

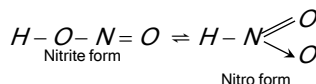
Chapter 29

Nitrogen Containing Compounds

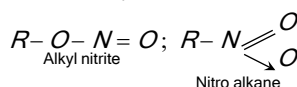
The important nitrogen containing organic compounds are alkyl nitrites ($RONO$), nitro-alkanes (RNO_2), aromatic nitro compounds ($ArNO_2$), alkyl cyanides (RCN), alkyl iso cyanides (RNC), amines ($-NH_2$), aryl diazonium salts (ArN_2Cl), amides ($-CONH_2$) and oximes ($>C=N OH$).

Alkyl nitrites and nitro alkanes

Nitrous acid exists in two tautomeric forms.



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



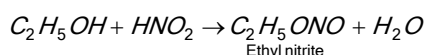
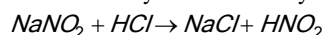
It is important to note that nitro alkanes are better regarded as nitro derivatives of alkanes, while alkyl nitrites are regarded as alkyl esters of nitrous acid.

(1) **Alkyl nitrites** : The most important alkyl nitrite is ethyl nitrite.

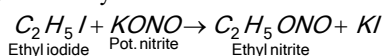
Ethyl nitrite (C_2H_5ONO)

(i) **General methods of preparation** : It is prepared

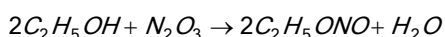
(a) By adding concentrated HCl or H_2SO_4 to aqueous solution of sodium nitrite and ethyl alcohol at very low temperature ($0^\circ C$).



(b) From Ethyl iodide



(c) By the action of N_2O_3 on ethyl alcohol.



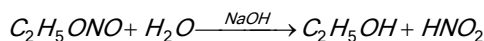
(ii) **Physical properties**

(a) At ordinary temperature it is a gas which can be liquified on cooling to a colourless liquid, (boiling point $17^\circ C$) having characteristic smell of apples.

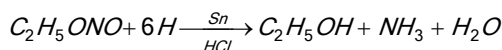
(b) It is insoluble in water but soluble in alcohol and ether.

(iii) **Chemical properties**

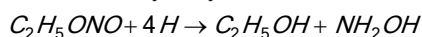
(a) **Hydrolysis** : It is hydrolysed by aqueous alkalies or acids into ethyl alcohol.



(b) **Reduction** :



Small amount of hydroxylamine is also formed.



(iv) **Uses**

(a) Ethyl nitrite dilates the blood vessels and thus accelerates pulse rate and lowers blood pressure, so it is used as a medicine for the treatment of asthma and heart diseases (angina pectoris).

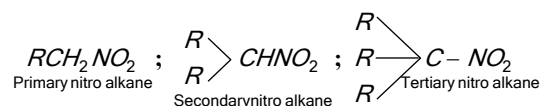
(b) Its 4% alcoholic solution (known as *sweet spirit of nitre*) is used in medicine as a diuretic.

(c) Since it is easily hydrolysed to form nitrous acids, it is used as a source of nitrous acid in organic synthesis.

□ **Isoamyl nitrite** is used as an antispasmodic in angina pectoris and as a restorative in cardiac failure.

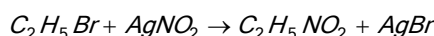
(2) **Nitro alkanes or Nitroparaffins** : Nitro alkanes are regarded as nitro derivatives of hydrocarbons.

(i) **Classification** : They are classified as primary, secondary and tertiary depending on the nature of carbon atom to which nitro groups is linked.



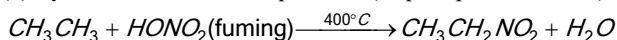
(ii) **General methods of preparation**

(a) By heating an alkyl halide with aqueous alcoholic solution of silver nitrite



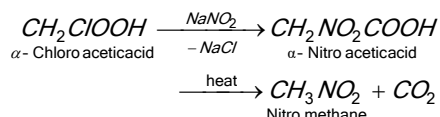
Some quantity of alkyl nitrite is also formed in this reaction. It can be removed by fractional distillation since alkyl nitrites have much lower boiling points as compared to nitro alkanes.

(b) By the direct nitration of paraffins (Vapour phase nitration)

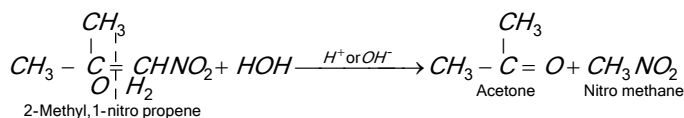


With higher alkanes, a mixture of different nitro alkanes is formed which can be separated by **fractional distillation**.

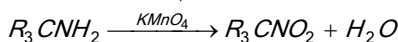
(c) By the action of sodium nitrite on α -halo carboxylic acids



(d) By the hydrolysis of α -nitro alkene with water or acid or alkali (Recent method)



(e) Tertiary nitro alkanes are obtained by the oxidation of *t*-alkyl amines with $KMnO_4$.



(iii) **Physical properties**

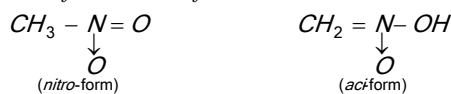
(a) Nitro alkanes are colourless, pleasant smelling liquids.

(b) These are sparingly soluble in water but readily soluble in organic solvents.

(c) Their boiling points are much higher than isomeric alkyl nitrites due to polar nature.

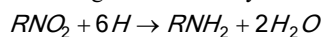
(d) Again due to polar nature, nitro alkanes are excellent solvents for polar and ionic compounds.

□ 1° and 2° - Nitro alkanes are known to exist as tautomeric mixture of nitro-form and aci-form.

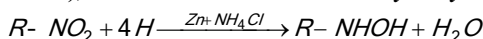


(iv) **Chemical properties**

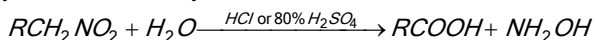
(a) **Reduction** : Nitro alkanes are reduced to corresponding primary amines with Sn and HCl or Fe and HCl or catalytic hydrogenation using nickel as catalyst.



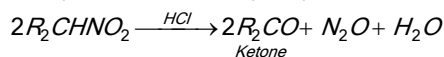
However, when reduced with a neutral reducing agent (**Zinc dust** + NH_4Cl), nitro alkanes form **substituted hydroxylamines**.



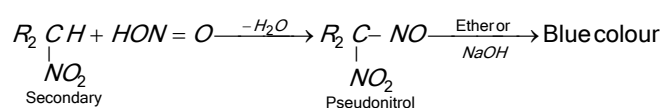
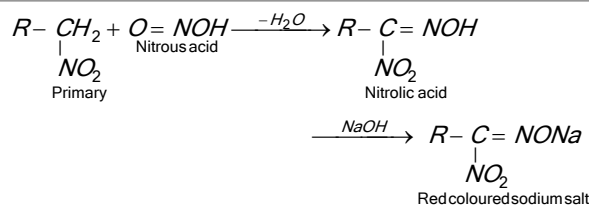
(b) **Hydrolysis** : Primary nitro alkanes on hydrolysis form hydroxylamine and carboxylic acid.



secondary nitro alkanes on hydrolysis form ketones.

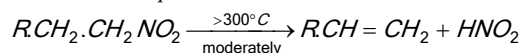


(c) **Action of nitrous acid** : Nitrous acid reacts with primary, secondary and tertiary nitro alkanes differently.

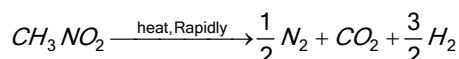


Tertiary nitro alkanes do not react with nitrous acid.

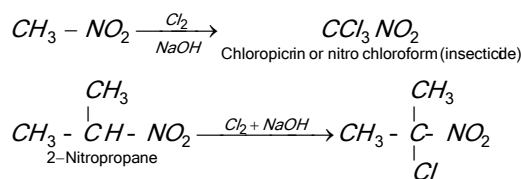
(d) **Thermal decomposition** :



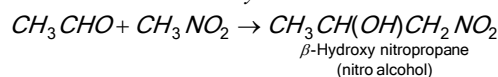
On rapid heating nitro alkanes decompose with great violence.



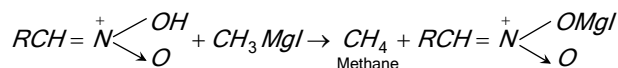
(e) **Halogenation** : Primary and secondary nitro alkanes are readily halogenated in the α -position by treatment with chlorine or bromine.



(f) **Condensation with aldehyde** :

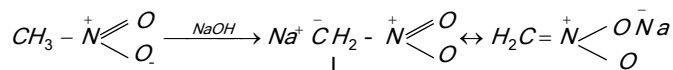


(g) **Reaction with grignard reagent** : The *aci*-form of nitroalkane reacts with Grignard reagent forming alkane.



□ The nitrogen of $-NO_2$ carrying a positive charge exerts a powerful $-I$ effect and thus activates the hydrogen atom of the α -carbon. Thus the important reactions of nitroalkanes are those which involve α -hydrogen atom of primary and secondary nitroalkanes (**tertiary nitroalkanes have no α -hydrogen atom and hence do not undergo such type of reactions**).

□ **Acidic character** : The α -hydrogen atom of primary and secondary nitroalkanes are weakly acidic and thus can be abstracted by strong alkalis like aq. $NaOH$. Therefore, 1° and 2° nitroalkanes dissolve in aq. $NaOH$ to form salts. For examples.



Thus 1° and 2° nitroalkanes are acidic mainly due to following two reasons,

(a) Strong electron withdrawing effect of the $-NO_2$ group.

(b) Resonance stabilisation of the carbanion (I) formed after the removal of proton.

The *aci*-form of nitroalkanes is relatively more acidic because it produces relatively more conjugate base.

(v) **Uses** : Nitro alkanes are used,

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

- (b) As an explosive.
(c) For the preparation of amines, hydroxylamines, chloropicrin
etc.

Table : 29.1 Distinction between Ethyl nitrite and Nitro ethane

Test	Ethyl nitrite (C_2H_5ONO) (Alkyl nitrite, $RONO$)	Nitro ethane ($C_2H_5NO_2$) (Nitro alkane, RNO_2)
Boiling point	Low, $17^\circ C$	Much higher, $115^\circ C$
Reduction with metal and acid (Sn/HCl) or with $LiAlH_4$.	Gives alcohol + hydroxyl amine or NH_3 . $C_2H_5ONO + 4H \rightarrow C_2H_5OH + NH_2OH$ $RONO + 6H \rightarrow ROH + NH_3 + H_2O$	Gives corresponding primary amine. $C_2H_5NO_2 + 6H \rightarrow C_2H_5NH_2 + 2H_2O$ $RNO_2 + 6H \rightarrow RNH_2 + 2H_2O$
Action of $NaOH$ (alkalies).	Readily hydrolysed to give corresponding alcohol and sodium nitrite (decomposition). $C_2H_5ONO + NaOH \rightarrow C_2H_5OH + NaNO_2$ $RONO + NaOH \rightarrow ROH + NaNO_2$	Not decomposed, <i>i.e.</i> , alcohols are not produced. But it may form soluble sodium salt, because in presence of alkali the nitro form changes into aci form, which dissolves in alkalies to form sodium salt. $CH_3 - CH = N \begin{matrix} OH \\ \diagdown \\ O \end{matrix} \xrightarrow{NaOH} CH_3 - CH = N \begin{matrix} ONa \\ \diagdown \\ O \end{matrix}$
Action of HNO_2 ($NaNO_2 + HCl$)	No action with nitrous acid.	Primary nitro alkanes forms nitrolic acid, which dissolve in alkali to give red solution. Secondary nitro alkane yields pseudo-nitrol, which dissolves in alkali to give blue solution. Tertiary nitro alkanes does not react with nitrous acid.

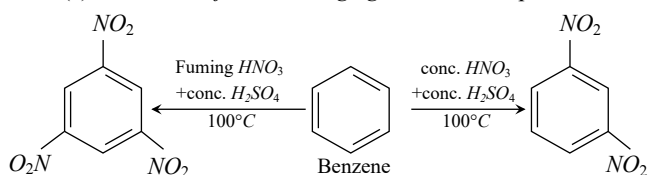
Aromatic Nitro Compounds

Aromatic nitro compounds are the derivatives of aromatic hydrocarbons in which one or more hydrogen atom (s) of the benzene nucleus has been replaced by nitro ($-NO_2$) group.

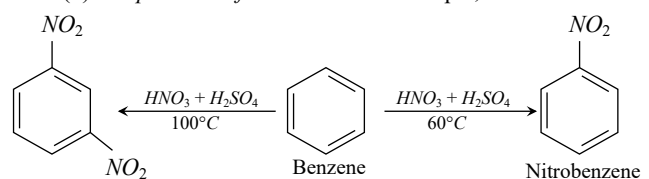
(1) Preparation

(i) **Nitration (Direct method)** : The number of $-NO_2$ groups introduced in benzene nucleus depends upon the nature and concentration of the nitrating agent, temperature of nitration and nature of the compound to be nitrated.

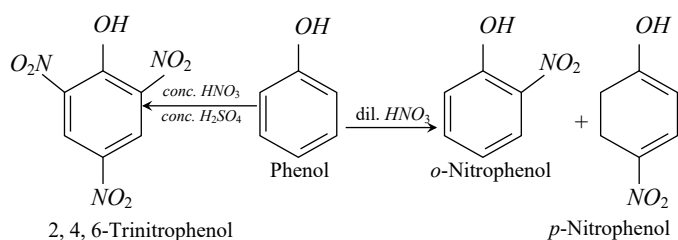
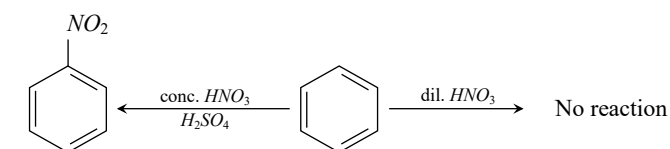
(a) *The nature of the nitrating agent* : For example,



(b) *Temperature of nitration* : For example,

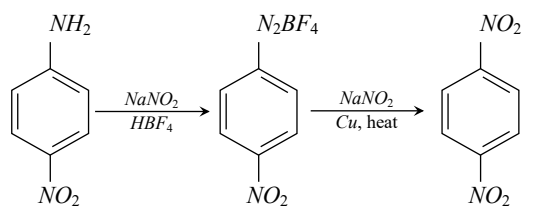


(c) *Nature of the compound to be nitrated* : Presence of electron-releasing group like $-OH$, $-NH_2$, $-CH_3$, $-OR$, etc., in the nucleus facilitates nitration. Thus aromatic compounds bearing these groups (i.e. phenol, aniline, toluene, etc.) can be nitrated readily as compared to benzene. Thus benzene is not affected by dilute HNO_3 while phenol, aniline and toluene forms the corresponding *ortho*- and *para*-nitro compounds.



On the other hand, nitration of aromatic compounds having electron withdrawing groups like $-NO_2$, $-SO_3H$ requires powerful nitrating agent (like fuming HNO_3 + conc. H_2SO_4) and a high temperature.

(ii) **Indirect method** : The aromatic nitro compounds which can not be prepared by direct method may be prepared from the corresponding amino compound.



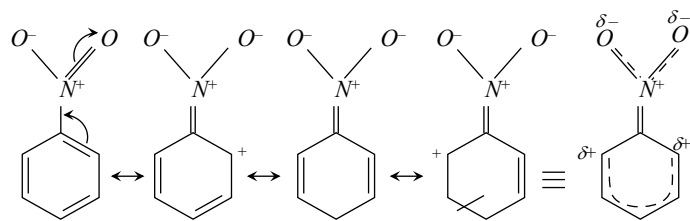
(2) Physical properties

(i) Aromatic nitro compounds are insoluble in water but soluble in organic solvents.

(ii) They are either pale yellow liquids or solids having distinct smells. For example, *nitro benzene (oil of Mirabane)* is a pale yellow liquid having a smell of bitter almonds.

(3) Chemical properties

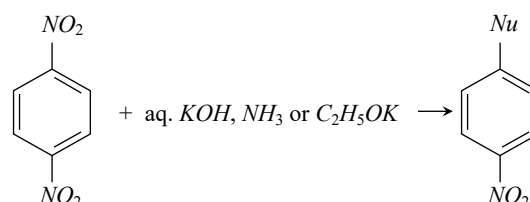
(i) Resonance in nitrobenzene imparts a partial double bond character to the bond between carbon of benzene nucleus and nitrogen of the $-NO_2$ group with the result the $-NO_2$ group is firmly bonded to the ring and therefore cannot be replaced other groups, i.e., it is very inert.



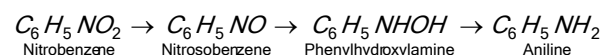
Resonating structures of nitrobenzene

Resonance hybrid of nitrobenzene

(ii) **Displacement of the $-NO_2$ group** : Although $-NO_2$ group of nitrobenzene cannot be replaced by other groups, but if a second $-NO_2$ group is present on the benzene ring of nitrobenzene in the *o*- or *p*- position, it can be replaced by a nucleophile. For example,

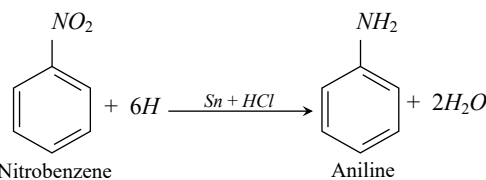


(iii) **Reduction** : Aromatic nitro compounds can be reduced to a variety of product as shown below in the case of nitrobenzene. (Where, $Nu = OH, NH_2$ or OC_2H_5)

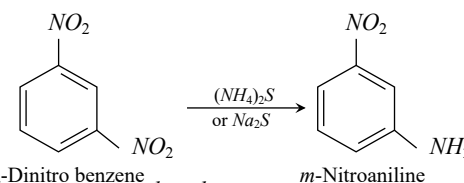


The nature of the final product depends mainly on the *nature (acidic, basic or neutral) of the reduction medium and the nature of the reducing agent.*

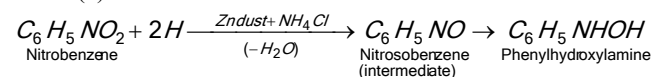
(a) Reduction in acidic medium



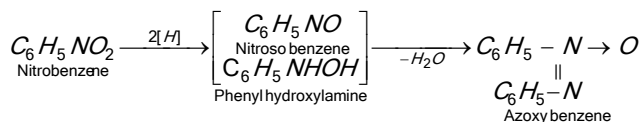
Reduction of dinitrobenzene with ammonium sulphide reduces only one $-NO_2$ group (**selective reduction**)



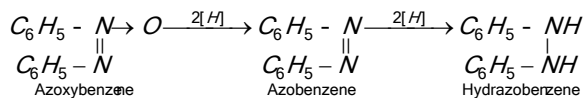
(b) Reduction in neutral medium :



(c) Reduction in alkaline medium :

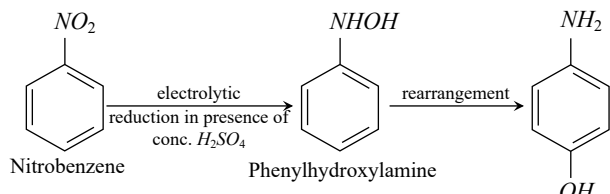


Azoxybenzene on further reduction yields azobenzene and hydrazobenzene.



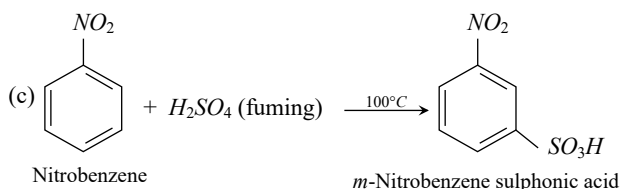
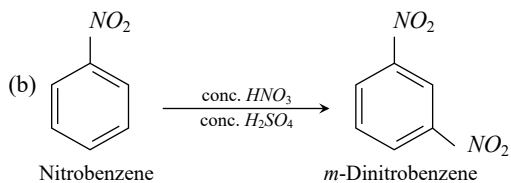
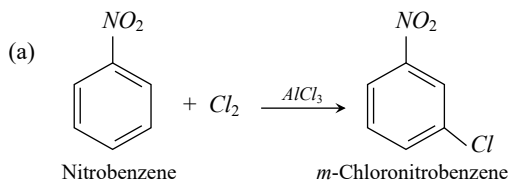
(d) **Electrolytic reduction** :

- **Weakly acidic medium** of electrolytic reduction gives **aniline**.
- **Strongly acidic medium** gives phenylhydroxylamine which rearranges to ***p*-aminophenol**.

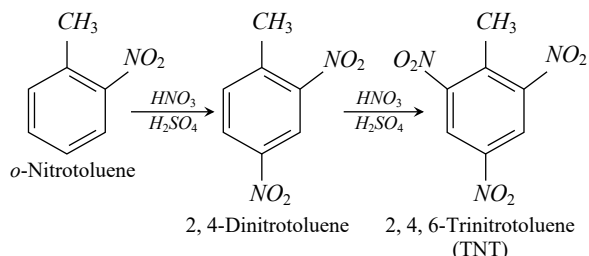


- **Alkaline medium** of electrolytic reduction gives ***m*-nitrophenol and di-nuclear reduction products** mentioned above in point (c).

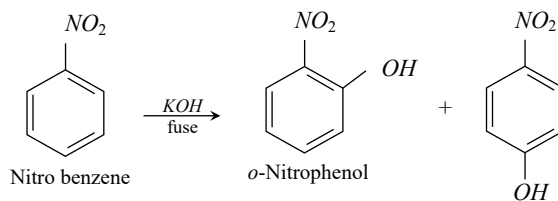
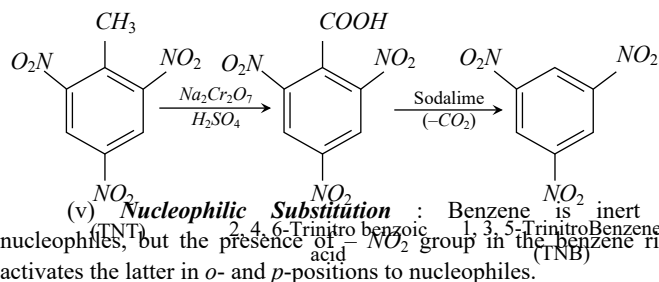
(iv) **Electrophilic substitution** : Since $-NO_2$ group is **deactivating and *m*-directing**, electrophilic substitution (halogenation, nitration and sulphonation) in simple aromatic nitro compounds (e.g. nitrobenzene) is very difficult as compared to that in benzene. Hence vigorous reaction conditions are used for such reaction and the new group enters the *m*-position.



Although nitrobenzene, itself undergoes electrophilic substitution under drastic conditions, nitrobenzene having activating groups like alkyl, $-OR$, $-NH_2$ etc. undergoes these reactions relatively more readily.

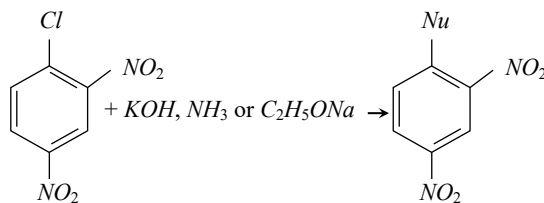


***Sym*-trinitrobenzene (TNB) is preferentially prepared from easily obtainable TNT rather than the direct nitration of benzene which even under drastic conditions of nitration gives poor yields.**



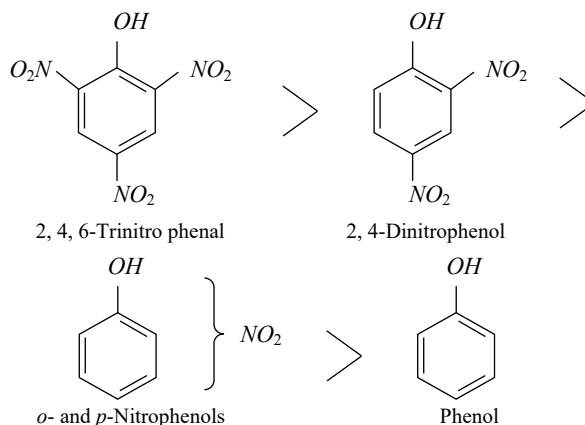
(vi) **Effect of the $-NO_2$ group on other nuclear substituents**

(a) **Effect on nuclear halogen** : The nuclear halogen is ordinarily inert, but if it carries one or more electron-withdrawing groups (like $-NO_2$) in *o*- or *p*-position, the halogen atom becomes active for nucleophilic substitutions and hence can be easily replaced by nucleophiles ($KOH, NH_3, NaOC_2H_5$).

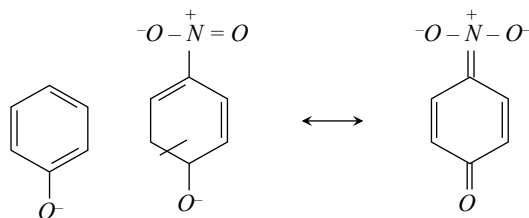


(b) **Effect on phenolic $-OH$ group** : The acidity of the phenolic hydroxyl group is markedly increased by the presence of $-NO_2$ group in *o*- and *p*-position.

The decreasing order of the acidity of nitrophenols follows following order

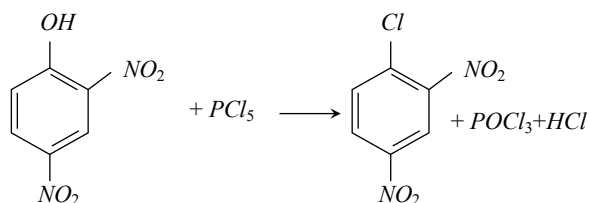


Increased acidity of *o*- and *p*-nitrophenols is because of the fact that the presence of electron-withdrawing $-NO_2$ group in *o*- and *p*-position (*s*) to phenolic $-OH$ group stabilises the phenoxide ions (recall that acidic nature of phenols is explained by resonance stabilisation of the phenoxide ion) to a greater extent.



Phenoxide ion
Due to increased acidity of phenols, the latter react with phosphorus pentachloride to give good yields of the corresponding chloro derivative, while phenol itself when treated with PCl_5 gives poor yield of chlorobenzene.

Extra stabilisation of p -nitrophenate ion due to $-NO_2$ group. The latter react with phosphorus pentachloride to give good yields of the corresponding chloro derivative, while phenol itself when treated with PCl_5 gives poor yield of chlorobenzene.



2, 4-Dinitrophenol

2, 4-Dinitrochlorobenzene

(4) Uses

(i) On account of their high polarity, aromatic nitro compounds are used as solvents.

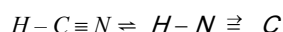
(ii) Nitro compounds like TNT, picric acid, TNB etc. are widely used as **explosives**.

(iii) These are used for the synthesis of aromatic amino compounds.

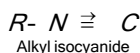
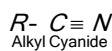
(iv) Nitro benzene is used in the preparation of shoe polish and scenting of cheap soaps.

Cyanides and Isocyanides

Hydrogen cyanide is known to exist as a tautomeric mixture.



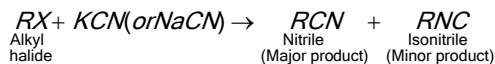
Hence, it forms two types of alkyl derivatives which are known as alkyl cyanides and alkyl isocyanides.



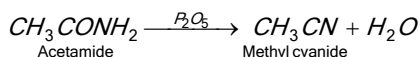
(1) Alkyl Cyanides

(i) Methods of preparation

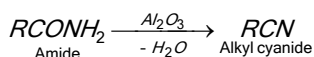
(a) *From alkyl halides* : The disadvantage of this method is that a mixture of nitrile and isonitrile is formed.



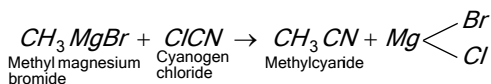
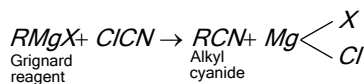
(b) *From acid amides* : $RCONH_2 \xrightarrow[-H_2O]{P_2O_5} RCN$



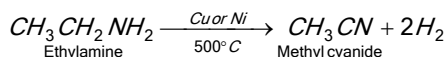
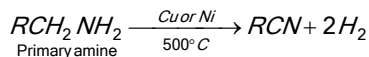
Industrially, alkyl cyanides are prepared by passing a mixture of carboxylic acid and ammonia over alumina at $500^\circ C$.



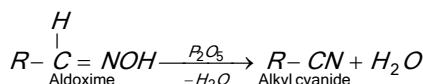
(c) *From Grignard reagent*



(d) *From primary amines* : Primary amines are dehydrogenated at high temperature to form alkyl cyanides. This is also a **commercial method**.



(e) *From oximes* :



(ii) Physical properties

(a) Alkyl cyanides are neutral substance with pleasant odour, similar to bitter almonds.

(b) Lower members containing upto 15 carbon atoms are liquids, while higher members are solids.

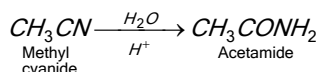
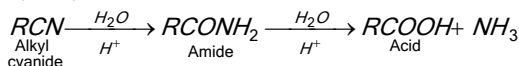
(c) They are soluble in water. The solubility decreases with the increase in number of carbon atoms in the molecule.

(d) They are soluble in organic solvents.

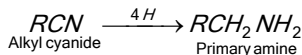
(e) They are poisonous but *less poisonous than HCN*

(iii) Chemical properties

(a) *Hydrolysis*



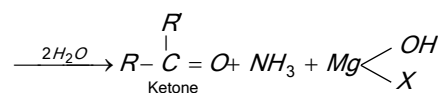
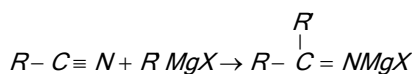
(b) *Reduction* : When reduced with hydrogen in presence of Pt or Ni , or $LiAlH_4$ (Lithium aluminium hydride) or sodium and alcohol, alkyl cyanides yield primary amines.

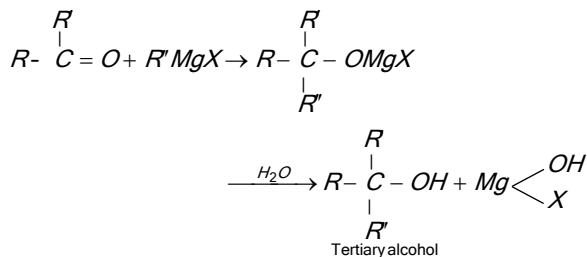


However, when a solution of alkyl cyanides in ether is reduced with stannous chloride and hydrochloric acid and then steam distilled, an aldehyde is formed (**Stephen's reaction**).

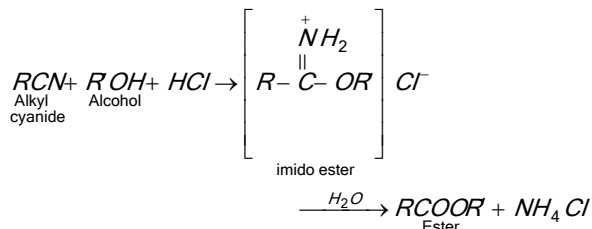


(c) *Reaction with Grignard reagent* : With grignard's reagent, an alkyl cyanide forms a ketone which further reacts to form a tertiary alcohol.





(d) Alcohololysis :

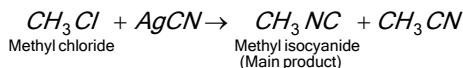
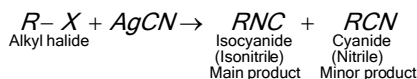


(iv) **Uses** : Alkyl cyanides are important intermediates in the organic synthesis of a large number of compounds like acids, amides, esters, amines etc.

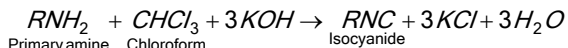
(2) Alkyl Isocyanides

(i) Methods of preparation

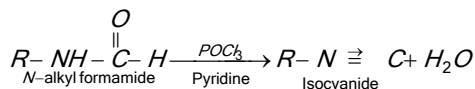
(a) From alkyl halides :



(b) From primary amines (Carbylamine reaction) :



(c) From N-alkyl formamides :



(ii) Physical properties

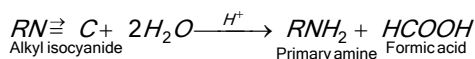
(a) Alkyl isocyanides are colourless, unpleasant smelling liquids.

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

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

(iii) Chemical properties

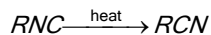
(a) Hydrolysis :



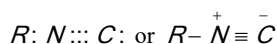
(b) Reduction : $R-\overset{\ominus}{N} \equiv C + 4H \xrightarrow[300^\circ C]{Ni} RNHCH_3$

Alkyl isocyanide secondary amine

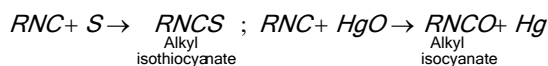
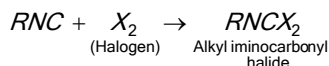
(c) **Action of heat** : When heated for sometime at 250°C, a small amount of isonitrile changes into isomeric nitrile.



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



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



(iv) **Uses** : Due to their unpleasant smell, alkyl isocyanides are used in detection of very minute leakage. Carbylamine reaction is used as a test for the detection of primary amino group.

□ **Methyl isocyanate (MIC) gas** was responsible for Bhopal gas tragedy in Dec. 1984.

□ Cyanides have more polar character than isocyanides. Hence cyanides have high boiling points and are more soluble in water. However, both isomers are more polar than alkylhalides, hence their boiling points are higher than the **corresponding alkyl halides**.

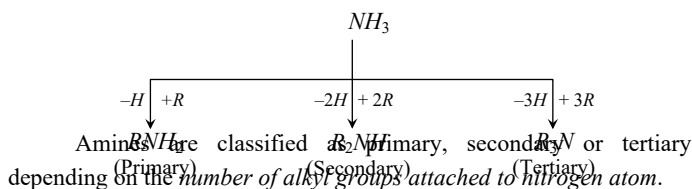
□ Being less polar, isocyanides are not attacked by OH⁻ ions.

Table : 29.2 Comparison of Alkyl Cyanides and Alkyl Isocyanides

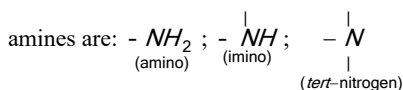
Test	Ethyl cyanide	Ethyl isocyanide
Smell	Strong but pleasant	Extremely unpleasant
Dipole moment	More (≈ 4D)	Less (≈ 3D)
B.P.	98°C (i.e. High)	78°C (i.e. low)
Solubility in water.	Soluble	Insoluble
Hydrolysis with acids	Gives propionic acid (Acid, in general)	Gives ethyl amine (1° amine, in general)
Hydrolysis with alkalis	Same as above	No action
Reduction	Gives propylamine (1° amine, in general)	Gives ethylmethyl amine (2° amine, in general)
Stephen's reaction	Gives propionaldehyde (Aldehyde, in general)	Does not occur
Heating (250°C)	No effect	Ethyl cyanide is formed

Amines

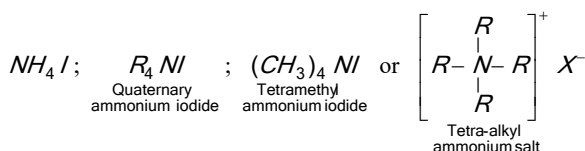
Amines are regarded as **derivatives of ammonia** in which one, two or all three hydrogen atoms are replaced by alkyl or aryl group.



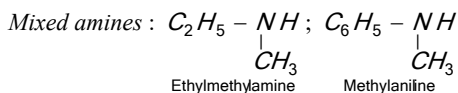
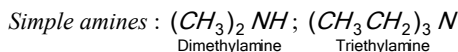
The characteristic groups in primary, secondary and tertiary



In addition to above amines, tetra-alkyl derivatives similar to ammonium salts also exist which are called **quaternary ammonium compounds**.



(1) **Simple and mixed amines** : Secondary and tertiary amines may be classified as **simple** or **mixed** amines according as all the alkyl or aryl groups attached to the nitrogen atom are same or different. For example,

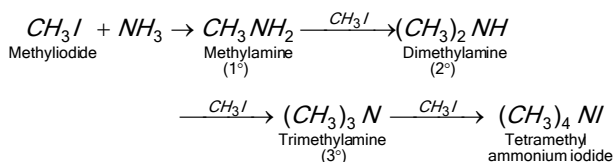


The aliphatic amines have *pyramidal shape* with one electron pair. In amines, N undergoes sp^3 hybridisation.

(2) General methods of preparation

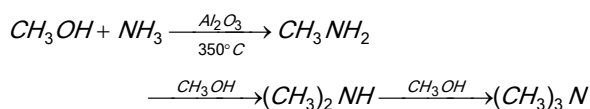
(i) **Methods yielding mixture of amines (Primary, secondary and tertiary)**

(a) **Hofmann's method** : The mixture of amines (1° , 2° and 3°) is formed by the **alkylation of ammonia with alkyl halides**.



The primary amine may be obtained in a good yield by using a large excess of ammonia. The process is also termed as **ammonolysis of alkyl halides**. It is a nucleophilic substitution reaction.

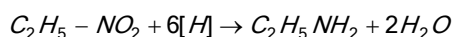
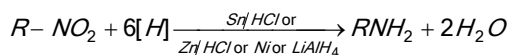
(b) **Ammonolysis of alcohols** :



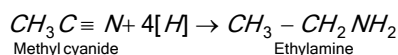
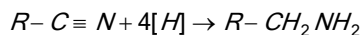
Primary amine may be obtained in a good yield by using a excess of ammonia.

(ii) **Methods yielding primary amines**

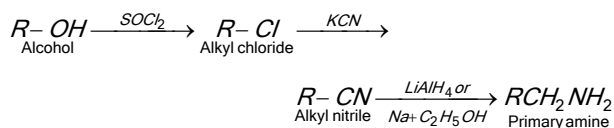
(a) **Reduction of nitro compounds**



(b) **Reduction of nitriles (Mendius reaction)**

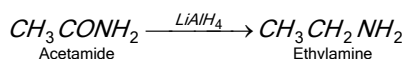
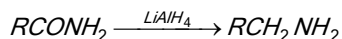


The start can be made from alcohol or alkyl halide.

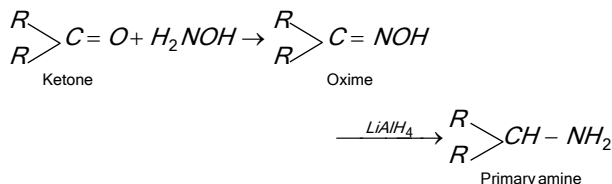
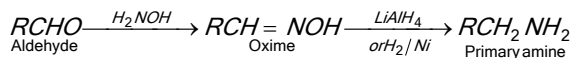


This sequence gives an amine containing one more carbon atom than alcohol.

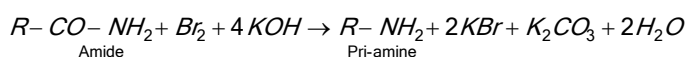
(c) **By reduction of amides with $LiAlH_4$**



(d) **By reduction of oximes** : The start can be made from an aldehyde or ketone.



(e) **Hofmann's bromamide reaction or degradation (Laboratory method)** : By this method the **amide** ($-CONH_2$) group is converted into **primary amino** ($-NH_2$) group.



This is the most convenient method for preparing primary amines.

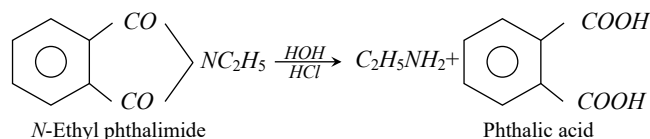
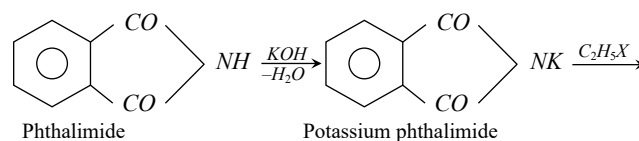
This method gives an **amine containing one carbon atom less than amide**.

(f) **Gabriel phthalimide synthesis** : This method involves the following three steps.

- Phthalimide is reacted with KOH to form potassium phthalimide.

- The potassium salt is treated with an alkyl halide.

- The product N -alkyl phthalimide is put to hydrolysis with hydrochloric acid when primary amine is formed.



When hydrolysis is difficult, the N -alkyl phthalimide can be treated with hydrazine to give the required amine.

