

Nitro Compounds

1 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 $-\text{NH}_2$ (amino) group.

[c] If two hydrogen atoms of NH_3 are replaced then it is called secondary amine and it possess $> \text{NH}$ (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] $-\text{NH}_2$ group is called Amino group.

[h] $-\text{NH}-$ group is called Imino group.

[i] $-\text{N}-$ group is called Nitrilo group.

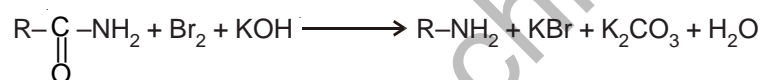
[j] N is in sp^3 hybridisation and tetrahedral geometry.

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



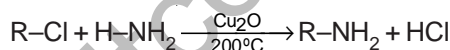
2. Methods of Preparation :

2.1 From Alkanamide :



Note : The reaction is called 'Hoffmann Bromamide reaction'.

2.2 From Alkylchloride :



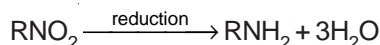
Note : In the above reaction Cu_2O neutralises the evolved HCl in form of $\text{Cu}_2\text{Cl}_2 + \text{H}_2\text{O}$ otherwise HCl forms additional salt with amines.

2.3 By reduction of Nitro compounds :

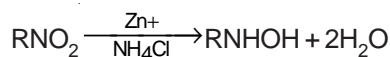
Nitro alkanes are reduced catalytically to primary amine.

[a] By LiAlH_4

[b] By Metal and acid (commonly used $\text{Sn} + \text{HCl}$ or $\text{Fe} + \text{HCl}$)



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.

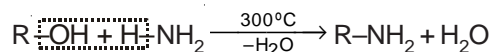


N-alkylhydroxyl amine

[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.



2.4 From Alcohol :



2.5 From Grignard reagent :



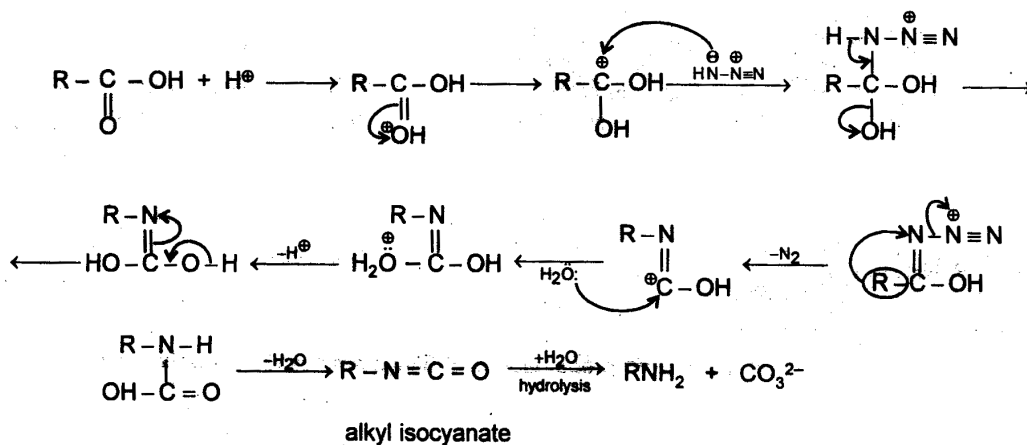
2.6 From Alkyl isocyanate (Alkaline Hydrolysis) :



2.7 From Alkanoic acid (Schmidt Reaction) ;



Mechanism :



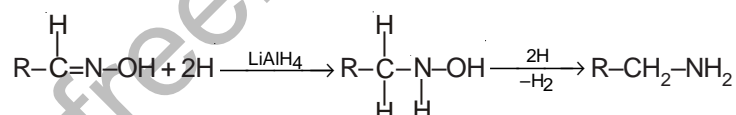
Note : Alkyl isocyanate can also be produced by heating the mixture of acyl halide and sodium azide, alkyl isocyanate, once it is formed, can easily be hydrolysed into primary amine and CO_3^{2-} .

2.8 By Alkyl cyanide (By reaction) :

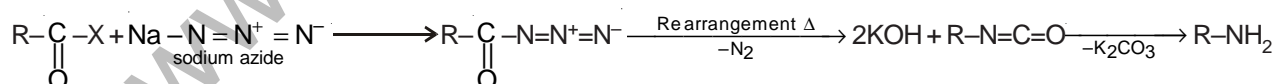


Note : When (Na + EtOH) is used as reducing agent then reaction is called 'Mandius Reaction'.

2.9 From Aldoxime (By Reduction) :

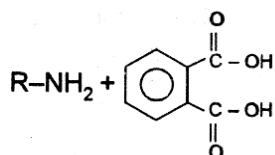
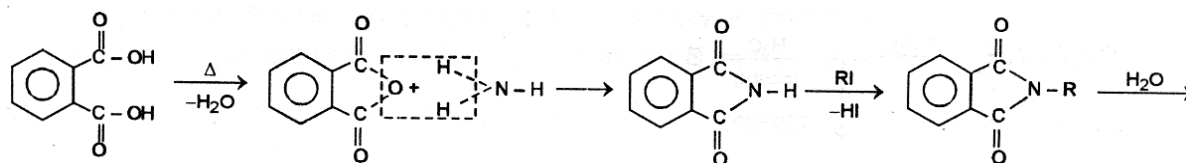


2.10 From Acyl halide :



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

2.11 From Phthalic acid :



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

2.12 By Aldehyde or ketone (reaction with H₂ and NH₃ in presence of catalyst) :

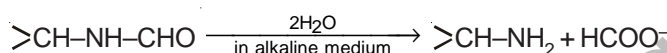
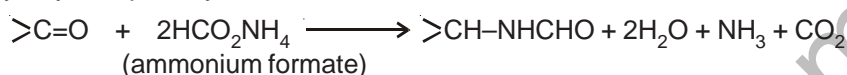
Primary amine can be produced by passing a mixture of aldehyde or ketone and large excess of ammonia and hydrogen under pressure (20–150 atm) over Raney nickel catalyst at 40–150°.



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

2.13 By reaction of aldehyde or ketones (with ammonium formate or with formamide and subsequent hydrolysis of product) :

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



3. 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 3° amines can form intermolecular 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 1° and 2° than that in alcohols and carboxylic acids. Because nitrogen is less electronegative than oxygen.
- [d] Boiling points of 1°, 2° and 3° amines follow the order.
1° > 2° > 3° amine.
- [e] Solubility in water follows the order.
1° > 2° > 3° amine.
This is all due to H-bonding.

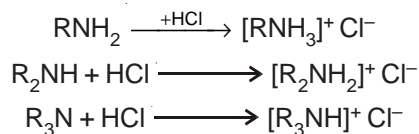
4. Chemical Properties :

- [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, affect its basicity.
- [d] Alkyl groups are electron releasing groups which increase electron density on nitrogen atom thus, we can expect the order of basicity of ammonia.
1°, 2° and 3° amines to be
3° > 2° > 1° ammonia
- [e] Some order factors like steric effect, solvation or hydration and mainly crowding on nitrogen atom by three bulky alkyl groups, decrease the basicity of 3° amines to a great extent and order follows :

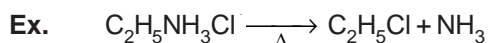
R ₂ NH	>	RNH ₂	>	R ₃ N	>	NH ₃
(2°)		(1°)		(3°)		(ammonia)
- [f] This can be also explained on basis of lesser capacity of 3° amine to form H-bonds with water which stabilizes R₂N⁺H on because it has only one H-atom.

5. Chemical Reaction :

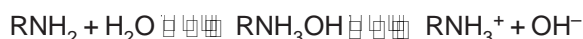
5.1 Salt Formation : Amine forms salt with mineral acids



These salts may undergo dealkylation at higher temp.



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

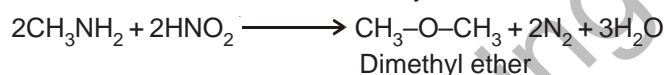
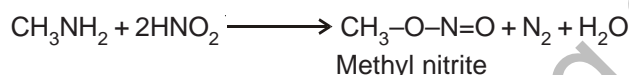


5.3 Reaction with HNO_2 : This reaction distinguishes 1°, 2° and 3° alcohols.

[a] Primary Amine : Except methyl amine, reaction happens at ordinary temp. to evolve N_2 gas.



Methylamine reacts in different way :



[b] Secondary Amine : Form nitroso amines with HNO_2 (NO gas is evolved)



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 **Liebermann's nitroso test** and used for identification of 2° amines.

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

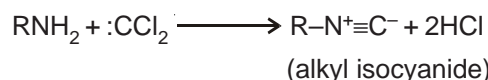
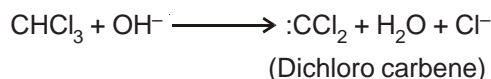


5.4 Isocyanide test or Carbylamine reaction :

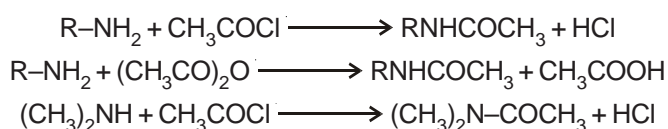
Primary amines when heated with chloroform and ethanolic KOH solution, alkyl isocyanides is produced which have characteristic foul smell. This reaction is characteristic to the primary amine. This test is known as **carbyl amines test or isocyanide test**.



The reaction proceeds via the formation of dichloro carbene ($:\text{CCl}_2$). In the absence of any lewis base catalyst when HCCl_3 reacts with base, $:\text{CCl}_2$ also produced, which is rapidly hydrolysed into CO , HCO_2^- and Cl^- .



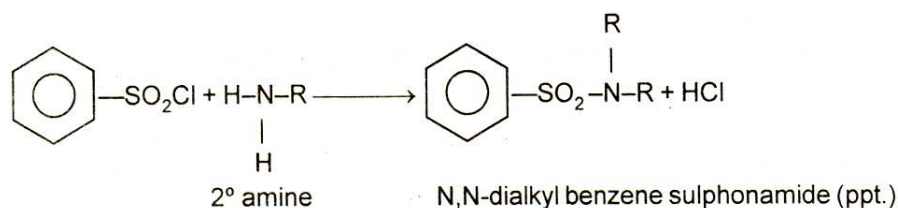
5.5 Acylation : 1° and 2° amines react with acetyl chloride or acetic anhydride to form acetyl derivatives.



Note : **[a]** Tertiary amines do not 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.

[b] Secondary amines form N, N-dialkyl benzene sulphonamide

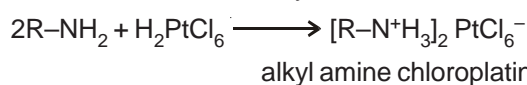
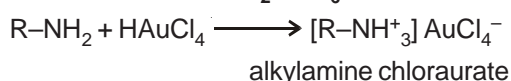


[c] Tertiary amines do not react because they do not possess a replacable Hydrogen atom.

5.12 Reaction with Nitrosyl chloride (TILDEN'S REAGNET) :

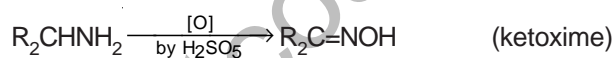
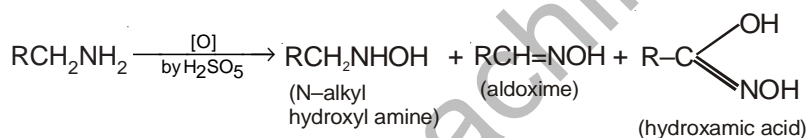


5.13 Reaction with HAuCl_4 (Chloroauric Acid) and H_2PtCl_6 (Chloroplatinic Acid) :



5.14 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.



6. Separation of Mixtures of Amines :

6.1 Fractional distillation :

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

6.2 Hofmann method :

This involves the treatment of the mixture with diethyl oxalate

[a] The primary amines forms a dialkyl oxamide, which is a solid.

[b] The secondary amine forms a dialkyl oxamic ester, which is an oily liquid.

[c] The tertiary amine does not react at all.

6.3 Hinsberg method :

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

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



[b] The secondary amine gives N, N-dialkyl benzene sulphonamide which is insoluble in KOH solution.

[c] The tertiary amine does not react at all.

7. Cyanides, Isocyanides, Alkyl Nitrites and Nitro Alkanes :

7.1 Introduction :

Hydrogen cyanide is known to exist as a tautomeric mixture



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



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 ₃ CN (Acetonitrile)	Methyl cyanide	Ethane nitrile
C ₂ H ₅ CN (Propionitrile)	Ethyl cyanide	Propane nitrile
C ₃ H ₇ CN	Propyl cyanide	Butane nitrile
C ₄ H ₉ CN	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 (Common name)	IUPAC names
CH ₃ NC	Methyl isocyanide (Methyl isonitrile)	Methylcarbylamine (Carbylamino methane)
C ₂ H ₅ NC	Ethyl isocyanide (Ethyl isonitrile)	Ethyl carbylamine (Carbylamino ethane)
C ₃ H ₇ NC	Propyl isocyanide (Propyl isonitrile)	(Propyl carbylamine (Carbylamino propane)

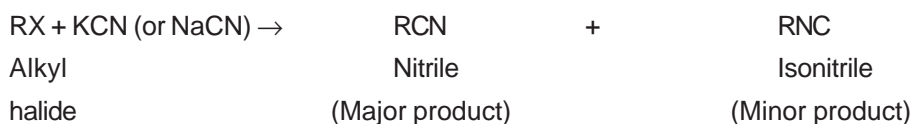
Isocyanides are also named as alkane isonitrile.

CH ₃ NC	Methane isonitrile
C ₂ H ₅ NC	Ethane isonitrile
C ₃ H ₇ NC	Propane isonitrile

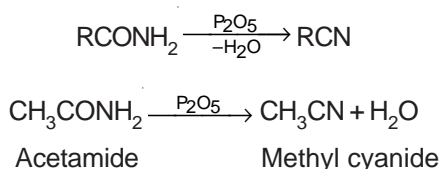
7.2 Alkyl cyanides :

7.2.1 Methods of Preparation :

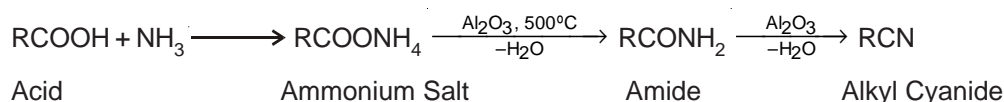
[i] From alkyl halides : The alkyl cyanides are prepared by refluxing an alcoholic solution of an alkyl halide with potassium cyanide. The disadvantage of this method is that a mixture of nitrile and isonitrile is formed.



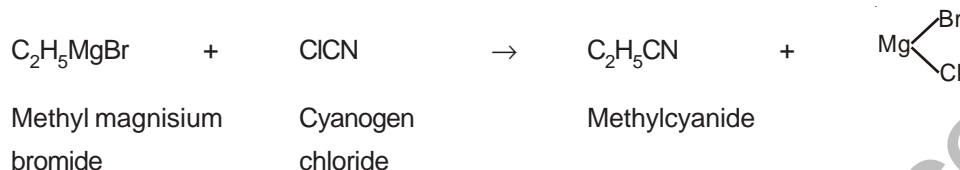
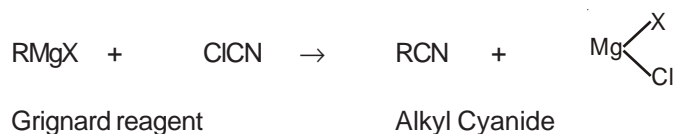
[ii] From acid amides : Pure nitriles are obtained by dehydration of acid amides with phosphorous pentoxide. Amides are distilled with phosphorus pentoxide, P₂O₅.



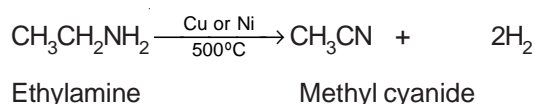
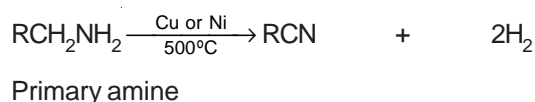
Industrially, alkyl cyanides are prepared by passing a mixture of carboxylic acid and ammonia over alumina at 500°C.



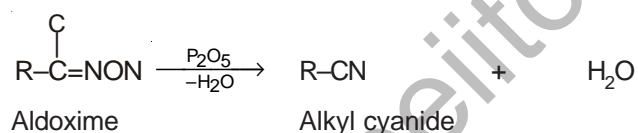
[iii] From Grignard reagent : Grignard reagent reacts with cyanogen chloride to form alkyl cyanides.



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



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



7.3 Physical properties :

[i] Alkyl cyanides are neutral substances with pleasant odour, similar to bitter almonds.

[ii] Lower members containing up to 15 carbon atoms are liquids, while higher members of carbon atoms in the molecule.

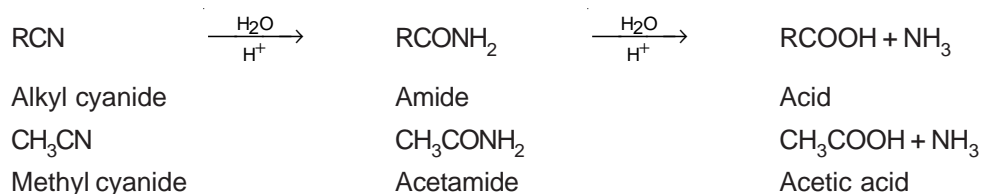
[iii] They are soluble in water. The solubility decreases with the increase in number of carbon atoms in the molecule.

[iv] They are soluble in organic solvents.

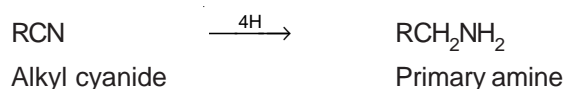
[v] They are poisonous but less poisonous than HCN.

7.4 Chemical properties :

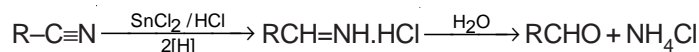
[i] **Hydrolysis :** Alkyl cyanides are hydrolysed by both acid and alkalies. On partial hydrolysis amides are formed while on complete hydrolysis acids are obtained.



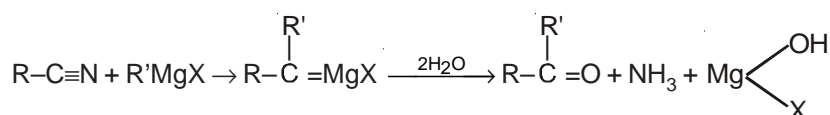
[ii] **Reduction :** When reduced with hydrogen in presence of Pt or Ni, or LiAlH₄ (Lithium aluminium hydride) or sodium and alcohol, alkyl cyanides yield primary amines.



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**).



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



[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.



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

7.5 Alkyl isocyanides :

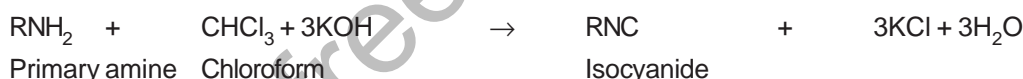
7.5.1 Methods of Preparation :

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

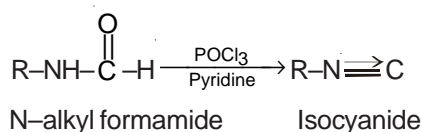


This method is, thus, not suitable for preparing isocyanides.

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



[iii] **From N-alkyl formamides** : N-alkyl formamides when dehydrated with POCl_3 in presence of pyridine give isocyanides.

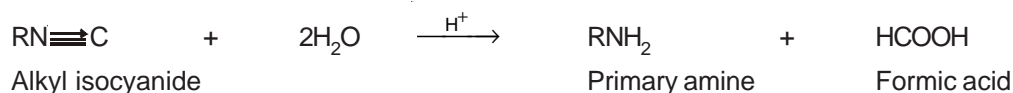


7.5.2 Physical Properties :

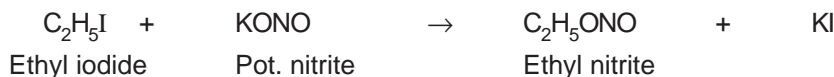
- [i] Alkyl isocyanides are colourless, unpleasant smelling liquids.
- [ii] The boiling points of isonitriles are lower than corresponding alkyl cyanides.
- [iii] They are insoluble in water but freely soluble in organic solvents.
- [iv] Isonitriles are much more poisonous than isomeric cyanides.

7.5.3 Chemical Properties :

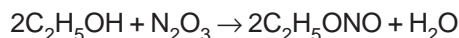
[i] **Hydrolysis** : Alkyl isocyanides are hydrolysed by dilute mineral acids (but not by alkalies) to form primary amines.



[ii] **From Ethyl iodide :**

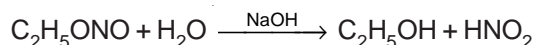


[iii] It is also prepared by the action of nitrogen trioxide, N_2O_3 on ethyl alcohol.

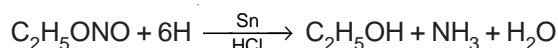


7.7.2 Properties : Ethyl nitrite is a gas at ordinary conditions. It has a characteristic smell of apples. It is insoluble in water.

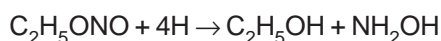
It is hydrolysed by aqueous alkalies or acids into ethyl alcohol.



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



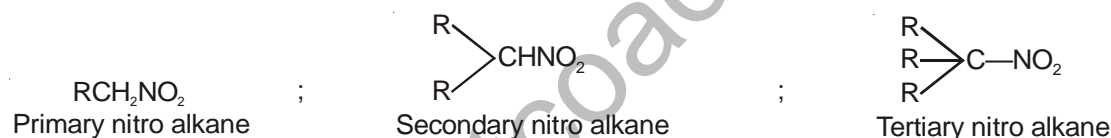
Small amount of hydroxylamine is also formed.



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

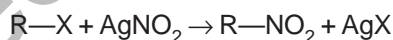
7.7.3 Nitro alkanes :

Nitro alkanes are the 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.



[a] General Methods of Preparation :

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

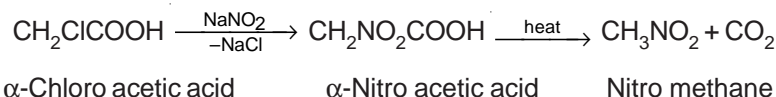


Some quantity of alkyl nitrite is also formed in the reaction. It can be removed by fractional distillation since alkyl nitrites have much lower boiling points as compared to nitro alkanes.

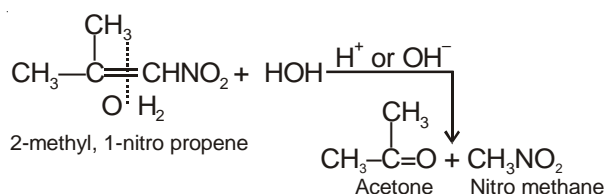
[ii] **Nitration :** Paraffins (alkanes) after hexane can be nitrated directly with concentrated nitric acid.

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

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



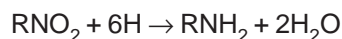
[iv] A recent method is by the hydrolysis of α -nitro alkene with water or acid or alkali.



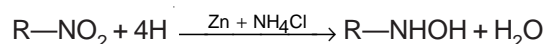
7.7.4 Physical properties : Nitro alkanes are colourless pleasant smelling liquids. Their boiling points are much higher than isomeric alkyl nitrites. They are less soluble in water but readily soluble in organic solvents.

7.7.5 Chemical properties :

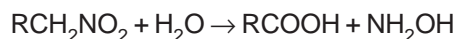
[i] **Reduction :** Nitro alkanes are reduced to corresponding primary amines with Sn and HCl or Iron and HCl or catalytic hydrogenation using nickel as catalyst.



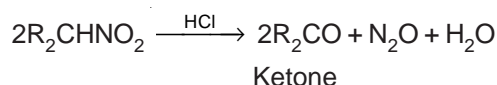
However when reduced with a neutral reducing agent (zinc dust + NH_4Cl), nitro alkanes form hydroxylamines.



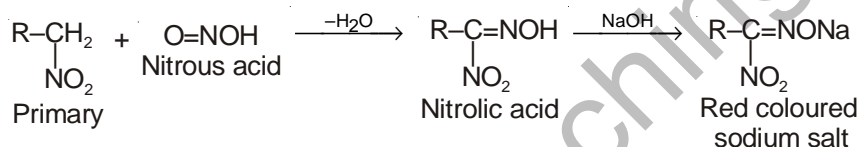
[ii] **Hydrolysis :** Primary nitro alkanes on hydrolysis with HCl or 80% H_2SO_4 produce hydroxylamine and carboxylic acid.



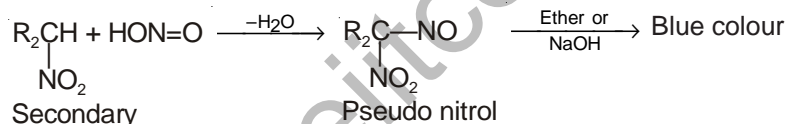
Secondary nitro alkanes on hydrolysis form ketones



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



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

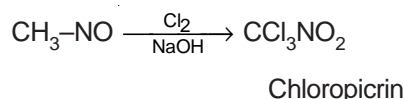


Tertiary nitro alkanes do not react with nitrous acid.

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.

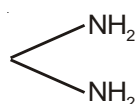
[v] **Halogenation :** Primary and secondary nitro alkanes are readily halogenated in the α -position by treatment with chlorine or bromine, Chloropicrin is formed when nitro methane reacts with Cl_2 in presence of NaOH. Chloropicrin is an important insecticide.



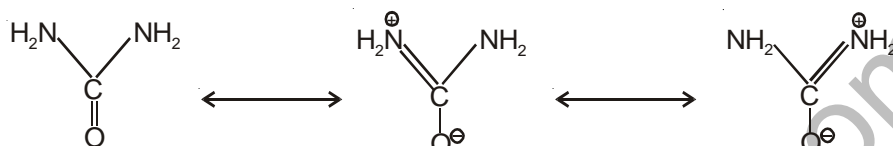
7.7.6 Uses : Nitro alkanes are used :

- [i] As solvents for substances such as cellulose acetate, synthetic rubber, etc.
- [ii] As explosives.
- [iii] For the preparation of amines, hydroxylamines, etc.

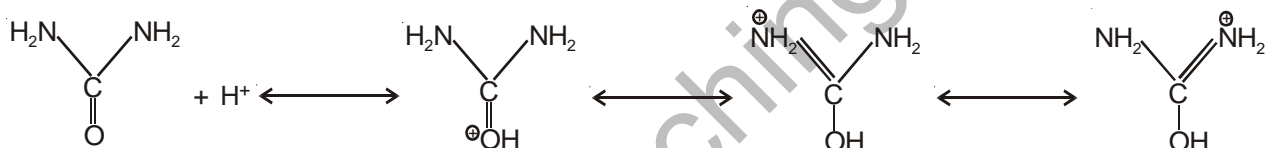
3. Physical Properties :

[a] Structure of Urea : The urea is represented by the diamide structure $\text{O}=\text{C}$  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 identical. Both length measurement of urea give the C–N distance as 1.37 Å, 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 resonance.



[b] Urea has been considered to be monoacidic base, because 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, odourless, crystalline solid.

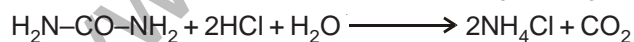
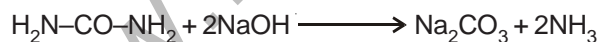
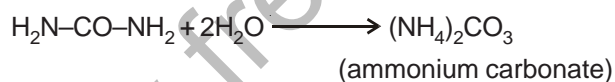
[d] It's boiling point is 132°C.

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

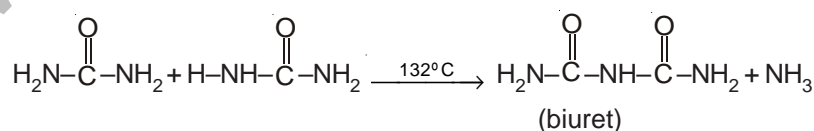
[f] Urea is used chiefly as a fertiliser. It can also be used for manufacturing urea formaldehyde resins and stabiliser for explosives (nitrocellulose).

4. Chemical Reactions :

4.1 Hydrolysis :



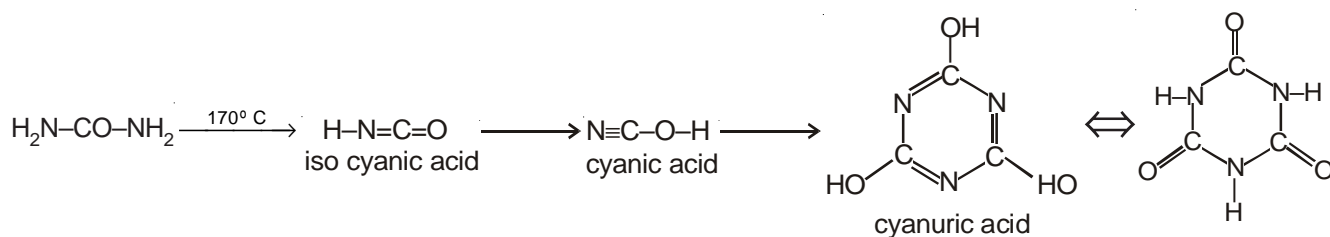
4.2 Effect of heat :



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.

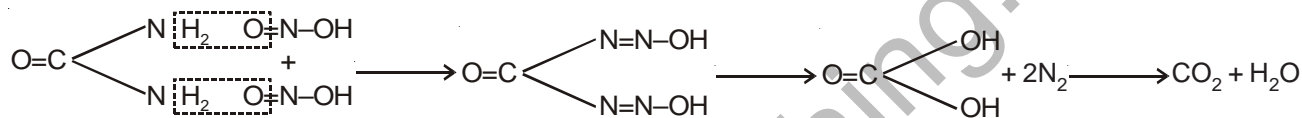


4.3 Salt Formation : It forms salts due to its weak basic nature. Urea is a feeble monoacid base ($K_b = 1.5 \times 10^{-14}$). It reacts with cold conc. nitric acid and oxalic acid to form salts.



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

4.4 Reaction with Nitrous acid :



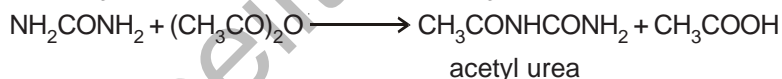
Thus, the total reaction is :



4.5 Reaction with Hypobromite solution :



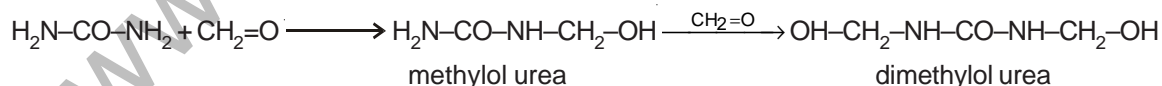
4.6 Acetylation : From Acetyl urea



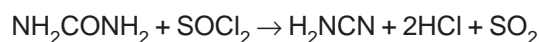
4.7 Reaction with Hydrazine (NH_2-NH_2) : Give semicarbazide :



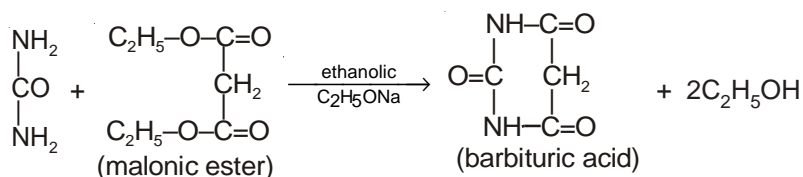
4.8 Condensation with Formaldehyde : Gives methylol urea then dimethylol urea which condenses to give Resins.



4.9 Reaction with SOCl_2 :

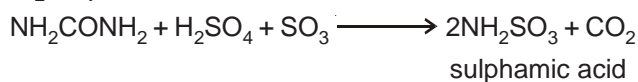


4.10 Reaction with Malonic ester :



Note : Barbituric acid is used as sedatives and hypnotics.

4.11 Reaction with fuming H_2SO_4 :

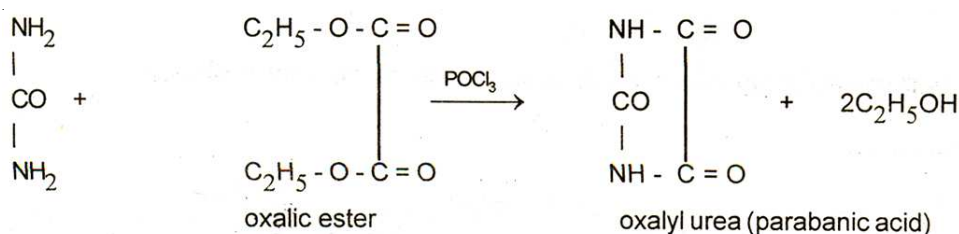


Sulphamic acid forms two things.

[a] Ammonium sulphamate used as flame proffing agent

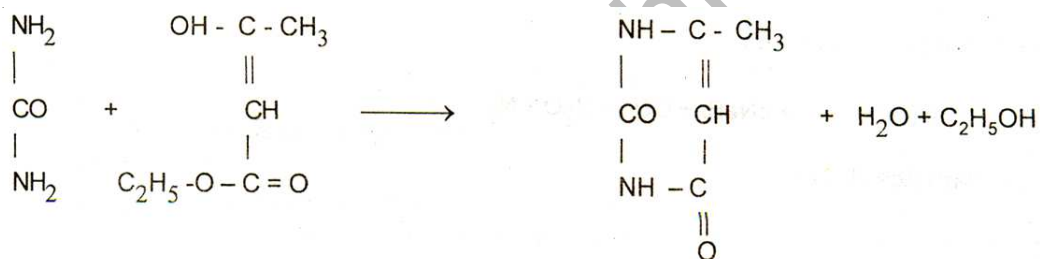
[b] Sodium cyclohexyl sulphamate (50 times sweeter than sugar)

4.12 Reaction with oxalic ester :

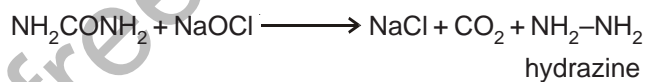


Note : Parabanic acid (Oxalyl urea) can also be produced when urea reacts with oxalic acid in presence of POCl_3 .

4.13 Reaction with Acetoacetic ester :



4.14 Reaction with NaOCl :



Nitro Benzene

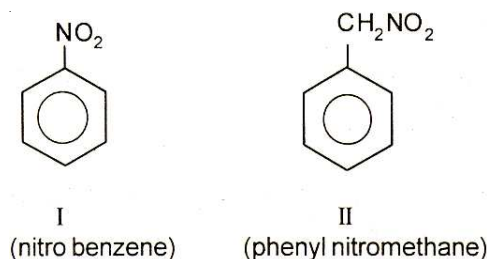
1 Introduction :

[a] Aromatic nitro compounds are obtained when hydrogen atom or atoms are of aromatic compound replaced by $-\text{NO}_2$ (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 benzene ring.

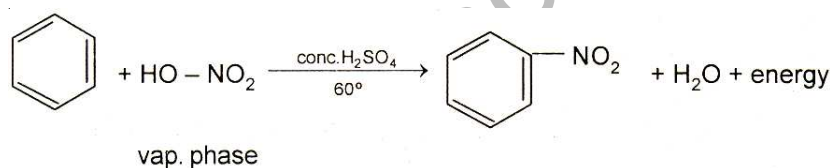


[c] Nitrobenzene is also called as 'oil of mirbane' or 'artificial oil of bitter almond's.

[d] It has a smell similar to benzaldehyde.

2. Methods of Preparation :

2.1 From Benzene (Nitration) :



Note :

[i] The reaction species is $^+\text{NO}_2$ (nitronium ion)

[ii] The above reaction is lab method of nitrobenzene preparation.

3. Physical Properties :

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

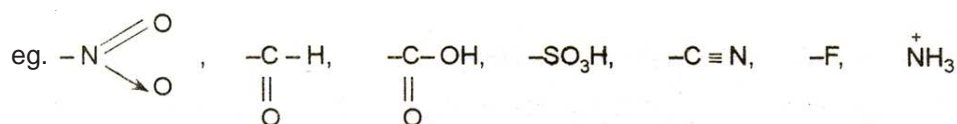
[b] It has odour like bitter almonds.

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

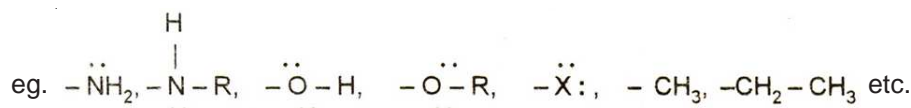
[d] Its boiling point is 211°C .

4. Resonance in nitrobenzene :

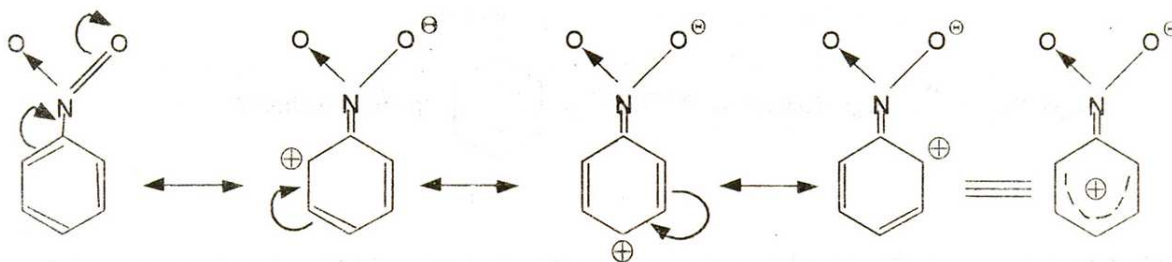
[a] The groups which can attract the electron from benzene ring or deactivate the benzene ring or make electron deficient to the benzene ring or shows $-I$ effect or shows $-M$ effect or $-R$ effect are called as meta directing groups. They do not show Friedel Craft reaction.



[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.



[c] Resonating structures of nitrobenzene.



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

5. Chemical Reactions :

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

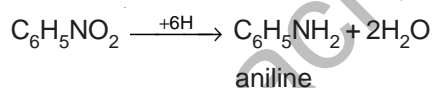
- 5.1 Reaction of $-\text{NO}_2$ group
- 5.2 Reaction of Benzene ring
- 5.3 Other reactions

5.1 Reaction of $-\text{NO}_2$ group :

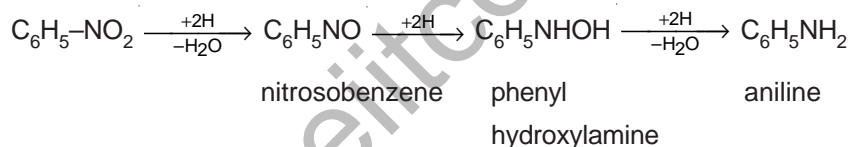
5.1.1 Reduction :

[a] Acidic medium :

Reagents : Sn/HCl or SnCl_2/HCl or $\text{Zn}/\text{CH}_3\text{COOH}$ etc.

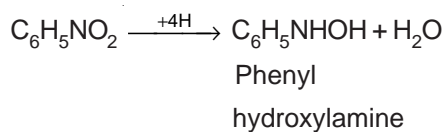


Propable intermediate steps :



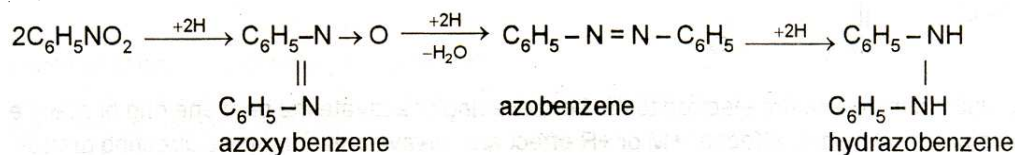
[b] Neutral Medium :

Reagents : $\text{Zn}/\text{NH}_4\text{Cl}$ or Zn/CaCl_2 or $\text{Al}-\text{Hg}/\text{NH}_4\text{Cl}$ etc.



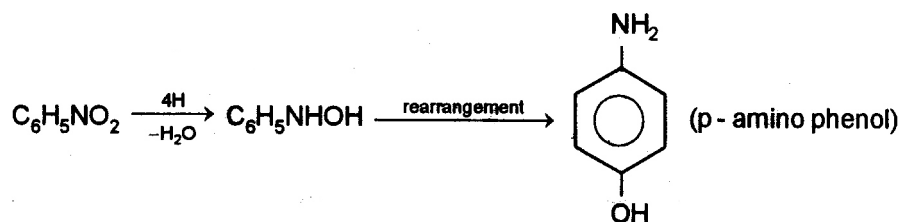
[c] Alkaline Medium :

Reagents : Zn/NaOH or $\text{SnCl}_2/\text{NaOH}$, or Glucose/ NaOH etc.

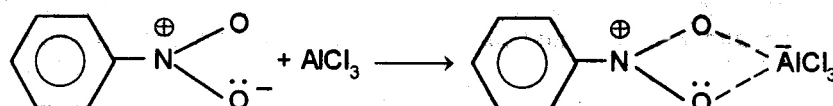


[d] Electrolytic reduction :

[Medium : conc, H₂SO₄]

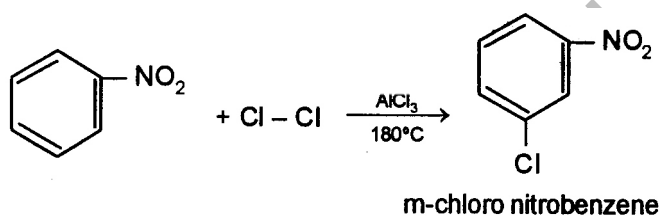


5.1.2 Reaction with AlCl₃ : Nitrobenzene behaves as weak base and makes a complex compound with aluminium chloride.

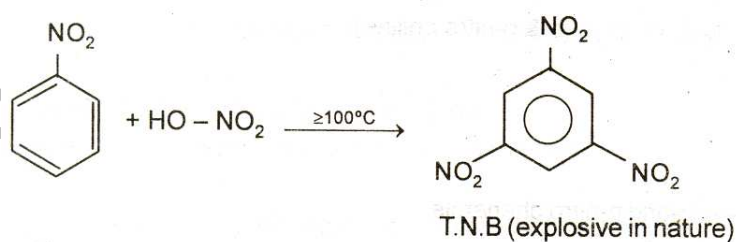
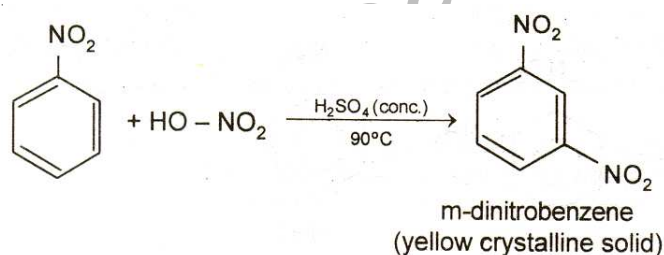


5.2 Reaction of Benzene ring :

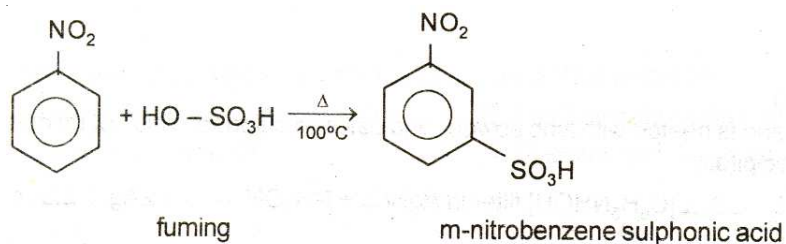
5.2.1 Halogenation :



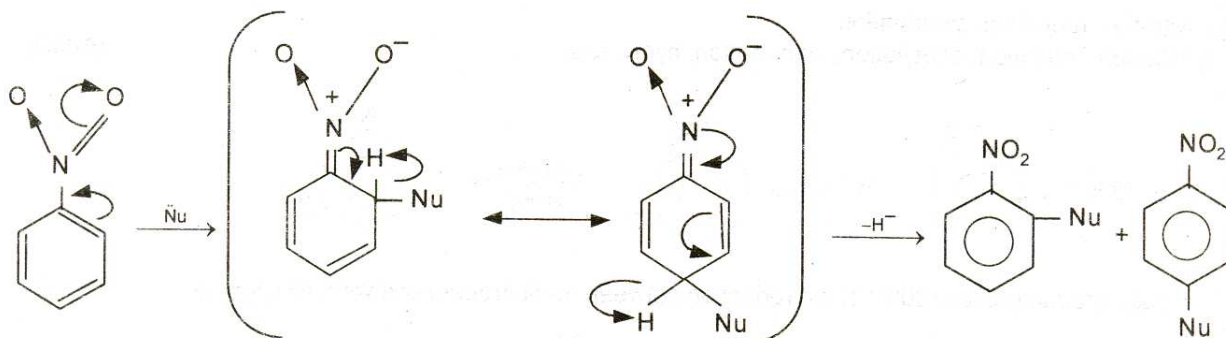
5.2.2 Nitration :



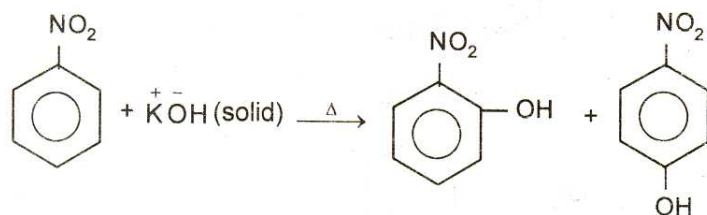
5.2.3 Sulphonation :



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

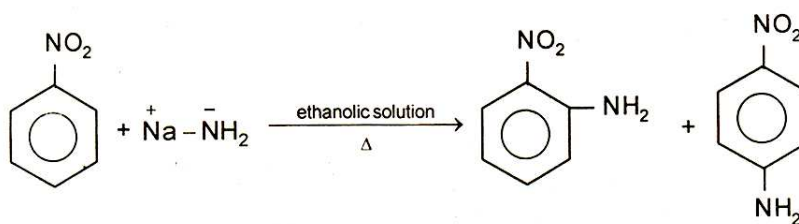


5.3.1 Reaction with Solid KOH :



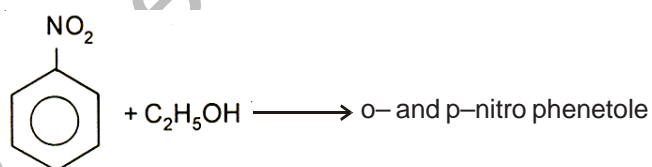
(o- & p-nitrophenol)

5.3.2 Reaction with Sodamide :



(o & p-nitro aniline)

5.3.3. Reaction with Ethanol :



6. 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.



Aniline

1 Introduction :

[a] Aniline is called phenyl derivative of ammonia.

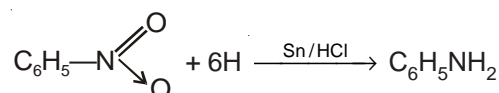
[b] It was initially obtained by the scientist 'Unverdorben'.

[c] Aniline is also called amino derivative of benzene because when a hydrogen atom is replaced by NH₂ group, aniline is obtained.

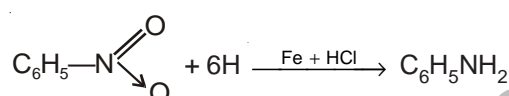
2. Method of Preparation :

2.1 From Nitrobenzene (Reduction in acidic medium) :

[a] Lab method :



[b] Industrial method :



2.2 From Benzamide :



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

2.3 From Chlorobenzene :

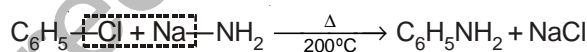
[a] With NH₃ :



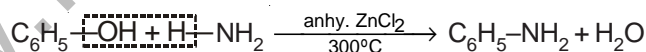
Note : We use Cu₂O to neutralize the formed HCl otherwise HCl forms additional salt with aniline.



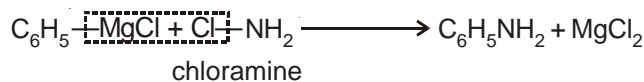
[b] With sodamide :



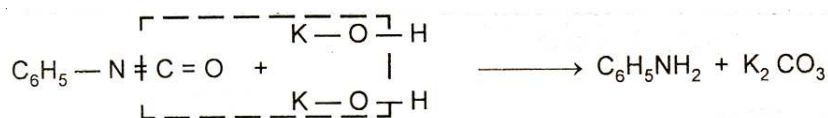
2.4 From Phenol :



2.5 From Grignard reagent :

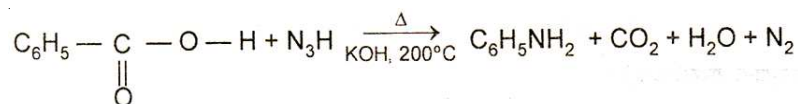


2.6 From phenyl isocyanate (By alkaline hydrolysis) :

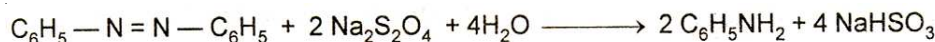


Note : The above method is called as 'wurtz method'.

2.7 From Benzoic acid (Schmidt reaction) :



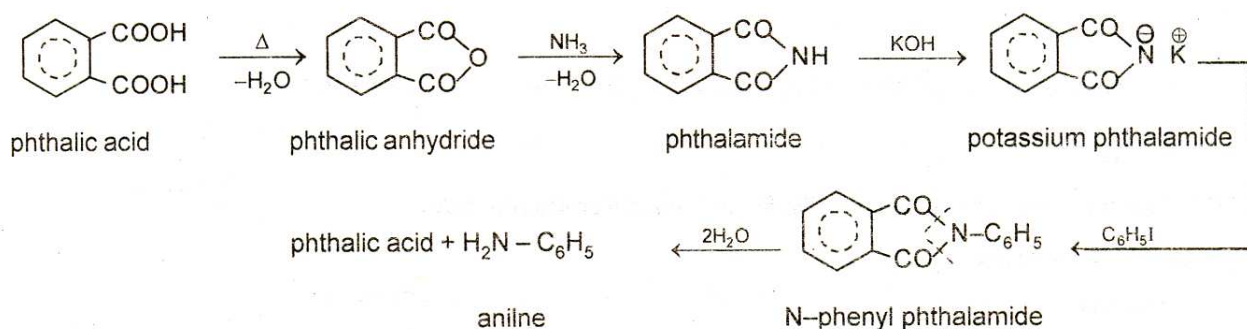
2.8 By reduction of azo and hydrazo compounds with sodium dithionite :



2.9 By Curtius reaction :



2.10 By Gabriel Phthalimide reaction :

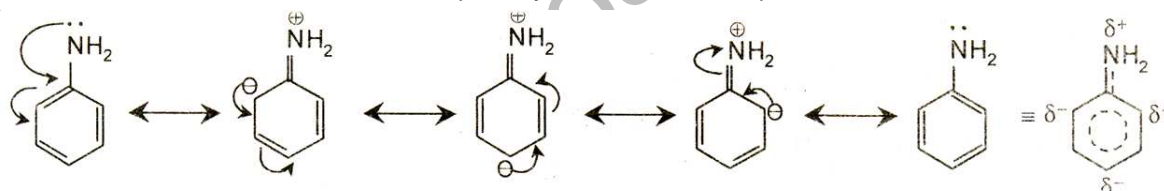


3. Physical properties :

- [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.

4. Resonance in Aniline :

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



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

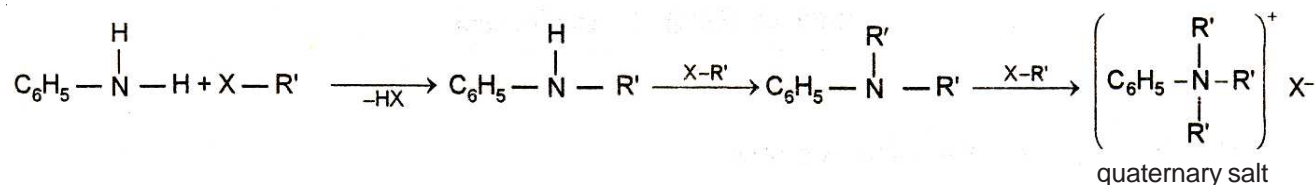
5. Chemical Reaction :

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

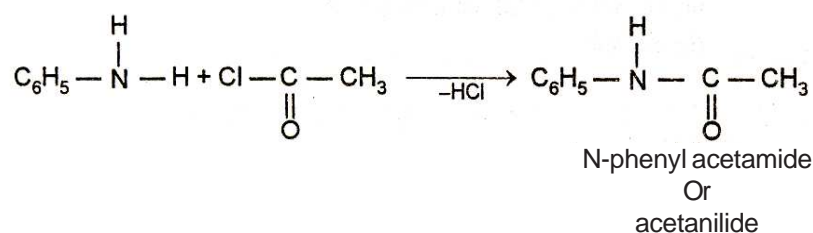
- 5.1 Reaction of —NH_2 group
- 5.2 Reactions of benzene ring
- 5.3 Other reactions

5.1 Reactions of —NH_2 group :

5.1.1 Alkylation :

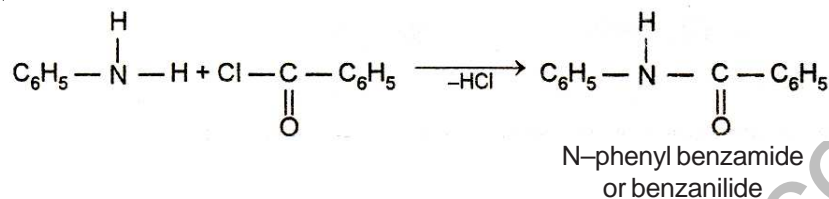


5.1.2 Acetylation :

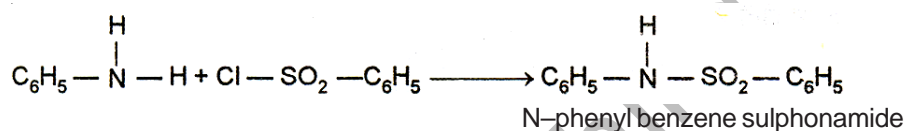


Note : The product formed is important because it is used in preservation of $-\text{NH}_2$ group in aniline.

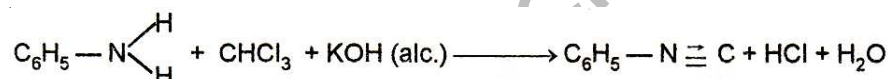
5.1.3 Schotten–baumann reaction :



5.1.4 Reaction with Hinsberg reagent :

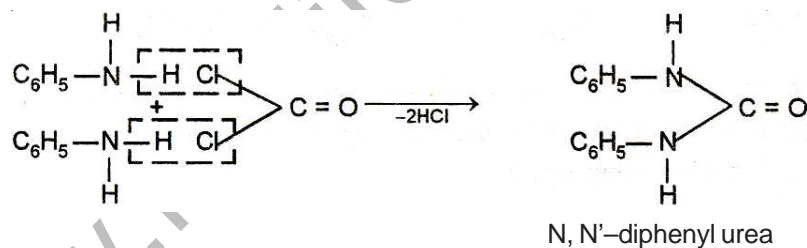


5.1.5 Hoffmann Carbylamine reaction (Isocyanide test) :



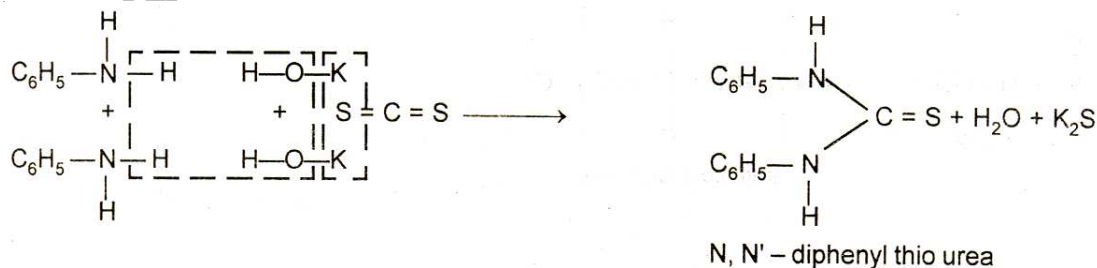
These isocyanides have a very offensive smell. Reaction is used for testing of primary amines.

5.1.6 Reaction with Phosgene :

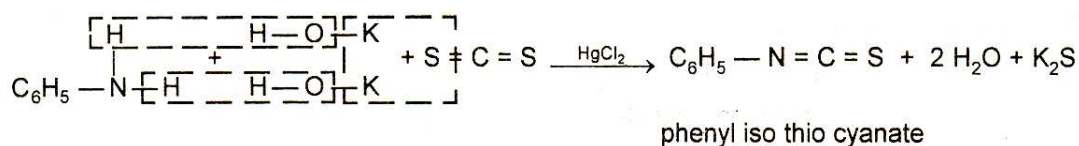


5.1.7 Reaction with Carbonyl disulphide :

[a] When aniline is in excess :

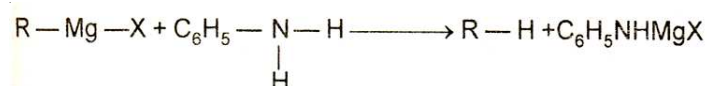


[b] When aniline is in lesser quantity :

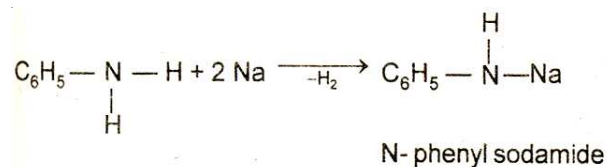


Note : This isothiocyanate has an odour like mustard oil so the reaction is called '**Hoffmann–mustard oil reaction**'.

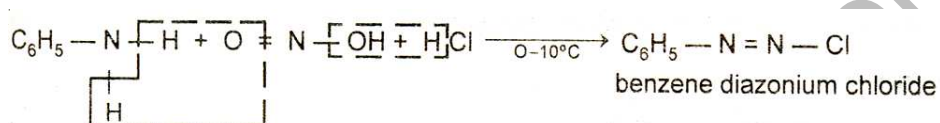
5.1.8 Reaction with Grignard reagent :



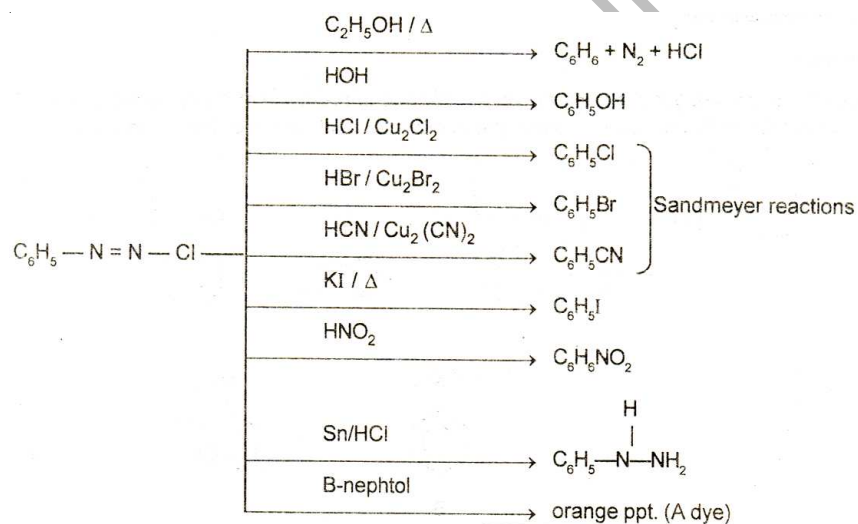
5.1.9 Reaction with Sodium metal :



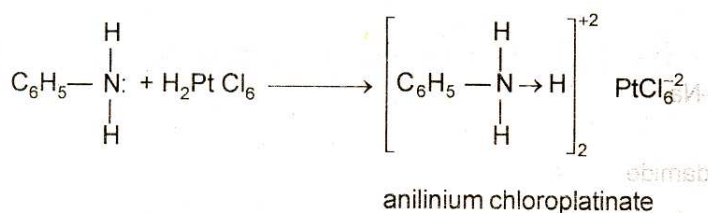
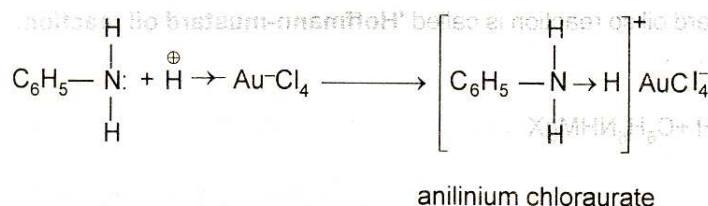
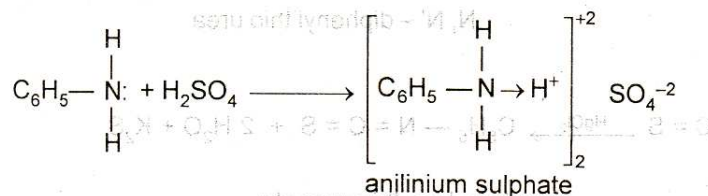
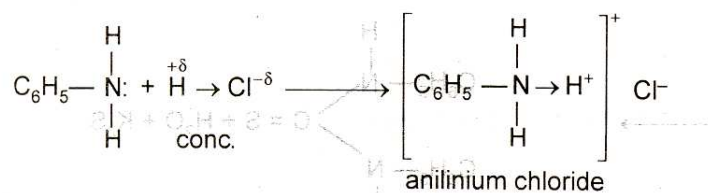
5.1.10 Reaction with HNO₂ and HCl (Diazotisation) :



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



5.1.11 Salt formation :



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

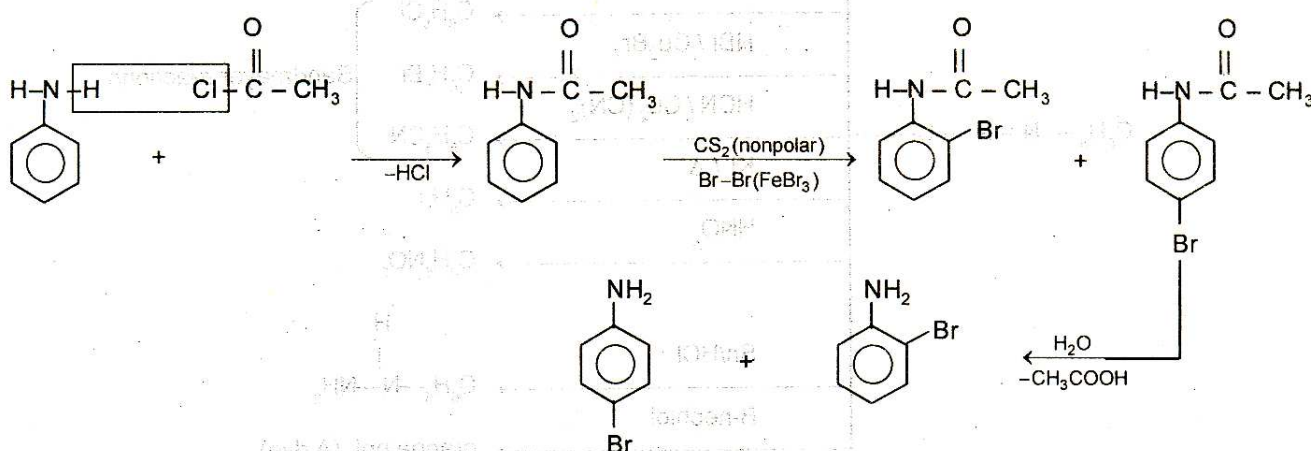
5.1.12 Reaction with Benzaldehyde :



5.2 Reaction of benzene ring :

5.2.1 Halogenation :

Aniline does not show halogenation or nitration directly due to presence of active hydrogen on $-\text{NH}_2$ group so for nitration, halogenations first we preserve $-\text{NH}_2$ 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.