



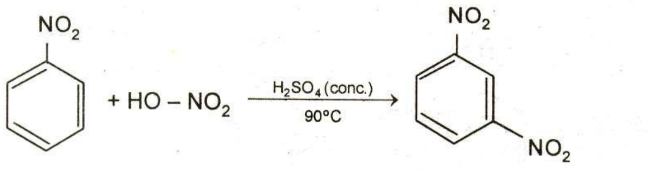
2 Reaction of Benzene ring :

2.1 Halogenation :

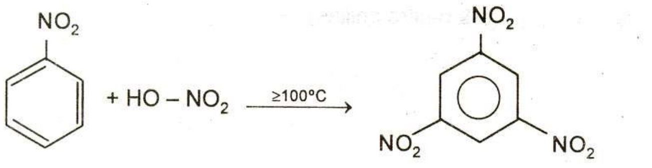


m-chloro nitrobenzene

2.2 Nitration :

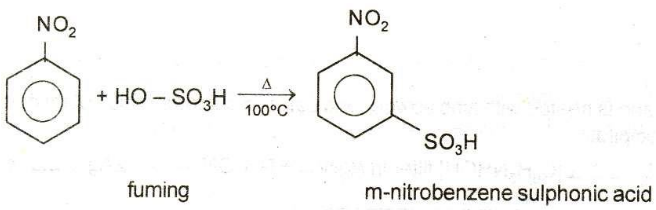


m-dinitrobenzene
(yellow crystalline solid)

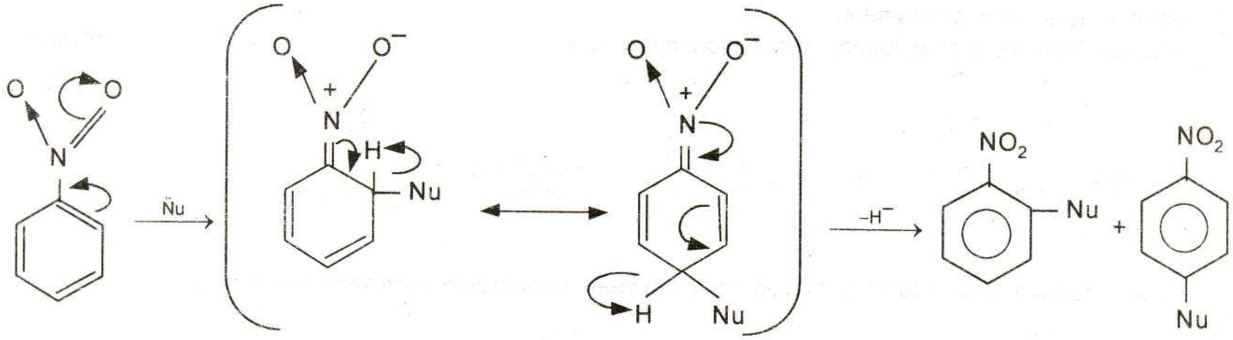


T.N.B (explosive in nature)

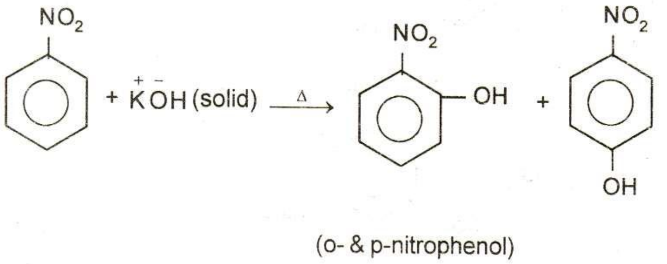
2.3 Sulphonation :



3. **Other Reactions :** Nitrobenzene shows nucleophilic substitution reaction also. It is accomplishes in the following way. **Mechanism of nucleophilic substitution reaction –** In nitrobenzene nucleophile attackes at o– & p– positions as these are the electron deficient centres.

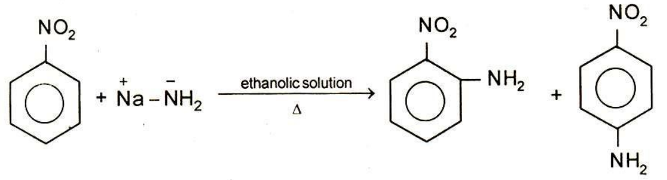


3.1 Reaction with Solid KOH :



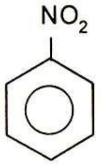
(o- & p-nitrophenol)

3.2 Reaction with Sodamide :



(o & p-nitro aniline)

3.3. Reaction with Ethanol :



+ $C_2H_5OH \longrightarrow$ o– and p–nitro phenetole

Test for Nitrobenzene :

[Mulliken and Barker's method]

The alcoholic solution of nitrobenzene is heated with zinc powder and calcium chloride. This hot mixture on filtration in Tollen's reagent gives a black precipitate.

$C_6H_5NO_2$ (alcoholic) + Zn + $CaCl_2 \xrightarrow{\Delta}$
$[C_6H_5NHOH]$ filter in $AgNO_3 + NH_4OH \longrightarrow$
2Ag ↓ Black precipitate

Aniline

Introduction :

[a] Aniline is called phenyl derivative of ammonia.

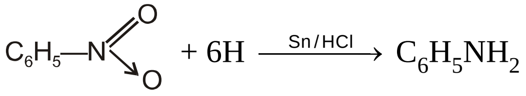
[b] It was initially obtained by the scientist 'Unverdorben'.

[c] Aniline is also called amino derivative of benzene because when a hydrogen atom is replaced by NH_2 group, aniline is obtained.

Method of Preparation :

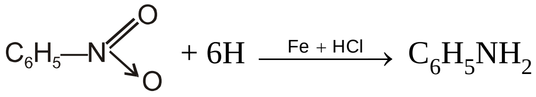
1. **From Nitrobenzene (Reduction in acidic medium) :**

[a] Lab method :



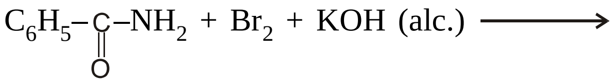
$$C_6H_5{-}N\overset{\nearrow O}{\underset{\searrow O}{}} + 6H \xrightarrow{Sn/HCl} C_6H_5NH_2$$

[b] Industrial method :



$$C_6H_5{-}N\overset{\nearrow O}{\underset{\searrow O}{}} + 6H \xrightarrow{Fe\ +\ HCl} C_6H_5NH_2$$

2. **From Benzamide :**



$$C_6H_5{-}\underset{\underset{O}{\|}}{C}{-}NH_2 + Br_2 + KOH\ (alc.) \longrightarrow$$

$C_6H_5NH_2 + K_2CO_3 + KBr + H_2O$

Note : The above reaction is called as **'Hofmann hypobromite reaction'.**

3. From Chlorobenzene :

[a] With NH_3 :

$$C_6H_5-\boxed{Cl + H}-NH_2 \xrightarrow[200^\circ C]{Cu_2O} C_6H_5\ NH_2 + HCl$$

Note : We use Cu_2O to neutralize the formed HCl otherwise HCl forms additional salt with aniline.

$$Cu_2O + 2HCl \longrightarrow Cu_2Cl_2 + H_2O$$

[b] With sodamide :

$$C_6H_5-\boxed{Cl + Na}-NH_2 \xrightarrow[200^\circ C]{\Delta} C_6H_5NH_2 + NaCl$$

4. From Phenol :

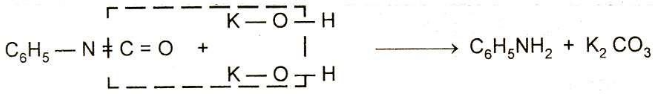
$$C_6H_5-\boxed{OH + H}-NH_2 \xrightarrow[300^\circ C]{\text{anhy. } ZnCl_2} C_6H_5-NH_2 + H_2O$$

5. From Grignard reagent :

$$C_6H_5-\boxed{MgCl + Cl}-NH_2 \longrightarrow C_6H_5NH_2 + MgCl_2$$

chloramine

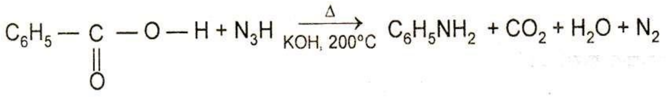
6. From phenyl isocyanate (By alkaline hydrolysis) :



$$C_6H_5-N=C=O + \begin{matrix}K-O-H\\ |\\ K-O-H\end{matrix} \longrightarrow C_6H_5NH_2 + K_2CO_3$$

Note : The above method is called as **'wurtz method'**.

7. From Benzoic acid (Schimdt reaction) :



$$C_6H_5-\underset{\underset{O}{\|}}{C}-O-H + N_3H \xrightarrow[KOH,\ 200^\circ C]{\Delta} C_6H_5NH_2 + CO_2 + H_2O + N_2$$

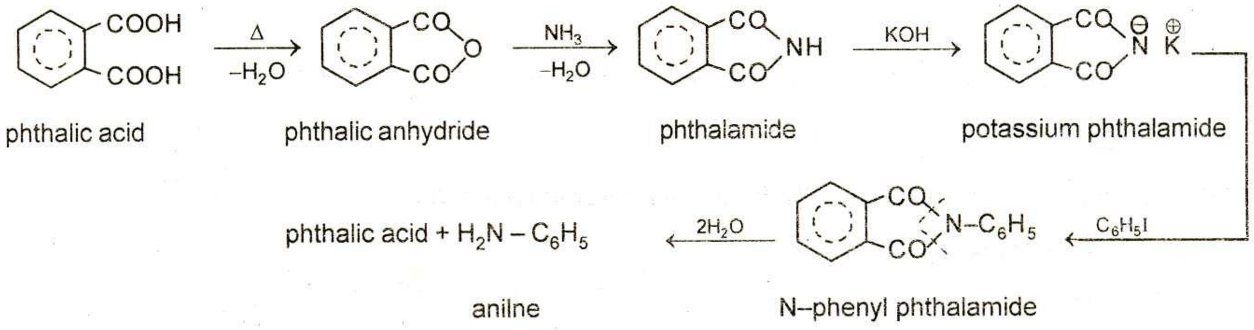
8. By reudction of azo and hydrazo compounds with sodium dithionite :

$$C_6H_5-N=N-C_6H_5 + 2\,Na_2S_2O_4 + 4H_2O \longrightarrow 2\,C_6H_5NH_2 + 4\,NaHSO_3$$

9. By curtius reaction :

$$C_6H_5COCl + NaN_3 \longrightarrow C_6H_5CON_3 + NaCl$$
$$C_6H_5CON_3 + H_2O \longrightarrow C_6H_5NH_2 + CO_2 + N_2$$

10. By Gabriel Phthalimide reaction :



Physical properties :

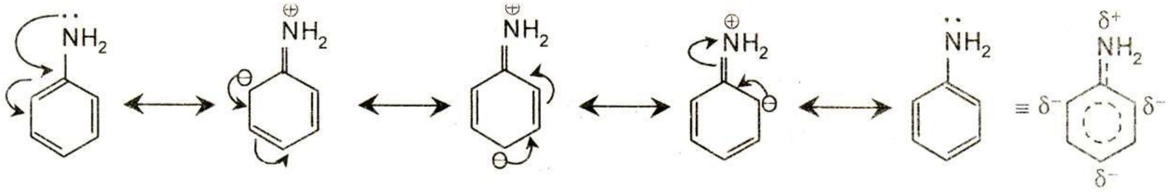
[a] Aniline is soluble in organic solvents as well as in water.

[b] Solubility in water is due to hydrogen bonding.

[c] It is colourless and poisonous liquid.

Resonance in Aniline :

Aniline is less basic than ammonia and primary amine because it possess resonance



It is evident from the above sturcutres that l.p. on N atom is delocalised and aniline behaves as a weak base. In these resonating structure, its ortho and para positions are electron richer (due to presence of negative charge) so electrophile attacks on these positions only. That's why we can say it is ortho & para directing.

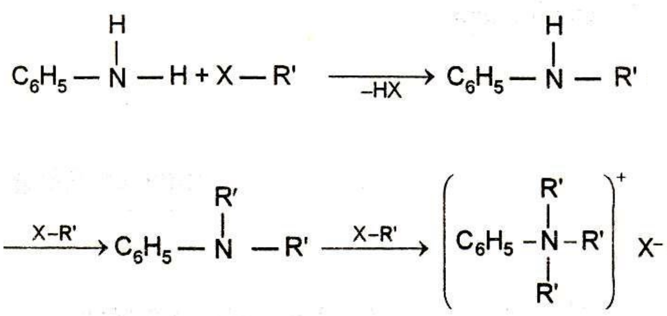
Chemical Reaction :

Chemical reactions of aniline are broadly classified in the following two ways :

1. Reaction of $-NH_2$ group
2. Reactions of benzene ring
3. Other reactions

1. Reactions of $-NH_2$ group :

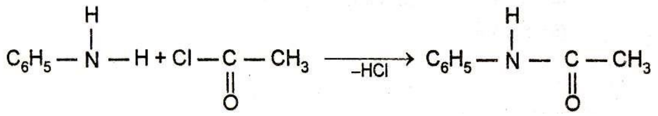
1.1 Alkylation :



$$C_6H_5-\overset{H}{N}-H + X-R' \xrightarrow{-HX} C_6H_5-\overset{H}{N}-R' \xrightarrow{X-R'} C_6H_5-\overset{R'}{N}-R' \xrightarrow{X-R'} \left(C_6H_5-\underset{R'}{\overset{R'}{N}}-R'\right)^+ X^-$$

quaternary salt

1.2 Acetylation :



$$C_6H_5-\overset{H}{N}-H + Cl-\underset{O}{\underset{\|}{C}}-CH_3 \xrightarrow{-HCl} C_6H_5-\overset{H}{N}-\underset{O}{\underset{\|}{C}}-CH_3$$

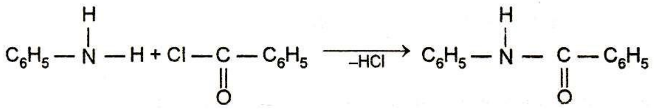
N-phenyl acetamide

Or

acetanilide

Note : The product formed is important because it is used in preservation of $-NH_2$ group in aniline.

1.3 Schotten–baumann reaction :

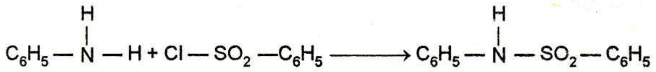


$$C_6H_5-\overset{H}{N}-H + Cl-\underset{O}{\underset{\|}{C}}-C_6H_5 \xrightarrow{-HCl} C_6H_5-\overset{H}{N}-\underset{O}{\underset{\|}{C}}-C_6H_5$$

N–phenyl benzamide

or benzanilide

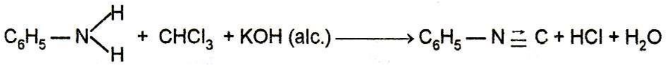
1.4 Reaction with Hinsberg reagent :



$$C_6H_5-\overset{H}{N}-H + Cl-SO_2-C_6H_5 \longrightarrow C_6H_5-\overset{H}{N}-SO_2-C_6H_5$$

N–phenyl benzene sulphonamide

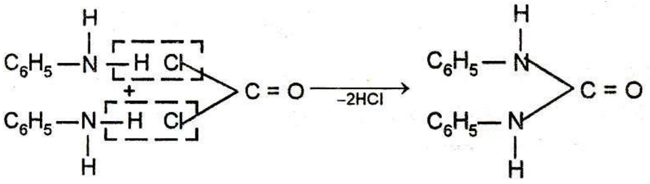
1.5 Hoffmann Carbylamine reaction (Isocyanide test) :



$$C_6H_5-NH_2 + CHCl_3 + KOH\ (alc.) \longrightarrow C_6H_5-N \overset{\rightarrow}{=} C + HCl + H_2O$$

There isocyanides has very offensive smell. Reaction is used for testing of primary amines.

1.6 Reaction with Phosgene :

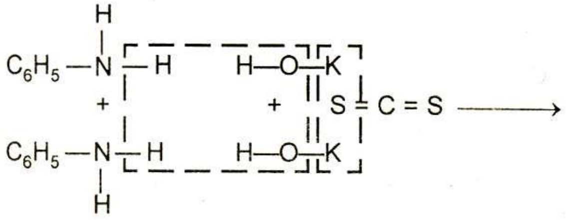


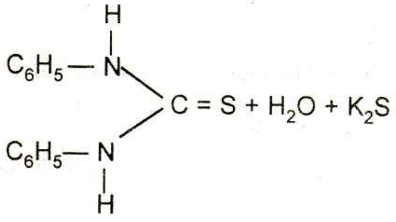
$$2\,C_6H_5-NH-H + Cl_2C=O \xrightarrow{-2HCl} (C_6H_5-NH)_2C=O$$

N, N'–diphenyl urea

1.7 Reaction with Carbondisulphide :

[a] When aniline is in excess :

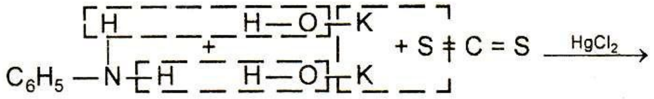




$$2\,C_6H_5-NH-H + 2\,KOH + S=C=S \longrightarrow (C_6H_5-NH)_2C=S + H_2O + K_2S$$

N, N' – diphenyl thio urea

[b] When aniline is in lesser quantity :



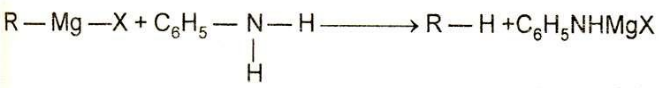
$$C_6H_5-NH_2 + 2\,KOH + S=C=S \xrightarrow{HgCl_2}$$

$C_6H_5-N=C=S + 2\,H_2O + K_2S$

phenyl iso thio cyanate

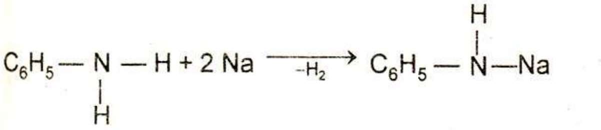
Note : There isothiocyanate has odour like mustard oil so reaction is called **'Hoffmann–mustard oil reaction.**

1.8 Reaction with Grignard reagent :



$R-Mg-X + C_6H_5-\underset{\substack{|\\ H}}{N}-H \longrightarrow R-H + C_6H_5NHMgX$

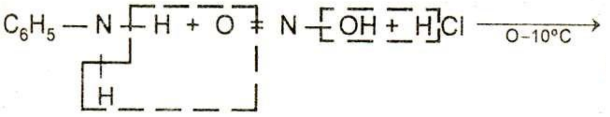
1.9 Reaction with Sodium metal :



$C_6H_5-\underset{\substack{|\\ H}}{N}-H + 2\,Na \xrightarrow[-H_2]{} C_6H_5-\overset{\substack{H\\ |}}{N}-Na$

N- phenyl sodamide

1.10 Reaction with HNO_2 and HCl (Diazotisation) :

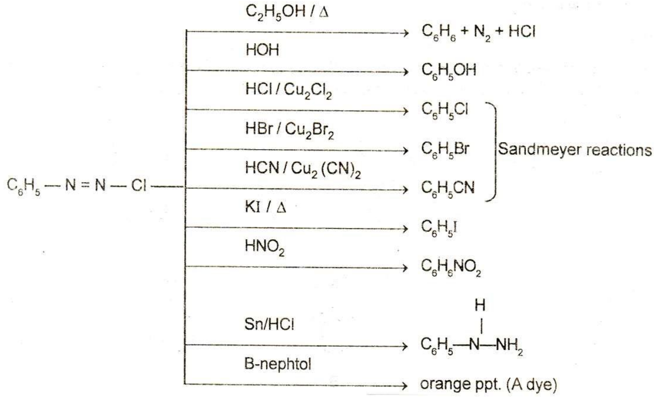


$C_6H_5-\underset{\substack{|\\ H}}{N}-H + O=N-OH + HCl \xrightarrow[O-10°C]{}$

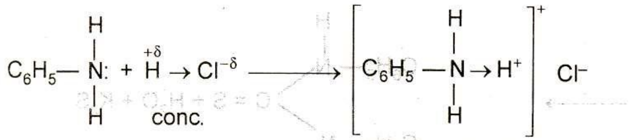
$C_6H_5-N=N-Cl$

benzene diazonium chloride

Note : It is an important compound because we can obtain a number of aromatic compounds from benzene diazonium chloride like.

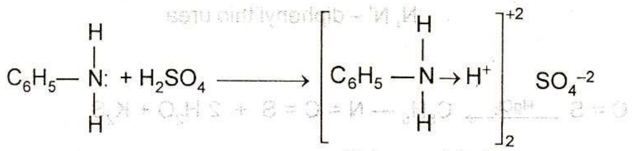


1.11 Salt formation :



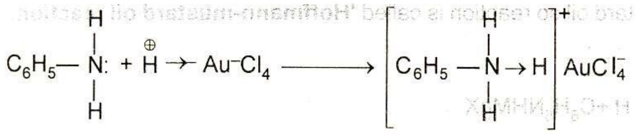
$C_6H_5-\overset{\substack{H\\ |}}{\underset{\substack{|\\ H}}{N}}: + \underset{conc.}{\overset{+\delta}{H}\to Cl^{-\delta}} \longrightarrow \left[C_6H_5-\overset{\substack{H\\ |}}{\underset{\substack{|\\ H}}{N}}\to H^+\right]^+ Cl^-$

anilinium chloride



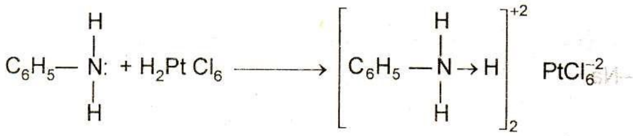
$C_6H_5-\overset{\substack{H\\ |}}{\underset{\substack{|\\ H}}{N}}: + H_2SO_4 \longrightarrow \left[C_6H_5-\overset{\substack{H\\ |}}{\underset{\substack{|\\ H}}{N}}\to H^+\right]_2^{+2} SO_4^{-2}$

anilinium sulphate



$C_6H_5-\overset{\substack{H\\ |}}{\underset{\substack{|\\ H}}{N}}: + \overset{\oplus}{H}\to Au^{-}Cl_4 \longrightarrow \left[C_6H_5-\overset{\substack{H\\ |}}{\underset{\substack{|\\ H}}{N}}\to H\right]^+ AuCl_4^-$

anilinium chloraurate



$C_6H_5-\overset{\substack{H\\ |}}{\underset{\substack{|\\ H}}{N}}: + H_2PtCl_6 \longrightarrow \left[C_6H_5-\overset{\substack{H\\ |}}{\underset{\substack{|\\ H}}{N}}\to H\right]_2^{+2} PtCl_6^{-2}$

anilinium chloroplatinate

Note : By the help of this salt we can calculate the mol. wt. of primary amine.

1.12 Reaction with Benzaldehyde :

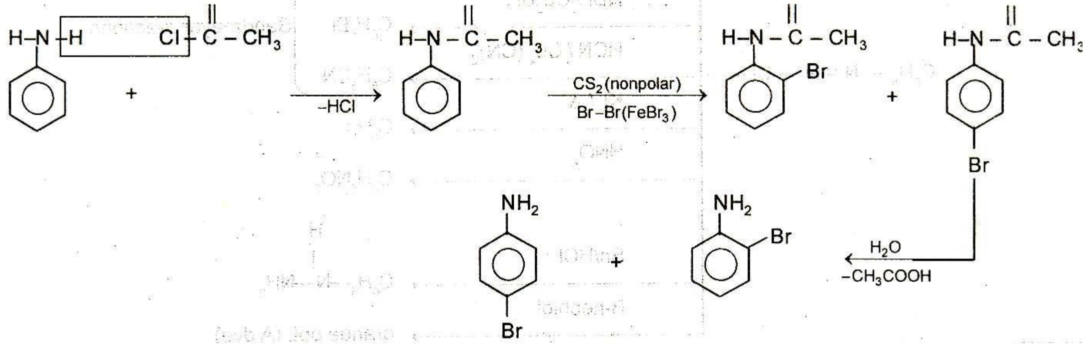
$C_6H_5NH_2 + C_6H_5CHO \longrightarrow C_6H_5–CH=N–C_6H_5$

(schiff base or anil)

2. Reaction of benzene ring :

2.1 Halogenation :

Aniline does not show halogenation or nitration directly due to presence of active hydrogen on $–NH_2$ group so for nitration, halogenations first we preserve $–NH_2$ group with acetyl chloride or by the formation of acetanilide.



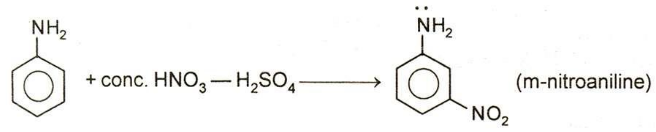
Note :

[i] Para product always yield more :

[ii] If reaction occurs in the presence of polar medium like bromine water, then product will be white ppt. of 2, 4, 6 tribromo aniline.

[iii] Aniline on iodination gives para–iodo product only.

2.2 Nitration :

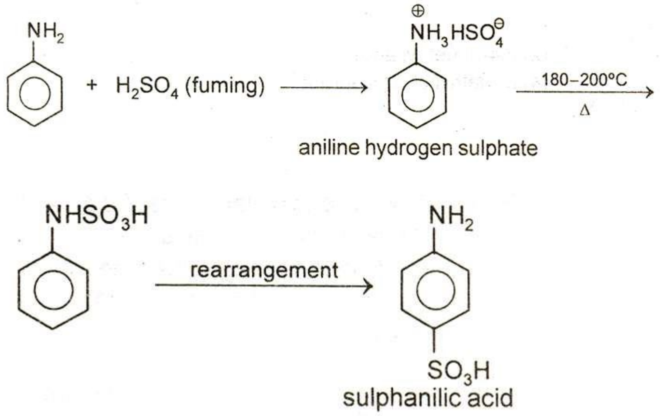


Note :

[i] Meta products is formed because intermediate anilinium ion is formed which is meta directing.

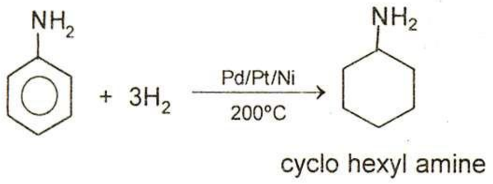
[ii] If nitration occurs with conc. HNO_3 then product will be yellow ppt. of 2, 4, 6 trinitroaniline.

2.3 Sulponation :

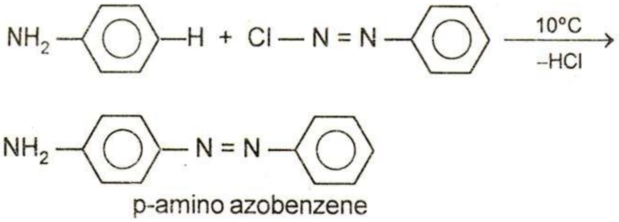


Note : Sulphanilic acid is used as hypnotic drug.

2.4 Reduction :



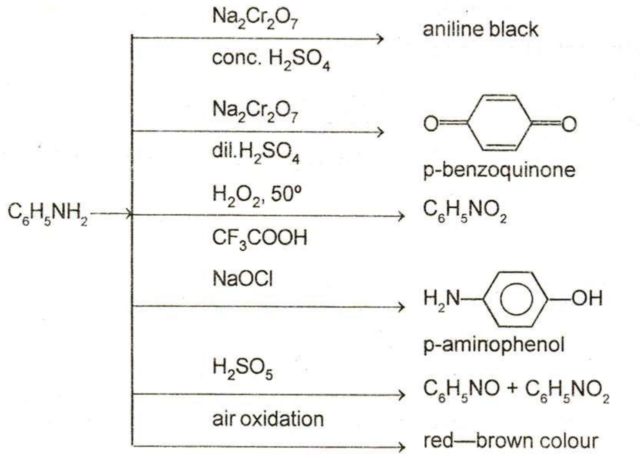
2.5 Reaction with benzene diazonium chloride :



3 Other reactions :

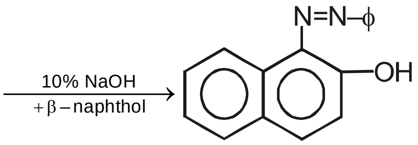
3.1 Oxidation :

Oxidation : Aniline forms different compounds on oxidation as follows :



3.2 Test for Aniline :

[a] Aniline $\xrightarrow[\text{HCl}(0-5^\circ)]{\text{NaNO}_2}$ $C_6H_5N_2Cl$



α-phenyl azo β–naphthol (orange–red dye)

[b] Aniline + NaOCl → p–

Aminophenol $\xrightarrow{\text{light}}$ Purple–colour

[c] Aniline $\xrightarrow[\text{KOH}]{\text{CHCl}_3}$ Phenyl isocyanide

(most unpleasant smell)