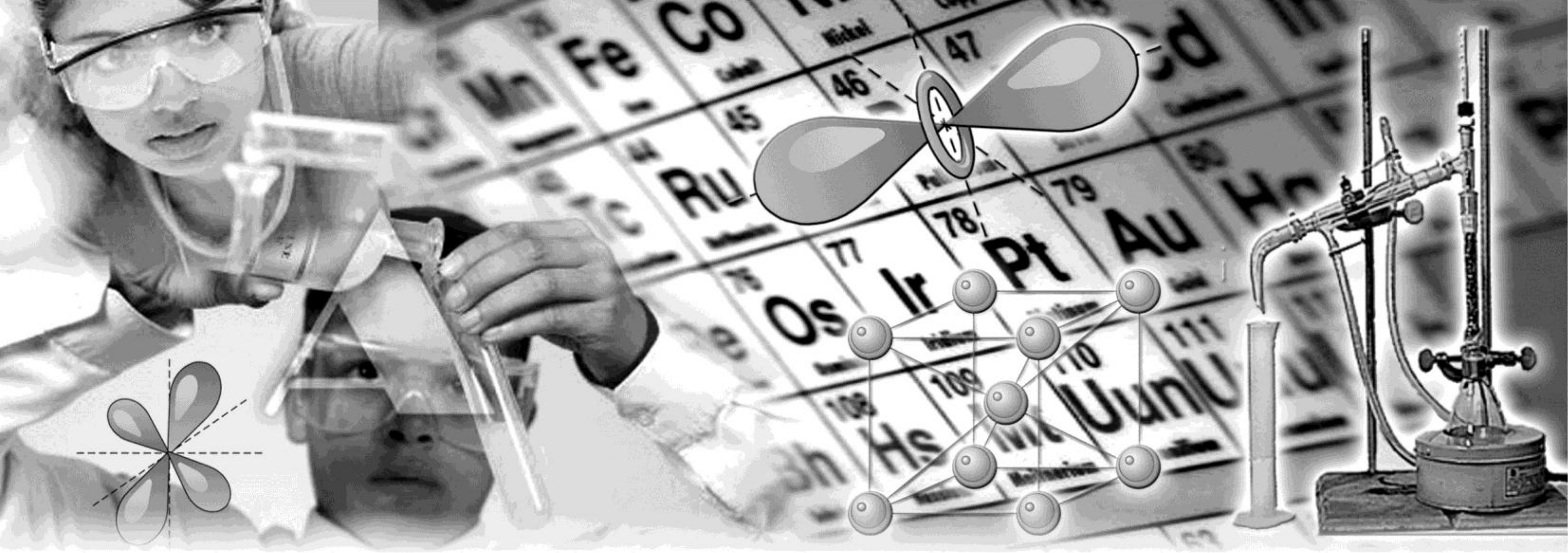


Chapter
29
Nitrogen Containing Compounds

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.

$$\underset{\text{Nitrite form}}{H-O-N=O} \rightleftharpoons \underset{\text{Nitro form}}{H-N\begin{matrix}\nearrow O\\ \searrow O\end{matrix}}$$

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

$$\underset{\text{Alkyl nitrite}}{R-O-N=O}\,;\ \underset{\text{Nitro alkane}}{R-N\begin{matrix}\nearrow O\\ \searrow O\end{matrix}}$$

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 ($0°C$).

$$NaNO_2 + HCl \rightarrow NaCl + HNO_2$$

$$C_2H_5OH + HNO_2 \rightarrow \underset{\text{Ethyl nitrite}}{C_2H_5ONO} + H_2O$$

(b) From Ethyl iodide

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + \underset{\text{Pot. nitrite}}{KONO} \rightarrow \underset{\text{Ethyl nitrite}}{C_2H_5ONO} + KI$$

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

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

(ii) ***Physical properties***

(a) At ordinary temperature it is a gas which can be liquified on cooling to a colourless liquid, *(boiling point 17°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.

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

(b) *Reduction* :

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

Small amount of hydroxylamine is also formed.

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

(iv) ***Uses***

(a) Ethyl nitrite dialates 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.

$$\underset{\text{Primary nitro alkane}}{RCH_2NO_2}\ ;\ \underset{\text{Secondary nitro alkane}}{\begin{matrix}R\\R\end{matrix}\!\!>CHNO_2}\ ;\ \underset{\text{Tertiary nitro alkane}}{\begin{matrix}R\\R\\R\end{matrix}\!\!>C-NO_2}$$

(ii) ***General methods of preparation***

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

$$C_2H_5Br + AgNO_2 \rightarrow C_2H_5NO_2 + AgBr$$

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)

$$CH_3CH_3 + HONO_2(\text{fuming}) \xrightarrow{400°C} CH_3CH_2NO_2 + H_2O$$

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

$$\underset{\alpha-\text{Chloro acetic acid}}{CH_2ClOOH} \xrightarrow[-NaCl]{NaNO_2} \underset{\alpha-\text{Nitro acetic acid}}{CH_2NO_2COOH}$$

$$\xrightarrow{\text{heat}} \underset{\text{Nitro methane}}{CH_3NO_2} + CO_2$$

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

$$\underset{\text{2-Methyl,1-nitro propene}}{CH_3 - \overset{CH_3}{\overset{|}{C}} = CHNO_2} + HOH \xrightarrow{H^+ \text{or} OH^-} \underset{\text{Acetone}}{CH_3 - \overset{CH_3}{\overset{|}{C}} = O} + \underset{\text{Nitro methane}}{CH_3NO_2}$$

(e) Tertiary nitro alkanes are obtained by the oxidation of *t*-alkyl amines with *KMnO*$_4$.

$$R_3CNH_2 \xrightarrow{KMnO_4} R_3CNO_2 + H_2O$$

(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.*

$$\underset{(\textit{nitro}\text{-form})}{CH_3 - \underset{\underset{O}{\downarrow}}{N} = O} \qquad \underset{(\textit{aci}\text{-form})}{CH_2 = \underset{\underset{O}{\downarrow}}{N} - OH}$$

(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.

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

However, when reduced with a neutral reducing agent (***Zinc dust + NH$_4$Cl***), nitro alkanes form ***substituted hydroxylamines.***

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

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

$$RCH_2NO_2 + H_2O \xrightarrow{HCl \text{ or } 80\% H_2SO_4} RCOOH + NH_2OH$$

secondary nitro alkanes on hydrolysis form ketones.

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

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

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

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

$$\underset{\text{Secondary}}{R_2\underset{\underset{NO_2}{|}}{CH}} + HON = O \xrightarrow{-H_2O} \underset{\text{Pseudo nitrol}}{R_2\underset{\underset{NO_2}{|}}{C} - NO} \xrightarrow[NaOH]{\text{Ether or}} \text{Blue colour}$$

Tertiary nitro alkanes do not react with nitrous acid.

(d) *Thermal decomposition* : .

$$R.CH_2.CH_2NO_2 \xrightarrow[\text{moderately}]{>300°C} R.CH = CH_2 + HNO_2$$

On rapid heating nitro alkanes decompose with great violence.

$$CH_3NO_2 \xrightarrow{\text{heat, Rapidly}} \frac{1}{2}N_2 + CO_2 + \frac{3}{2}H_2$$

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

$$CH_3 - NO_2 \xrightarrow[NaOH]{Cl_2} \underset{\text{Chloropicrin or nitro chloroform (insecticide)}}{CCl_3NO_2}$$

$$\underset{\text{2–Nitropropane}}{CH_3 - \overset{CH_3}{\overset{|}{C}}H - NO_2} \xrightarrow{Cl_2 + NaOH} CH_3 - \underset{\underset{Cl}{|}}{\overset{CH_3}{\overset{|}{C}}} - NO_2$$

(f) *Condensation with aldehyde* :

$$CH_3CHO + CH_3NO_2 \rightarrow \underset{\beta\text{-Hydroxy nitropropane (nitro alcohol)}}{CH_3CH(OH)CH_2NO_2}$$

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

$$RCH = \overset{+}{N}\begin{matrix} OH \\ O^- \end{matrix} + CH_3MgI \rightarrow \underset{\text{Methane}}{CH_4} + RCH = \overset{+}{N}\begin{matrix} OMgI \\ O^- \end{matrix}$$

❑ *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 alkalies like aq. NaOH. Therefore, 1° and 2° nitroalkanes dissolve in aq. NaOH to form salts. For examples.*

$$CH_3 - \overset{+}{N}\begin{matrix} O \\ O^- \end{matrix} \xrightarrow{NaOH} Na^+ \underset{\text{I}}{\overset{-}{C}H_2} - \overset{+}{N}\begin{matrix} O \\ O^- \end{matrix} \leftrightarrow H_2C = \overset{+}{N}\begin{matrix} O\overset{-}{N}a \\ O^- \end{matrix}$$

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)	Nitro ethane ($C_2H_5NO_2$)

	(Alkyl nitrite, *RONO*)	(Nitro alkane, *RNO₂*)
Boiling point	Low, 17°*C*	Much higher, 115°*C*
Reduction with metal and acid (*Sn/HCl*) or with *LiAlH₄*	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.e.,* 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. $CH_3-CH=N\begin{smallmatrix}OH\\ \searrow O\end{smallmatrix} \xrightarrow{NaOH} CH_3-CH=N\begin{smallmatrix}ONa\\ \searrow O\end{smallmatrix}$
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.

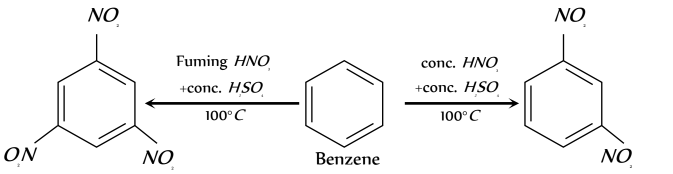
Aromatic Nitro Compounds

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**

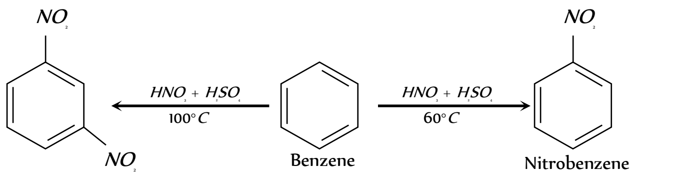
(i) ***Nitration (Direct method)*** : The number of – NO_2 groups introduced in benzene nucleus depends upon the nature and concentration of the nitrating agent, temperature of nitration and nature of the compound to be nitrated.

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



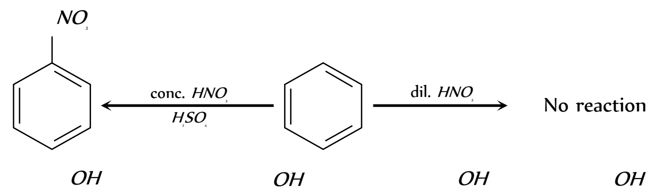
Syn-Trinitro benzene   *m*-Dinitrobenzene

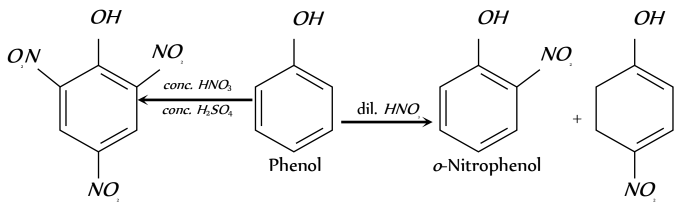
(b) *Temperature of nitration* : For example,



m-Dinitro benzene

(c) *Nature of the compound to be nitrated : Presence of electron-releasing group like –OH, –NH₂, –CH₃, –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.

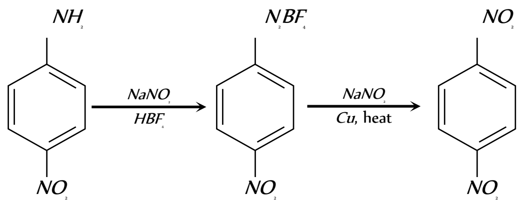




2, 4, 6-Trinitrophenol   *p*-Nitrophenol

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.



p-Nitroaniline   *p*-Dinitroaniline

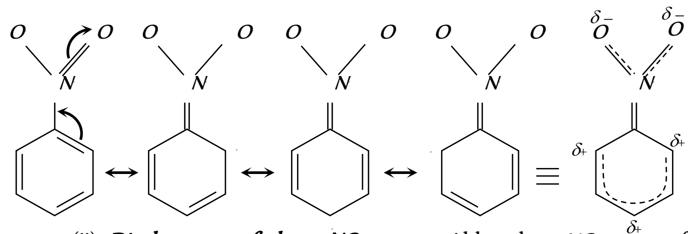
(2) **Physical properties**

(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.*

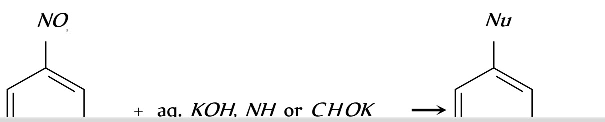
(3) **Chemical properties**

(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 – NO₂ group*** : Although – NO_2 group of nitrobenzene cannot be replaced by other groups, but if another – 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,

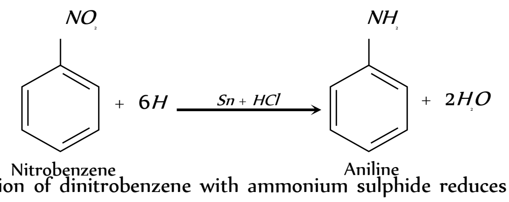


(iii) ***Reduction*** : Aromatic nitro compounds can be reduced to a variety of product as shown below in the case of nitrobenzene.

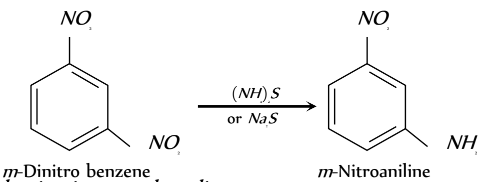
$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \rightarrow \underset{\text{Nitrosobenzene}}{C_6H_5NO} \rightarrow \underset{\text{Phenylhydroxylamine}}{C_6H_5NHOH} \rightarrow \underset{\text{Aniline}}{C_6H_5NH_2}$$

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* :

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 2H \xrightarrow[(-H_2O)]{Zn\ dust\ +NH_4Cl} \underset{\substack{\text{Nitrosobenzene}\\ \text{(intermediate)}}}{C_6H_5NO} \rightarrow \underset{\text{Phenylhydroxylamine}}{C_6H_5NHOH}$$

(c) *Reduction in alkaline medium* :

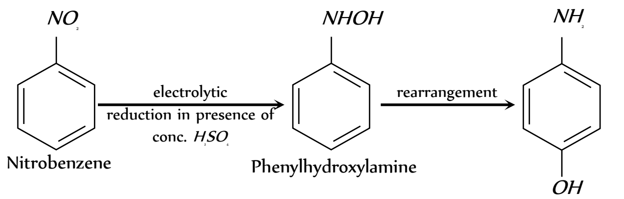
$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow{2[H]} \left[\begin{matrix} \underset{\text{Nitroso benzene}}{C_6H_5NO} \\ \underset{\text{Phenyl hydroxylamine}}{C_6H_5NHOH} \end{matrix}\right] \xrightarrow{-H_2O} \underset{\text{Azoxy benzene}}{\begin{matrix} C_6H_5-N \rightarrow O \\ \| \\ C_6H_5-N \end{matrix}}$$

Azoxybenzene on further reduction yields azobenzene and hydrazobenzene.

$$\underset{\text{Azoxybenzene}}{\begin{matrix} C_6H_5-N \rightarrow O \\ \| \\ C_6H_5-N \end{matrix}} \xrightarrow{2[H]} \underset{\text{Azobenzene}}{\begin{matrix} C_6H_5-N \\ \| \\ C_6H_5-N \end{matrix}} \xrightarrow{2[H]} \underset{\text{Hydrazobenzene}}{\begin{matrix} C_6H_5-NH \\ | \\ C_6H_5-NH \end{matrix}}$$

(d) *Electrolytic reduction* :

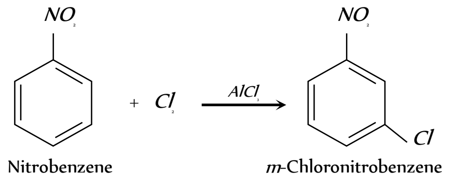
- *Weakly acidic medium* of electrolytic reduction gives **aniline.**
- *Strongly acidic medium* gives phenylhydroxylamine which rearranges to ***p*-aminophenol.**



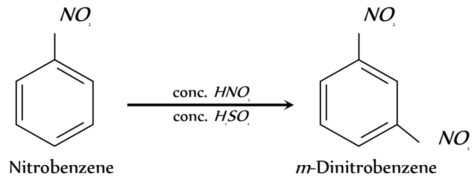
- Alkaline medium of electrolytic reduction gives all the **mono- and di-nuclear reduction products** mentioned above in point (c).

(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.

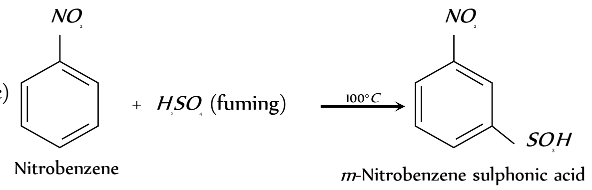
(a)



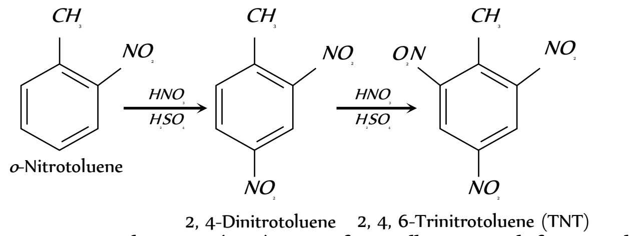
(b)



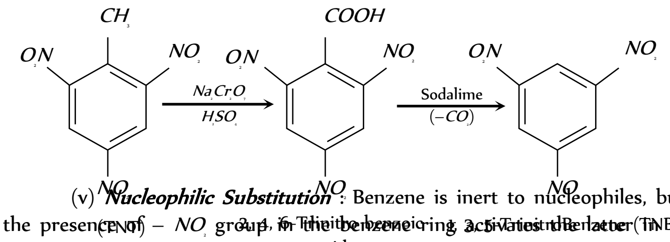
(c)



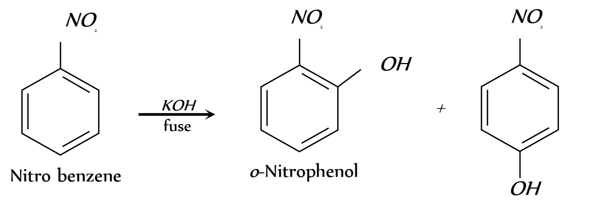
Although nitrobenzene, itself undergoes electrophilic substitution under drastic conditions, nitrobenzene having activating groups like alkyl, $-OR$, $-NH_2$ etc. undergoes these reactions relatively more readily.



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.

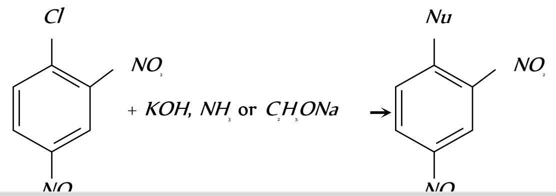


(v) ***Nucleophilic Substitution*** : Benzene is inert to nucleophiles, but the presence of $-NO_2$ group in the benzene ring activates the *o*- and *p*-positions to nucleophiles.



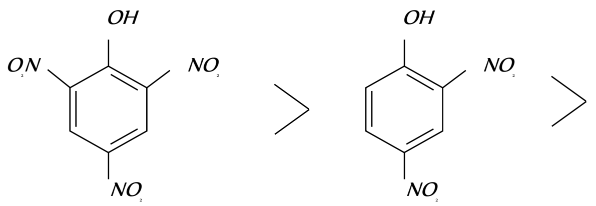
(vi) ***Effect of the*** $-NO_2$ ***group on other nuclear substituents***

(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 $(KOH, NH_3, NaOC_2H_5)$.

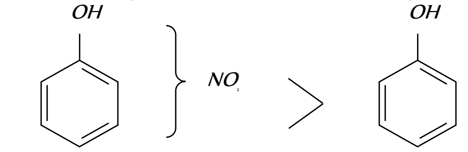


(b) *Effect on phenolic –OH group* : The acidity of the phenolic hydroxyl group is markedly increased by the presence of $-NO_2$ group in *o*- and *p*-position.

The decreasing order of the acidity of nitrophenols follows following order

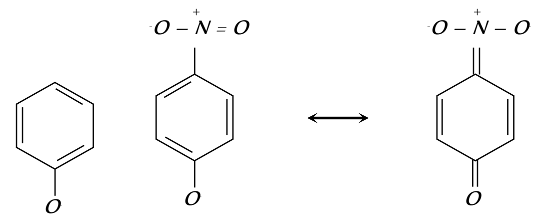


2, 4, 6-Trinitro phenal   2, 4-Dinitrophenol



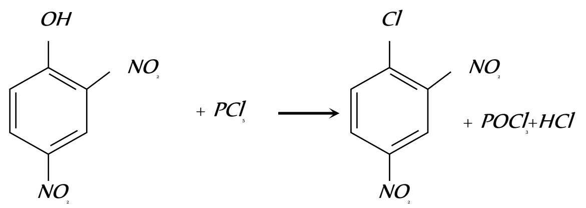
o- and *p*-Nitrophenols   Phenol

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 (no $-NO_2$ group)   Extra stabilisation of *p*-nitrophenate ion due to $-NO_2$ group

Due to increased acidity of nitrophenols, 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.

$$H-C\equiv N \rightleftharpoons H-N \overrightarrow{\leftarrow} C$$

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

$$\underset{\text{AlkylCyanide}}{R-C\equiv N} \qquad \underset{\text{Alkylisocyanide}}{R-N \overrightarrow{\leftarrow} C}$$

(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.

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

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

$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{P_2O_5} \underset{\text{Methyl cyanide}}{CH_3CN} + H_2O$$

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

$$\underset{\text{Acid}}{RCOOH} + NH_3 \rightarrow \underset{\text{Ammonium salt}}{RCOONH_4} \xrightarrow[-H_2O]{Al_2O_3}$$

$$\underset{\text{Amide}}{RCONH_2} \xrightarrow[-H_2O]{Al_2O_3} \underset{\text{Alkylcyanide}}{RCN}$$

(c) *From Grignard reagent*

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

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

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

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

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

(e) *From oximes* :

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

(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*

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

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

$$\xrightarrow[H^+]{H_2O} \underset{\text{Aceticacid}}{CH_3COOH} + NH_3$$

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

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

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

$$R-C\equiv N \xrightarrow[{[2H]}]{SnCl_2/HCl} \underset{\text{Imine hydrochloride}}{RCH=NH.HCl} \xrightarrow{H_2O} \underset{\text{Aldehyde}}{RCHO} + NH_4Cl$$

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

$$R-C\equiv N + R'MgX \rightarrow R-\overset{R'}{\overset{|}{C}}=NMgX$$

$$\xrightarrow{2H_2O} \underset{\text{Ketone}}{R-\overset{R'}{\overset{|}{C}}=O} + NH_3 + Mg\begin{matrix} OH \\ X \end{matrix}$$

$$R-\overset{R'}{\overset{|}{C}}=O + R''MgX \rightarrow R-\underset{R''}{\underset{|}{\overset{R'}{\overset{|}{C}}}}-OMgX$$

$$\xrightarrow{H_2O} \underset{\text{Tertiaryalcohol}}{R-\underset{R''}{\underset{|}{\overset{R'}{\overset{|}{C}}}}-OH} + Mg\begin{matrix} OH \\ X \end{matrix}$$

(d) *Alcoholoysis* :

$$\underset{\text{Alkyl cyanide}}{RCN} + \underset{\text{Alcohol}}{R'OH} + HCl \rightarrow \underset{\text{imido ester}}{\left[R-\overset{\overset{+}{N}H_2}{\overset{||}{C}}-OR'\right]}Cl^-$$

$$\xrightarrow{H_2O} \underset{\text{Ester}}{RCOOR'} + NH_4Cl$$

(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* :

$$\underset{\text{Alkylhalide}}{R-X} + AgCN \rightarrow \underset{\substack{\text{Isocyanide} \\ \text{(Isonitrile)} \\ \text{Main product}}}{RNC} + \underset{\substack{\text{Cyanide} \\ \text{(Nitrile)} \\ \text{Minor product}}}{RCN}$$

$$\underset{\text{Methyl chloride}}{CH_3Cl} + AgCN \rightarrow \underset{\substack{\text{Methyl isocyanide} \\ \text{(Main product)}}}{CH_3NC} + CH_3CN$$

(b) *From primary amines* (*Carbylamine reaction*) :

$$\underset{\text{Primary amine}}{RNH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH \rightarrow \underset{\text{Isocyanide}}{RNC} + 3KCl + 3H_2O$$

(c) *From N-alkyl formamides* :

$$\underset{N-\text{alkylformamide}}{R-NH-\overset{O}{\overset{||}{C}}-H} \xrightarrow[\text{Pyridine}]{POCl_3} \underset{\text{Isocyanide}}{R-N \rightleftarrows C} + H_2O$$

(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* :

$$\underset{\text{Alkylisocyanide}}{RN \rightleftarrows C} + 2H_2O \xrightarrow{H^+} \underset{\text{Primary amine}}{RNH_2} + \underset{\text{Formic acid}}{HCOOH}$$

(b) *Reduction* : $\underset{\text{Alkylisocyanide}}{R-N \rightleftarrows C} + 4H \xrightarrow[300^oC]{Ni} \underset{\text{secondary amine}}{RNHCH_3}$

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

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

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

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

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

$$RNC + \underset{\text{(Halogen)}}{X_2} \rightarrow \underset{\text{Alkyliminocarbonyl halide}}{RNCX_2}$$

$$RNC + S \rightarrow \underset{\text{Alkyl isothiocyanate}}{RNCS} \quad ; \quad RNC + HgO \rightarrow \underset{\text{Alkyl isocyanate}}{RNCO} + Hg$$

(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)	Give ethyl amine (1° amine, in general)
Hydrolysis with alkalies	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.

$$NH_3 \xrightarrow{-H,\ +R} \underset{\text{(Primary)}}{RNH_2};\quad NH_3 \xrightarrow{-2H,\ +2R} \underset{\text{(Secondary)}}{R_2NH};\quad NH_3 \xrightarrow{-3H,\ +3R} \underset{\text{(Tertiary)}}{R_3N}$$

Amines are classified as primary, secondary or tertiary depending on the *number of alkyl groups attached to nitrogen atom.*

The characteristic groups in primary, secondary and tertiary amines are: $\underset{\text{(amino)}}{-NH_2}$; $\underset{\text{(imino)}}{-\overset{|}{N}H}$; $\underset{(tert\text{–nitrogen})}{-\overset{|}{\underset{|}{N}}}$

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

$$NH_4I;\quad \underset{\text{Quaternary ammonium iodide}}{R_4NI};\quad \underset{\text{Tetramethyl ammonium iodide}}{(CH_3)_4NI}\ \text{ or }\ \underset{\text{Tetra-alkyl ammonium salt}}{\left[R-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{N}}-R\right]^+}X^-$$

(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,

Simple amines : $\underset{\text{Dimethylamine}}{(CH_3)_2NH}$; $\underset{\text{Triethylamine}}{(CH_3CH_2)_3N}$

Mixed amines : $\underset{\text{Ethylmethylamine}}{C_2H_5-\underset{\underset{CH_3}{|}}{N}H}$; $\underset{\text{Methylaniline}}{C_6H_5-\underset{\underset{CH_3}{|}}{N}H}$

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

$$\underset{\text{Methyliodide}}{CH_3I} + NH_3 \rightarrow \underset{\substack{\text{Methylamine}\\(1^\circ)}}{CH_3NH_2} \xrightarrow{CH_3I} \underset{\substack{\text{Dimethylamine}\\(2^\circ)}}{(CH_3)_2NH}$$

$$\xrightarrow{CH_3I} \underset{\substack{\text{Trimethylamine}\\(3^\circ)}}{(CH_3)_3N} \xrightarrow{CH_3I} \underset{\substack{\text{Tetramethyl}\\\text{ammonium iodide}}}{(CH_3)_4NI}$$

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* :

$$CH_3OH + NH_3 \xrightarrow[350°C]{Al_2O_3} CH_3NH_2$$

$$\xrightarrow{CH_3OH} (CH_3)_2NH \xrightarrow{CH_3OH} (CH_3)_3N$$

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*

$$R-NO_2 + 6[H] \xrightarrow[Zn/HCl \text{ or } Ni \text{ or } LiAlH_4]{Sn/HCl \text{ or}} RNH_2 + 2H_2O$$

$$C_2H_5-NO_2 + 6[H] \rightarrow C_2H_5NH_2 + 2H_2O$$

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

$$R-C\equiv N + 4[H] \rightarrow R-CH_2NH_2$$

$$\underset{\text{Methyl cyanide}}{CH_3C\equiv N} + 4[H] \rightarrow \underset{\text{Ethylamine}}{CH_3-CH_2NH_2}$$

The start can be made from alcohol or alkyl halide.

$$\underset{\text{Alcohol}}{R-OH} \xrightarrow{SOCl_2} \underset{\text{Alkylchloride}}{R-Cl} \xrightarrow{KCN}$$

$$\underset{\text{Alkylnitrile}}{R-CN} \xrightarrow[Na+C_2H_5OH]{LiAlH_4 or} \underset{\text{Primary amine}}{RCH_2NH_2}$$

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

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

$$RCONH_2 \xrightarrow{LiAlH_4} RCH_2NH_2$$

$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{LiAlH_4} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

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

$$\underset{\text{Aldehyde}}{RCHO} \xrightarrow{H_2NOH} \underset{\text{Oxime}}{RCH=NOH} \xrightarrow[or H_2/Ni]{LiAlH_4} \underset{\text{Primary amine}}{RCH_2NH_2}$$

$$\underset{\text{Ketone}}{\begin{matrix}R\\R\end{matrix}\!\!>C=O} + H_2NOH \rightarrow \underset{\text{Oxime}}{\begin{matrix}R\\R\end{matrix}\!\!>C=NOH}$$

$$\xrightarrow{LiAlH_4} \underset{\text{Primary amine}}{\begin{matrix}R\\R\end{matrix}\!\!>CH-NH_2}$$

(e) *Hofmann's bromamide reaction or degradation (Laboratory method)* : By this method the *amide (–CONH) group is converted into primary amino (– NH) group.*

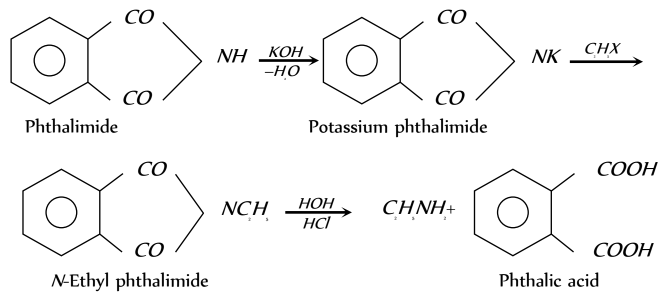
$$\underset{\text{Amide}}{R-CO-NH_2} + Br_2 + 4KOH \rightarrow \underset{\text{Pri-amine}}{R-NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

This is the most convenient method for preparing primary amines.

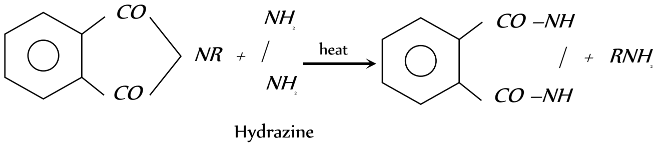
This method gives an ***amine containing one carbon atom less than amide.***

(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.



(g) *By decarboxylation of α-amino acids*

$$R\underset{\underset{NH_2}{|}}{C}HCOOH \xrightarrow[\text{heat}]{Ba(OH)_2} RCH_2NH_2$$

$$\underset{\substack{\alpha\text{-amino aceticacid}\\ \text{(Glycine)}}}{\underset{\underset{NH_2}{|}}{CH_2}-COOH} \xrightarrow[\text{heat}]{Ba(OH)_2} \underset{\text{Methyl amine}}{CH_3NH_2}$$

(h) *By means of a Grignard reagent and chloramine* :

$$RMgX + ClNH_2 \rightarrow RNH_2 + MgXCl$$

(i) *By hydrolysis of Isocyanides or Isocyanates*

$$\underset{\text{Alkylisocyanide}}{R-N \equiv C} + 2H_2O \xrightarrow{(HCl)} \underset{\text{Alkylamine}}{R-NH_2} + HCOOH$$

$$\underset{\text{methyl isonitile}}{CH_3-NC} + 2HOH \xrightarrow{H^+} CH_3-NH_2 + HCOOH$$

$$\underset{\text{Methyl isocyanate}}{CH_3-N=C=O} + 2KOH \rightarrow CH_3-NH_2 + K_2CO_3$$

$$\underset{\text{Alkylisocyanate}}{R-NCO} + 2KOH \rightarrow R-NH_2 + K_2CO_3$$

(j) *By Schmidt reaction* :

$$\underset{\text{Acid}}{R-COOH} + \underset{\substack{\text{Hydrazoic}\\ \text{acid}}}{N_3H} \xrightarrow{Conc.H_2SO_4} \underset{\substack{\text{Alkyl}\\ \text{amine}}}{R-NH_2} + N_2 + CO_2$$

In this reaction the acyl azide ($R-CON_3$) and alkyl isocyanate ($R-NCO$) are formed as an intermediate.

$$R-COOH + N_3H \rightarrow \underset{\text{Acylazide}}{RCON_3} + H_2O$$

$$\underset{\text{Acylazide}}{RCON_3} \rightarrow \underset{\text{Alkylisocyanate}}{R-N=C=O} + N_2$$

$$R-N=C=O + H_2O \rightarrow \underset{\text{Alkylamine}}{R-NH_2} + CO_2$$

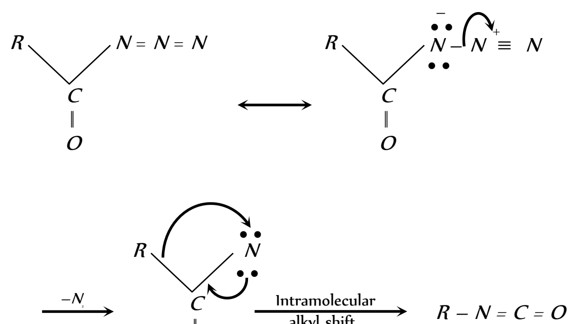
The overall reaction which proceeds by the elimination of nitrogen from acyl azide followed by acidic or alkaline hydrolysis to yield primary amine containing one carbonless, is called ***Curtius Degradation***.

The method uses acid chloride to prepare primary amine through acyl azide.

$$R-\overset{\overset{O}{||}}{C}-OH \xrightarrow{SOCl_2} \underset{\text{Acyl chloride}}{R-\overset{\overset{O}{||}}{C}-Cl} \xrightarrow{NaN_3} \underset{\text{Acylazide}}{R-\overset{\overset{O}{||}}{C}-N_3}$$

$$R-\overset{\overset{O}{||}}{C}-N_3 \xrightarrow{-N_2} R-N=C=O \xrightarrow[\text{heat}]{2NaOH} R-NH_2 + Na_2CO_3$$

The mechanism of **curtius rearrangement** is very similar to Hofmann degradation.



Schmidt reaction converts $R-COOH$ to $R-NH_2$ which is a modification of curtius degradation. In this reaction a carboxylic acid is warmed with sodium azide (NaN_3) and conc. H_2SO_4. The carboxylic acid is directly converted to the primary amine without the necessity of isolating alkyl azide.

$$R-\overset{\overset{O}{||}}{C}-OH \xrightarrow[heat]{NaN_3+H_2SO_4(conc.)} RNH_2 + N_2 + CO_2$$

$$(NaN_3 + H_2SO_4 \rightarrow N_3H + NaHSO_4)$$

(k) *By Ritter reaction* : It is a good method for preparing primary amines having α-tertiary alkyl group.

$$\underset{\text{Tert-butyl alcohol}}{(CH_3)_3C-OH} + H_2SO_4 + HCN \rightarrow \underset{\substack{\text{Tert–butylamine}\\ (1°\text{amine})}}{(CH_3)_3C-NH_2}$$

$$\Big[R_3C-OH \xrightarrow{H^+} H_2O + \underset{\text{Tert-carboniumion}}{R_3C^+} \xrightarrow{HCN} R_3C\overset{+}{N} \equiv CH$$

$$\xrightarrow{H_2O} CHO-R_3CNH \xrightarrow{OH^-} \underset{\text{Pri-amine}}{R_3C-NH_2} + HCOO^-\Big]$$

(l) *Reductive amination of aldehydes and ketones* :

$$\underset{\text{Aldehyde}}{R-\overset{\overset{O}{||}}{C}-H} + NH_3 + H_2 \xrightarrow[300\,atm]{Ni,150°C} \underset{\text{Primary amine}}{R-CH_2-NH_2} + H_2O$$

$$\Big[R-\overset{\overset{H}{|}}{C}=O + H_2HN \xrightarrow{(-H_2O)} [R-\underset{\text{Imine}}{\overset{\overset{H}{|}}{C}}=NH]$$

$$\xrightarrow[Ni]{H_2} RCH_2-NH_2\Big]$$

$$\underset{\text{Ketone}}{R-\overset{\overset{O}{||}}{C}-CH_3} + NH_3 + H_2 \xrightarrow[300\,atm]{Ni,150°C} R-\overset{\overset{CH_3}{|}}{CH}-NH_2$$

This reaction probably takes place through the formation of an imine (Schiff's base).

The primary amine can also be converted into sec. or tert. amines by the following steps

$$R-CHO + R'NH_2 \xrightarrow{H_2/Ni} \underset{\text{Sec. amine}}{RCH_2NHR'}$$

$$RNH_2 + 2H_2C=O + 2HCOOH$$

$$\rightarrow \underset{\text{Tert.-amine}}{RN(CH_3)_2} + 2H_2O + 2CO_2$$

(m) *By reduction of azide with* $NaBH_4$

$$\underset{\substack{\text{Alkylhalide}\\ (1°\text{or}2°)}}{R-X} + \underset{\substack{\text{Sodium}\\ \text{azide}}}{NaN_3} \rightarrow \underset{\substack{\text{Alkyl}\\ \text{azide}}}{RN_3} \xrightarrow[H_2O]{NaBH_4} \underset{1°\text{amine}}{RNH_2}$$

(n) *By Leuckart reaction* : Aldehydes or ketones react with ammonium formate or with formamide to give formyl derivative of primary amine.

$$>C=O + \underset{\text{Amm. formate}}{2HCOONH_4} \rightarrow >CHNH-\overset{\overset{O}{||}}{C}-H$$

$$+2H_2O + CO_2 + NH_3$$

$$>C=O + \underset{\text{Formamide}}{2HCONH_2} \rightarrow >CHNH-\overset{\overset{O}{||}}{C}-H + CO_2 + NH_3$$

These formyl derivatives are readily hydrolysed by acid to yield primary amine.

$$\begin{matrix}R\\R\end{matrix}\!\!>CHNH-\overset{\overset{O}{||}}{C}-H + HOH \xrightarrow{H^+}$$

$$\begin{matrix} R \\ R \end{matrix}\!\!> CHNH_2 + H_2O + CO_2$$

This is called Leuckart reaction, *i.e.,*

$$\underset{\text{Ketone}}{\begin{matrix} R \\ R' \end{matrix}\!\!> C = O} + \underset{\text{Amm. formate}}{HCOONH_4} \xrightarrow[\Delta]{180-200°C} \underset{\text{Primary amine}}{\begin{matrix} R \\ R' \end{matrix}\!\!> CHNH_2} + H_2O + CO_2$$

❑ *On commercial scale, ethylamine is obtained by heating a mixture of ethylene and ammonia at 450°C under 20 atmospheric pressure in presence of cobalt catalyst.*

$$\underset{\text{Ethylene}}{CH_2 = CH_2} + NH_3 \xrightarrow[450°C, 20\,atm]{\text{Cobalt catalyst}} CH_3CH_2NH_2$$

(iii) ***Methods yielding secondary amines***

(a) *Reaction of primary amines with alkyl halides*

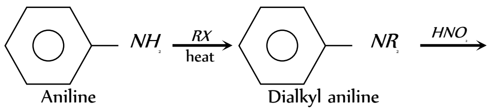
$$R - NH_2 + R - X \xrightarrow{\Delta} R_2NH + HX \rightarrow \underset{\text{dialkylammonium salt}}{R_2\overset{+}{N}H_2\overset{-}{X}}$$

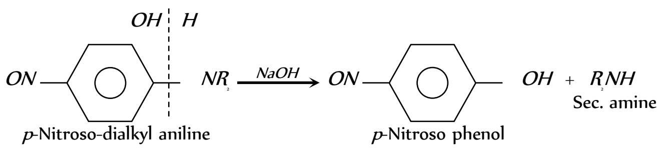
$$R_2\overset{+}{N}H_2\overset{-}{X} + NaOH \rightarrow \underset{\text{Secondary amine}}{R_2NH} + H_2O + NaX$$

(b) *Reduction of isonitriles* : $\underset{\text{Alkylisonitrile}}{R - NC} + 4[H] \xrightarrow{Pt} \underset{\text{Sec. amine}}{RNHCH_3}$

Secondary amine formed by this method always possesses one $-CH_3$ group linked directly to nitrogen.

(c) *Reaction of p-nitroso-dialkyl aniline with strong alkali solution* :





This is one of the best method for preparing pure secondary amines.

(d) *Hydrolysis of dialkyl cyanamide*

$$\left[\underset{\substack{\text{Calcium}\\\text{cyanamide}}}{CaN - CN} \xrightarrow{2NaOH} \underset{\substack{\text{Sodium}\\\text{cyanamide}}}{Na_2N - CN} \xrightarrow{2RX} \underset{\substack{\text{Dialkyl}\\\text{cyanamide}}}{R_2N - CN}\right]$$

$$R_2N - CN + 2HOH \xrightarrow[OH^-]{H^+ or} \underset{\text{Dialkylamine}}{R_2NH} + CO_2 + NH_3$$

(e) *Reduction of N-substituted amides* : Reduction of *N*-substituted amides with $LiAlH_4$ yields secondary amines.

Alkyl β-amino ketones are formed by the action of ketone with formaldehyde and NH_3 (or primary or secondary amines).

The product is referred to as Mannich base and the reaction is called **Mannich Reaction.**

$$CH_3COCH_3 + HCHO + RNH_2 \xrightarrow{heat} CH_3COCH_2CH_2NHR$$

Which can be reduced to alkyl amines.

$$\underset{N\text{-Alkylacid amide}}{R - CONHR'} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{Sec. amine}}{RCH_2NHR'} + H_2O$$

(iv) ***Methods yielding tertiary amines***

(a) *Reaction of alkylhalides with ammonia*

$$3RX + NH_3 \rightarrow R_3N + 3HX \rightarrow \underset{\text{Trialkylammonium salt}}{R_3\overset{+}{N}H\overset{-}{X}}$$

$$R_3\overset{+}{N}H\overset{-}{X} + NaOH \rightarrow R_3N + NaX + H_2O$$

(b) *Reduction of N, N-disubstituted amides* : The carbonyl group is converted into $-CH_2$ group.

$$\underset{\substack{N,N\text{-disubstituted}\\\text{amide}}}{RCONR'_2} \xrightarrow[4[H]]{LiAlH_4} \underset{\text{ter. amine}}{RCH_2NR'_2} + H_2O$$

(c) *Decomposition of tetra-ammonium hydroxides* : The tetra-alkyl ammonium hydroxides are formed when corresponding halides are treated with moist silver oxide.

$$R_4\overset{+}{N}\overset{-}{I} + AgOH \rightarrow R_4\overset{+}{N}O\overset{-}{H} + AgI$$

The hydroxides thus formed on heating decompose into tertiary amines. Tetramethyl ammonium hydroxide gives methyl alcohol as one of the products while all other tetra-alkyl ammonium hydroxides give an olefin and water besides tertiary amines.

$$(CH_3)_4NOH \rightarrow (CH_3)_3N + CH_3OH$$

$$(R)_4NOH \rightarrow (R)_3N + \text{olefin} + H_2O$$

(3) **Separation of mixture of amines :** When the mixture consists of salts of primary, secondary and tertiary amines along with quaternary salt, ***it is first distilled with KOH solution***. The mixture of three amines distils over leaving behind non-volatile quaternary salt.

$$RNH_2.HI \text{ or } RN\overset{+}{H}_3 - \overset{-}{I} + \overset{+}{K}O\overset{-}{H} \rightarrow \underset{\substack{\text{Primary amine}\\\text{(Volatile) Distillate}}}{RNH_2} + KI + H_2O$$

$$R_2NH.HI \text{ or } R_2N\overset{+}{H}_2 - \overset{-}{I} + \overset{+}{K}O\overset{-}{H} \rightarrow R_2NH + KI + H_2O$$

$$R_3N.HI \text{ or } R_3N\overset{+}{H} - \overset{-}{I} + \overset{+}{K}O\overset{-}{H} \rightarrow R_3N + KI + H_2O$$

$R_4\overset{+}{N}\overset{-}{I}$ (non-volatile tetra-alkyl ammonium salt) has no reaction with *KOH*, however remains as residue.

This mixture is separated into primary, secondary and tertiary amines by the application of following methods.

(i) ***Fractional distillation*** : The boiling points of primary, secondary and tertiary amines are quite different, *i.e., the boiling point of $C_2H_5NH_2$ is 17°C, $(C_2H_5)_2NH$ is* 56°C and $(C_2H_5)_3N$ is 95°C and thus, these can be separated by fractional distillation. This method is used satisfactorily in industry.

(ii) ***Hofmann's method*** : The mixture of three amines is treated with diethyl oxalate. The primary amine forms a solid oxamide, a secondary amine gives a liquid oxamic ester while tertiary amine does not react.

$$\underset{\text{Diethyl oxalate}}{\begin{matrix} CO\,OC_2H_5 \\ | \\ CO\,OC_2H_5 \end{matrix}} + \underset{\substack{\text{Primary}\\\text{amine}}}{\begin{matrix} H\,NHR \\ \\ H\,NHR \end{matrix}} \xrightarrow{-2C_2H_5OH} \underset{\substack{\text{Dialkyloxamide}\\\text{(Solid)}}}{\begin{matrix} CONHR \\ | \\ CONHR \end{matrix}}$$

$$\underset{\text{Diethyl oxalate}}{\begin{matrix} COOC_2H_5 \\ | \\ COOC_2H_5 \end{matrix}} + \underset{\substack{\text{Secondary}\\\text{amine}}}{HNR_2} \xrightarrow{-C_2H_5OH} \underset{\substack{\text{Dialkyloxamic ester}\\\text{(liquid)}}}{\begin{matrix} CONR_2 \\ | \\ COOC_2H_5 \end{matrix}}$$

Primary amine is recovered when solid oxamide is heated with caustic potash solution and collected as distillate on distilling the reaction mixture.

$$\begin{array}{l} CO\,\boxed{NHR \quad H}\,OK \\ | \qquad\qquad + \\ CO\,\boxed{NHR \quad H}\,OK \end{array} \rightarrow \begin{array}{l} COOK \\ | \\ \underset{\text{Pot. oxalate}}{COOK} \end{array} + \underset{\substack{\text{Primary amine} \\ \text{(Distillate)}}}{2RNH_2}$$

The liquid (mixture of oxamic ester+ tertiary amine) is subjected to fractional distillation when tertiary amine distils over.

The remaining liquid is distilled with KOH to recover secondary amine.

$$\begin{array}{l} CONR_2 \\ | \\ COOC_2H_5 \end{array} + \begin{array}{l} HOK \\ \\ HOK \end{array} \rightarrow \underset{\substack{\text{Secondary} \\ \text{amine}}}{R_2NH} + \begin{array}{l} COOK \\ | \\ \underset{\text{Pot. oxalate}}{COOK} \end{array} + C_2H_5OH$$

(iii) ***Hinsberg's method*** **:** It involves the treatment of the mixture with benzene sulphonyl chloride, *i.e.,* ***Hinsberg's reagent*** ($C_6H_5SO_2Cl$). The solution is then made alkaline with aqueous alkali to form *sodium or potassium salt of monoalkyl benzene sulphonamide* (soluble in water).

$$C_6H_5SO_2Cl + \underset{\substack{\text{Primary} \\ \text{amine}}}{HNHR} \rightarrow \underset{\substack{N\text{-Alkyl benzene} \\ \text{sulphonamide}}}{C_6H_5SO_2NHR}$$

$$\xrightarrow{NaOH} \underset{\text{Soluble salt}}{C_6H_5SO_2N(Na)R}$$

The secondary amine forms *N,N*-dialkyl benzene sulphonamide which does not form any salt with $NaOH$ and remains as insoluble in alkali solution.

$$C_6H_5SO_2Cl + \underset{\text{Sec. amine}}{HNR_2} \rightarrow C_6H_5SO_2NR_2$$

$$\xrightarrow{NaOH} \underset{\substack{\text{(Insoluble in water,} \\ \text{soluble in ether)}}}{\text{No reaction}}$$

Tertiary amine does not react.

The above alkaline mixture of the amines is extracted with ether.

Two distinct layers are formed. Lower layer, the aqueous layer consists of sodium salt of *N*-alkyl benzene sulphonamide (primary amine) and upper layer, the ether layer consists of *N,N*-dialkyl benzene sulphonamide (secondary amine) and tertiary amine.

Two layers are separated. The upper layer is fractionally distilled. One fraction obtained is tertiary amine and the other fraction is treated with concentrated HCl to recover secondary amine hydrochloride which gives free secondary amine on distillation with $NaOH$.

$$C_6H_5SO_2NR_2 + HCl + H_2O \rightarrow C_6H_5SO_2.OH + R_2NH.HCl$$

$$R_2NH.HCl + NaOH \rightarrow \underset{\text{Sec. amine}}{R_2NH} + NaCl + H_2O$$

The aqueous layer is acidified and hydrolysed with dilute HCl. The hydrochloride formed is then distilled with $NaOH$ when primary amine distils over.

$$C_6H_5SO_2N(Na)R + HCl \rightarrow \underset{\substack{\text{Sulphonamide of} \\ \text{primary amine}}}{C_6H_5SO_2NHR} + NaCl$$

$$C_6H_5SO_2NHR + HCl + H_2O \rightarrow C_6H_5SO_2.OH + \underset{\substack{\text{Primary amine} \\ \text{hydrochloride}}}{RNH_2.HCl}$$

$$RNH_2.HCl + NaOH \rightarrow RNH_2 + NaCl + H_2O$$

(4) **Physical properties**

(i) Lower amines are gases or low boiling point liquids and possess a ***characteristic ammonia like smell (fishy odour).*** Higher members are solids.

(ii) *The boiling points rise gradually with increase of molecular mass.* Amines are polar compounds like NH_3 and have comparatively higher boiling points than non-polar compounds of similar molecular masses. This is due to the presence of ***intermolecular hydrogen bonding.***

$$\begin{array}{ccccc} & H & & H & & H \\ & | & & | & & | \\ H - & N:---H- & & N:---H- & & N:--- \\ & | & & | & & | \\ & R & & R & & R \end{array}$$

Hydrogen bonding in amines

(iii) Amines are soluble in water. This is due to hydrogen bonding between amine and water molecules. Amines are also soluble in benzene and ether.

$$\begin{array}{l} \qquad\qquad\quad H \qquad\qquad\qquad\quad H \\ \qquad\qquad\quad | \qquad\qquad\qquad\quad\; | \\ H - \ddot{O}:---H-N:---H-\ddot{O}:---H-N:--- \\ \quad\;\; | \qquad\qquad\quad | \qquad\qquad\; | \qquad\qquad\; | \\ \quad\; H \qquad\qquad\; R \qquad\qquad H \qquad\qquad R \end{array}$$

Hydrogen bonding between amine and water molecules

Solubility decreases with increase of molecular mass.

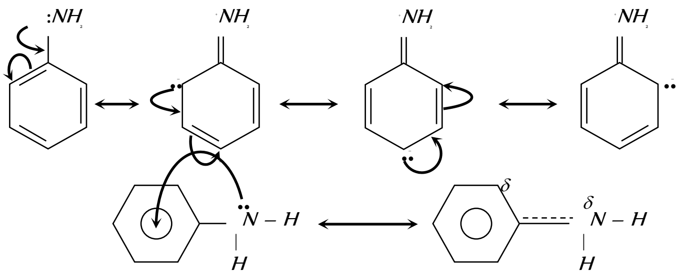
(5) **Chemical properties :** The main reactions of amines are due to the presence of a lone pair of electrons on nitrogen atom. Amines are **electrophilic reagents** as the lone pair of electrons can be donated to electron seeking reagents, (*i.e.*, electrophiles).

Except the amines containing tertiary butyl group, all *lower aliphatic amines are stronger bases than ammonia because of + I (inductive) effect.* The alkyl groups, which are electron releasing groups, increase the electron density around the nitrogen thereby increasing the availability of the lone pair of electrons to proton or Lewis acids and making the amine more basic (larger K_b). Thus, it is expected that the basic nature of amines should be in the order tertiary > secondary > primary, but the *observed order in the case of lower members is found to be as* ***secondary > primary > tertiary.*** This anomalous behaviour of tertiary amines is ***due to steric factors,*** *i.e.,* crowding of alkyl groups cover nitrogen atom from all sides and thus makes the approach and bonding by a proton relatively difficult which results the maximum steric strain in tertiary amines. The electrons are there but the path is blocked, resulting the reduced in its basicity.

(i) The order of basic nature of various amines has been found ***to vary with nature of alkyl groups.***

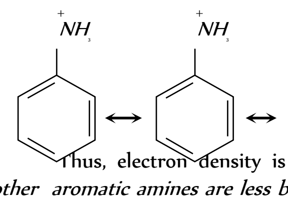
Alkyl group	**Relative strength**
CH_3-	$R_2NH > RNH_2 > R_3N > NH_3$
C_2H_5-	$R_2NH > RNH_2 > NH_3 > R_3N$
$(CH_3)_2CH-$	$RNH_2 > NH_3 > R_2NH > R_3N$
$(CH_3)_3C-$	$NH_3 > RNH_2 > R_2NH > R_3N$

(ii) ***Basic nature of aromatic amines*** **:** In aniline or other aromatic amines, the lone pair present on nitrogen atom *is delocalized with benzene ring by resonance.*



Resonance hybrid

But anilinium ion is less resonance stabilized than aniline.



No other resonating structure possible

Thus, electron density is less on N atom due to which *aniline or other aromatic amines are less basic than aliphatic amines.*

However, any group which when present on benzene ring has electron withdrawing effect (– NO_2, – CN, – SO_3H, – COOH – Cl, C_6H_5, etc.) decreases basicity of aniline (Nitroaniline is less basic than aniline as nitro group is electron withdrawing group (– *I* group) and aniline is more basic than diphenyl amine), *while a group which has electron repelling effect (– NH_2, – OR, R –, etc.) increases basicity of aniline.* Toluidine is more basic than aniline as – CH_3 group is electron repelling group (+ *I* group).

Further *greater the value of K_b or lower the value of pK_b, stronger will be the base.* The basic character of some amines have the following order,

$$R_2NH > RNH_2 > C_6H_5CH_2NH_2 > NH_3 > C_6H_5NH_2$$

N-alkylated anilines are stronger bases than aniline because of steric effect. Ethyl group being bigger than methyl has more steric effect, so *N*-ethyl aniline is stronger base than *N*-methyl aniline. Thus, basic character is,

$$C_6H_5N(C_2H_5)_2 > C_6H_5NHC_2H_5 > C_6H_5N(CH_3)_2$$
$$> C_6H_5NHCH_3 > C_6H_5NH_2NH_3 > C_6H_5NHC_2H_5$$
$$> C_6H_5NHCH_3 > C_6H_5NH_2 > C_6H_5NHC_6H_5$$

In Toluidines –*p*-isomer > *m*- > *o*-

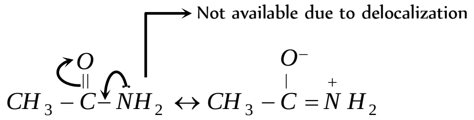
Chloroanilines–*p*-isomer>*m*-> *o*-

Phenylene diamines –*p*-isomer > *m*- > *o*-

Nitroanilines–*m*-isomer > *p*- > *o*-

❑ *Aniline is less basic than ammonia. The phenyl group exerts –I (inductive) effect, i.e., it withdraws electrons. This results to the lower availability of electrons on nitrogen for protonation.*

❑ *Ethylamine and acetamide both contain an amino group but acetamide does not show basic nature. This is because lone pair of electrons on nitrogen is delocalised by resonance with the carbonyl group which makes it less available for protonation.*



❑ *The compounds with least 's' character (sp^3-hybridized) is most basic and with more 's' character (sp-hybridized) is least basic. Examples in decreasing order of basicity are,*

$$CH_3\ddot{N}H_2 \underset{(sp^3)}{} > CH_3-\ddot{N}=CHCH_3 \underset{(sp^2)}{} > CH_3-C\equiv\ddot{N} \underset{(sp)}{}$$

$$CH_3CH_2CH_2NH_2 > H_2C=CHCH_2NH_2 > HC\equiv CCH_2NH_2$$

$$(CH_3)_2NH > CH_3NH_2 > NH_3 > C_6H_5NH_2$$

❑ *Electron withdrawing (C_6H_5 –) groups decrease electron density on nitrogen atom and thereby decreasing basicity.*

$$(CH_3)_2NH > CH_3NH_2 > C_6H_5NHCH_3 > C_6H_5NH_2$$

$$CH_3CH_2NH_2 > HO(CH_2)_3NH_2 > HO(CH_2)_2NH_2$$

❑ *Electron withdrawing inductive effect of the –OH group decreases the electron density on nitrogen. This effect diminishes with distance from the amino group.*

$$CH_3CH_2NH_2 > C_6H_5CONH_2 > CH_3CONH_2$$

(iii) ***Salt formation*** : Amines being basic in nature, combine with mineral acids to form salts.

$$R-NH_2 + HCl \rightarrow \underset{\text{Alkylammonium chloride}}{R\overset{+}{N}H_3\overline{C}l}$$

$$2R-NH_2 + H_2SO_4 \rightarrow \underset{\text{Alkylammonium sulphate}}{(R\overset{+}{N}H_3)_2SO_4^-}$$

(iv) ***Nature of aqueous solution*** : Solutions of amines are alkaline in nature.

$$RNH_2 + HOH \rightleftharpoons R\overset{+}{N}H_3OH^- \rightleftharpoons [RNH_3]^+ + OH^-$$

$$R_2NH + HOH \rightleftharpoons R_2\overset{+}{N}H_2OH^- \rightleftharpoons [R_2NH_2]^+ + OH^-$$

$$R_3N + HOH \rightleftharpoons R_3\overset{+}{N}HOH^- \rightleftharpoons [R_3NH]^+ + OH^-$$

The aqueous solutions of amines behaves like NH_4OH and give ferric hydroxide precipitate with ferric chloride and blue solution with copper sulphate.

$$3RNH_3OH + FeCl_3 \rightarrow Fe(OH)_3 + 3RNH_3Cl$$

(v) ***Reaction with alkyl halides (Alkylation)***

$$\underset{\text{Pri.amine}}{RNH_2} \xrightarrow[-HX]{R'X} \underset{\text{Sec.amine}}{RNHR'} \xrightarrow[-HX]{R'X} \underset{\text{Tert.amine}}{R-NR'_2} \xrightarrow{R'X} \underset{\text{Quaternary salt}}{(R-\overset{+}{N}R'_3)X^-}$$

(vi) ***Reaction with acetyl chloride (Acylation)***

$$\underset{\text{Pri. amine}}{RNH_2} + ClOCCH_3 \xrightarrow{-HCl} \underset{N\text{-Alkylacetamide}}{RNHOCCH_3}$$

$$\underset{\text{Sec. amine}}{R_2NH} + ClOCCH_3 \xrightarrow{-HCl} \underset{N,N\text{-Dialkylacetamide}}{R_2NOCCH_3}$$

Tertiary amines do not react since they do not have replaceable hydrogen on nitrogen.

Therefore, all these above reactions are used to distinguish between $1^o, 2^o$ and 3^o -amines.

(vii) ***Action of sodium***

$$\underset{1^o\text{ amine}}{2RNH_2} + 2Na \xrightarrow{\Delta} \underset{\text{Sod. salt}}{2[RNH]^- Na^+} + H_2\uparrow$$

$$\underset{2^o\text{ amine}}{2R_2NH} + 2Na \xrightarrow{\Delta} \underset{\text{Sod.salt}}{2[R_2N]^- Na^+} + H_2\uparrow$$

(viii) ***Action of halogens***

$$\underset{\text{Alkylamine}}{RNH_2} \xrightarrow[NaOH]{X_2} RNHX \xrightarrow[NaOH]{X_2} \underset{\text{Dihalo-alkyl amine}}{RNX_2}$$

$$\underset{\text{Dialkylamine}}{R_2NH} \xrightarrow[NaOH]{X_2} \underset{\text{Halo-dialkyl amine}}{R_2NX}$$

(ix) ***Reaction with Grignard reagent***

$$RNH_2 + Mg\begin{cases}CH_3\\ I\end{cases} \rightarrow CH_4 + RNH-Mg-I$$

$$R_2NH + CH_3-Mg-I \rightarrow CH_4 + R_2N-Mg-I$$

(x) ***Carbylamine reaction*** : This reaction is shown by only ***primary amines.*** This is a test of primary amines and is used to distinguish primary amines from secondary and tertiary amines.

$$RNH_2 + CHCl_3 + \underset{\text{(Alc.)}}{3KOH} \rightarrow \underset{\substack{\text{Alkylisocyanide}\\ \text{(carbyl amine)}}}{RNC} + 3KCl + 3H_2O$$

Isocyanides are bad smelling compounds and can be easily detected.

(xi) ***Reaction with nitrous acid***

(a) Primary amines form alcohols with nitrous acid ($NaNO_2$+ HCl). Nitrogen is eliminated.

$$\underset{\text{Pri. amine}}{RNH_2} + HONO \rightarrow \underset{\text{Alcohol}}{ROH} + N_2 + H_2O$$

Methyl amine is an exception to this reaction, *i.e.,*

$$CH_3NH_2 + 2HONO \rightarrow \underset{\text{Methyl nitrite}}{CH_3-O-N=O} + N_2 + 2H_2O$$

$$2CH_3NH_2 + 2HONO \rightarrow \underset{\text{Dimethyl ether}}{CH_3-O-CH_3} + 2N_2 + 3H_2O$$

(b) Secondary amines form nitrosoamines which are water insoluble yellow oily liquids.

$$\underset{\text{Sec. amine}}{R_2NH} + HONO \rightarrow \underset{\text{Dialkyl nitrosoamine}}{R_2NNO} + H_2O$$

Nitrosoamine on warming with phenol and conc. H_2SO_4 give a brown or red colour which soon changes to blue green. The colour changes to red on dilution and further changes to blue or violet with alkali. This colour change is referred to **Liebermann's nitroso reaction** and is used for the test of secondary amines.

(c) Tertiary amines react nitrous acid to form nitrite salts which are soluble in water. These salts on heating give alcohols and nitrosoamines.

$$\underset{\text{Tert.amine}}{R_3N} + HONO \rightarrow \underset{\text{Trialkylammoniumnitrite}}{[R_3NH]^+NO_2^-} \xrightarrow{heat} \underset{\text{Alcohol}}{R-OH} + \underset{\text{Nitrosoamine}}{R_2N\!-\!N=O}$$

This reaction (nitrous acid test) is used to make distinction between primary, secondary and tertiary amines.

(xii) ***Reaction with carbon di sulphide*** **:** This **Hofmann's mustard oil reaction** is used as a **test for primary amines.**

$$\underset{1^\circ}{RNH_2} \xrightarrow[\text{heat}]{S=C=S} \underset{\text{Alkyldithiocarbamic acid}}{S=C\begin{matrix} NHR \\ SH \end{matrix}} \xrightarrow{HgCl_2} \underset{\substack{\text{Alkylisothiocyanate} \\ \text{(Mustard oil smell)}}}{RNC=S} + \underset{\text{Black ppt.}}{HgS} + 2HCl$$

$$\underset{2^\circ}{R_2NH} \xrightarrow{S=C=S} \underset{\text{Dialkyldithiocarbamic acid}}{S=C\begin{matrix} NR_2 \\ SH \end{matrix}} \xrightarrow{HgCl_2} \text{No reaction}$$

(xiii) ***Oxidation*** **:** All the three types of amines undergo oxidation. The product depends upon the nature of oxidising agent, class of amine and the nature of the alkyl group.

(a) *Oxidation of primary amines*

$$\underset{\text{Pri. amine}}{RCH_2NH_2} \xrightarrow[KMnO_4]{[O]} \underset{\text{Aldimine}}{RCH=NH} \xrightarrow{H_2O} \underset{\text{Aldehyde}}{RCHO} + NH_3$$

$$R_2CHNH_2 \xrightarrow[KMnO_4]{[O]} \underset{\text{Ketimine}}{R_2C=NH} \xrightarrow{H_2O} \underset{\text{Ketone}}{R_2CO} + NH_3$$

(b) *Oxidation of secondary amines*

$$\underset{\text{Sec. amine}}{R_2NH} \xrightarrow[KMnO_4]{[O]} \underset{\text{Tetra-alkylhydrazine}}{R_2N-NR_2} \; ; \; R_2NH \xrightarrow[H_2SO_5]{[O]} \underset{\text{Dialkylhydroxylamine}}{R_2NOH}$$

(c) *Oxidation of tertiary amines* : Tertiary amines are not oxidised by potassium permanganate but are oxidised by Caro's acid or Fenton's reagent to amine oxides.

$$\underset{\text{Tert.amine}}{R_3N} + [O] \rightarrow \underset{\text{Amine oxide}}{[R_3N \rightarrow O]}$$

(xiv) ***Reaction with other electrophilic reagents***

$$\underset{\text{Pri. amine}}{RNH_2} + \underset{\text{Aldehyde}}{O=CHR'} \rightarrow \underset{\text{Schiff's base}}{RN=CH\,R'}$$

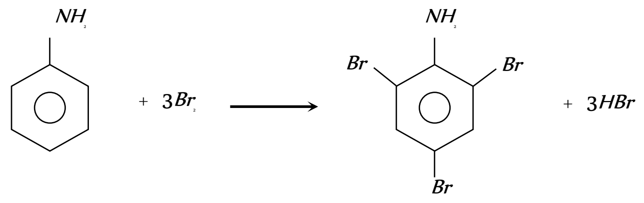
$$2RNH_2 + \underset{\substack{\text{Carbonyl} \\ \text{chloride}}}{Cl-\overset{\overset{O}{||}}{C}-Cl} \rightarrow \underset{\substack{\text{Dialkylurea} \\ \text{(Symmetrical)}}}{RNH-\overset{\overset{O}{||}}{C}-NHR} + 2HCl$$

$$RNHH + \underset{\text{Isocyanate}}{O=C=N-R'} \rightarrow \underset{\substack{\text{Dialkylurea} \\ \text{(Unsymmetrical)}}}{RNH-\overset{\overset{O}{||}}{C}-HNR'}$$

$$RNHH + \underset{\text{Isothiocyanate}}{S=C=N-R'} \rightarrow \underset{\text{Dialkyl thiourea}}{RNH-\overset{\overset{S}{||}}{C}-NHR'}$$

(xv) ***Ring substitution in aromatic amines*** **:** Aniline is more reactive than benzene. The *presence of amino group activates the aromatic ring and directs the incoming group preferably to ortho and para positions.*

(a) *Halogenation*

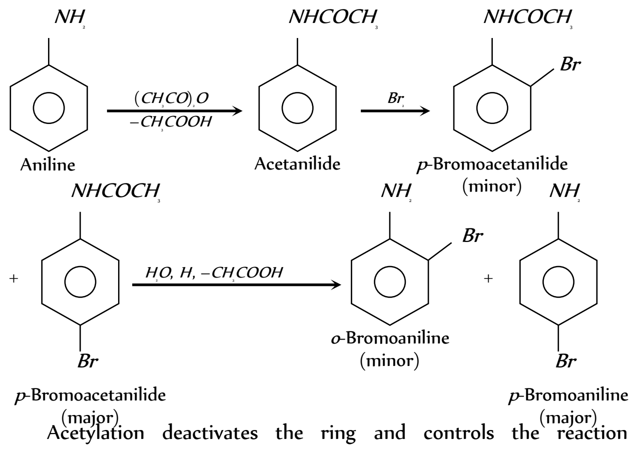


2, 4, 6-Tri Bromoaniline (white ppt.)

This reaction is used as a test for aniline.

However, if monosubstituted derivative is desired, aniline is first acetylated with acetic anhydride and then halogenation is carried out. After halogenation, the acetyl group is removed by hydrolysis and only monosubstituted halogen derivative is obtained.

It may be noted that $-NH_2$ group directs the attacking group at *o-* and *p*-positions and therefore, both *o-* and *p*-derivatives are obtained.

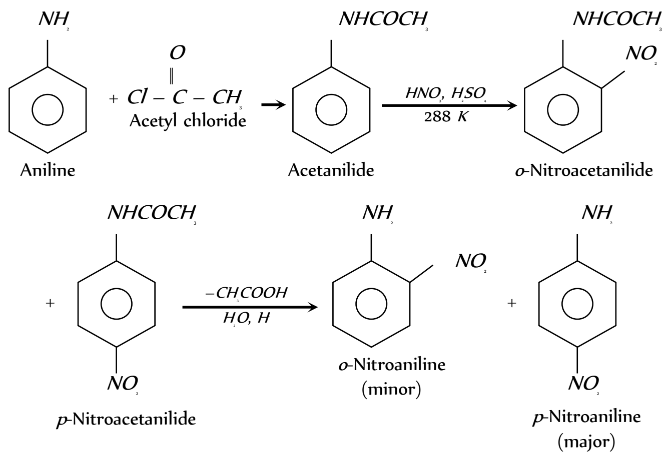


Acetylation deactivates the ring and controls the reaction to monosubstitution stage only because *acetyl group is electron withdrawing group and therefore, the electron pair of N-atom is withdrawn towards the carbonyl group.*

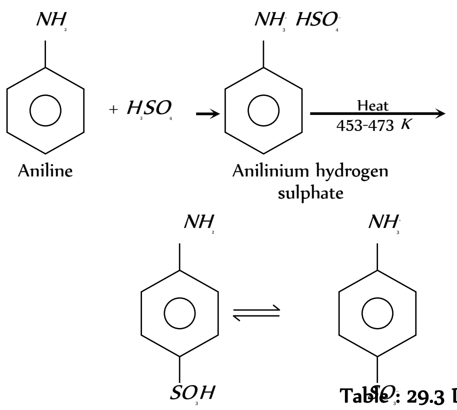
(b) *Nitration* : Aromatic amines cannot be nitrated directly because they are readily oxidized. This is because, HNO_3 is a strong *oxidising agent and results in partial oxidation of the ring to form a black mass.*

Therefore, to solve this problem, nitration is carried out by *protecting the $-NH_2$ group by acetylation. The acetylation deactivates the ring and therefore, controls the reaction.*

The hydrolysis of nitroacetanilides removes the protecting acyl group and gives back amines.



(c) *Sulphonation*



Sulphanilic acid (I) Zwitter ion structure (II)

The sulphanilic acid exists as a dipolar ion (structure II) which has acidic and basic groups in the same molecule. Such ions are called ***Zwitter ions or inner salts.***

(6) **Uses**

(i) Ethylamine is used in solvent extraction processes in ***petroleum refining*** and as a **stabiliser** for ***rubber latex.***

(ii) The quaternary ammonium salts derived from long chain aliphatic tertiary amines are widely used as detergents.

(iii) Aliphatic amines of low molecular mass are used as solvents.

Table : 29.3 Distinction between primary, secondary and tertiary amines

Test	Primary amine	Secondary amine	Tertiary amine
Action of $CHCl_3$ and alcoholic KOH. (Carbylamine test)	Bad smelling carbylamine (Isocyanide) is formed.	No action.	No action.
Action of CS_2 and $HgCl_2$ (Mustard oil test)	Alkyl isothiocyanate is formed which has pungent smell like mustard oil.	No action.	No action
Action of nitrous acid.	Alcohol is formed with evolution of nitrogen.	Forms nitrosoamine which gives green colour with phenol and conc. H_2SO_4 (Liebermann's test).	Forms nitrite in cold which on heating gives nitrosoa- mine which responds to Liebermann's test.
Action of acetyl chloride.	Acetyl derivative is formed.	Acetyl derivative is formed.	No action.
Action of Hinsberg's reagent.	Monoalkyl sulphonamide is formed which is soluble in KOH.	Dialkyl sulphonamide is formed which is insoluble in KOH.	No action.
Action of methyl iodide.	3 molecules (moles) of CH_3I to form quaternary salt with one mole of primary amine.	2 moles of CH_3I to form quaternary salt with one mole of secondary amine.	One mole of CH_3I to form quaternary salt with one mole of tertiary amine.

❑ *Aniline does not form alcohol with nitrous acid but it forms benzene diazonium chloride which* ***shows dye test.***

Aniline

Aniline was first prepared by ***Unverdorben (1826) by dry distillation of indigo.*** In the laboratory, it can be prepared by the reduction of nitrobenzene with tin and hydrochloric acid.

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 6H \xrightarrow{Sn, HCl} \underset{\text{Aniline}}{C_6H_5NH_2} + 2H_2O$$

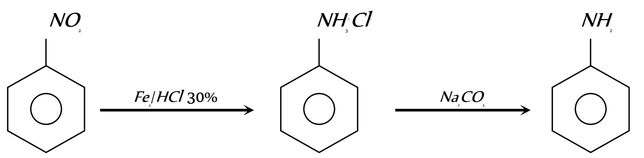
Aniline produced combines with $H_2SnCl_6 (SnCl_4 + 2HCl)$ to form a double salt.

$$2C_6H_5NH_2 + SnCl_4 + 2HCl \rightarrow \underset{\text{Double salt}}{(C_6H_5NH_3)_2\, SnCl_6}$$

From double salt, aniline is obtained by treating with conc. caustic soda solution.

$$(C_6H_5NH_3)_2SnCl_6 + 8NaOH \rightarrow 2C_6H_5NH_2$$
$$+ 6NaCl + Na_2SnO_3 + 5H_2O$$

On a commercial scale, aniline is obtained by reducing nitrobenzene with iron filings and hydrochloric acid.



Aniline is also obtained on a large scale by the action of amine on chlorobenzene at 200°*C* under 300-400 *atm* pressure in presence of cuprous catalyst.

$$2C_6H_5Cl + 2NH_3 + Cu_2O \xrightarrow[300-400\ atm]{200°C} 2C_6H_5NH_2 + Cu_2Cl_2 + H_2O$$

Properties Aniline when freshly prepared is a ***colourless oily liquid (b.p. 184°C).*** It has a characteristic unpleasant odour and is not poisonous in nature. It is heavier than water and is only slightly soluble. It is soluble in alcohol, ether and benzene. Its colour changes to dark brown on standing.

It shows all the characteristic reactions discussed earlier.

Uses : (1) It is used in the preparation of diazonium compounds which are used in dye industry.

(2) Anils (Schiff's bases from aniline) are used as antioxidants in rubber industry.

(3) It is used for the manufacture of its some derivatives such as acetamide, sulphanilic acid and sulpha drugs, etc.

(4) It is used as an accelerator in vulcanizing rubber.

Some important conversions

(1) **Conversion of methylamine to ethylamine (Ascent)**

$$\underset{\text{Methylamine}}{CH_3NH_2} \xrightarrow{HNO_2} \underset{\text{Methyl alcohol}}{CH_3OH} \xrightarrow{PI_3} \underset{\text{Methyl iodide}}{CH_3I}$$
$$\xrightarrow{NaCN} \underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow{LiAlH_4} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

(2) **Conversion of ethylamine to methylamine (Descent)**

$$\underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow{HNO_2} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

$$\xrightarrow{[O]} \underset{\text{Aceticacid}}{CH_3COOH} \xrightarrow{SOCl_2} \underset{\text{Acetylchloride}}{CH_3COCl}$$

$$\xrightarrow{NH_3} \underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[KOH]{Br_2} \underset{\text{Methylamine}}{CH_3NH_2}$$

(3) **Conversion of ethylamine to acetone**

$$\underset{\text{Ethylamine}}{C_2H_5NH_2} \xrightarrow{HNO_2} \underset{\text{Ethylalcohol}}{C_2H_5OH} \xrightarrow[H_2SO_4]{K_2Cr_2O_7}$$

$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Aceticacid}}{CH_3COOH} \xrightarrow{Ca(OH)_2} \underset{\text{Calciumacetate}}{(CH_3COO)_2Ca}$$

$$\xrightarrow{heat} \underset{\text{Acetone}}{CH_3COCH_3}$$

(4) **Conversion of propionic acid to**

(i) Ethylamine, (ii) *n*-Butylamine.

(i) $\underset{\text{Propionic aicd}}{CH_3CH_2COOH} \xrightarrow{SOCl_2} \underset{\text{Propionyl chloride}}{CH_3CH_2COCl} \xrightarrow{NH_3}$

$$\underset{\text{Propionamide}}{CH_3CH_2CONH_2} \xrightarrow[KOH]{Br_2} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

or $C_2H_5COOH \xrightarrow[H_2SO_4(conc.)]{N_3H} C_2H_5NH_2$

(ii) $\underset{\text{Propionic acid}}{CH_3CH_2COOH} \xrightarrow[Ether]{LiAlH_4} \underset{n\text{-Propyl alcohol}}{CH_3CH_2CH_2OH} \xrightarrow{PBr_5}$

$$\underset{\text{Propyl bromide}}{CH_3CH_2CH_2Br} \xrightarrow{KCN} \underset{\text{Propyl cyanide}}{CH_3CH_2CH_2CN}$$

$$\xrightarrow[\text{or } LiAlH_4]{Na+C_2H_5OH} \underset{n\text{-Butylamine}}{CH_3CH_2CH_2CH_2NH_2}$$

(5) **Conversion of ethylene to 1,4-diaminobutane**

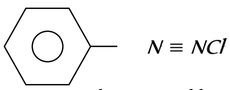
$$\underset{\text{Ethylene}}{CH_2=CH_2} \xrightarrow[CCl_4]{Br_2} \underset{\text{Ethylene bromide}}{CH_2Br.CH_2Br} \xrightarrow{NaCN}$$

$$\underset{\text{Ethylenecyanide}}{NCCH_2CH_2CN} \xrightarrow{LiAlH_4} \underset{\text{1,4-Diaminobutane}}{NH_2CH_2CH_2CH_2CH_2NH_2}$$

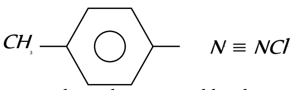
Diazonium salts

The diazonium salts have the general formula $ArN_2^+X^-$, where X may be an anion like *Cl, Br* etc. and the group $N_2^+(-N\equiv N^+)$ is called diazonium ion group.

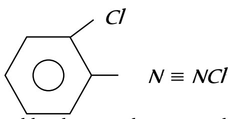
(1) **Nomenclature :** The diazonium salts are named by adding the word diazonium to the name of the parent aromatic compound to which they are related followed by the name of the anion. For example,



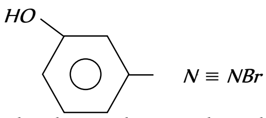
Benzenediazonium chloride



p-Toluenediazonium chloride

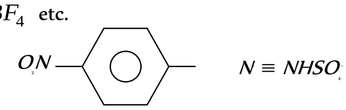


o-chlorobenzenediazonium chloride



m-Hydroxybenzenediazonium bromide

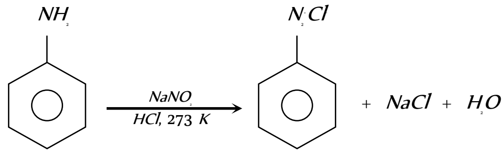
The diazonium salt may contain other anions also such as NO_3^-, HSO_4^-, BF_4 etc.



p-Nitrobenzenediazonium hydrogen sulphate

(2) **Preparation of diazonium salts :**

$$NaNO_2 + HCl \rightarrow NaCl + HONO$$



Aniline Benzene diazonium chloride

The reaction of converting aromatic primary amine to diazonium salt is called **diazotisation.**

(3) **Physical properties of diazonium salts**

(i) Diazonium salts are generally colourless, crystalline solids.

(ii) These are readily soluble in water but less soluble in alcohol.

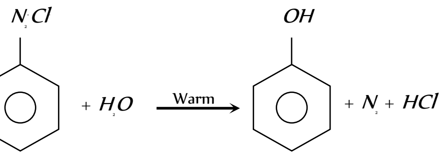
(iii) They are unstable and explode in dry state. Therefore, they are generally used in solution state.

(iv) Their aqueous solutions are neutral to litmus and conduct electricity due to the presence of ions.

(4) **Chemical properties of diazonium salts**

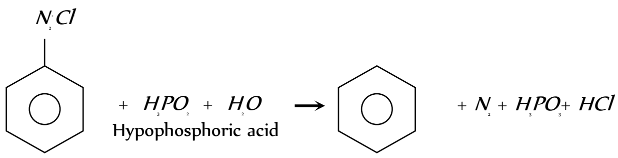
(i) ***Substitution reaction* :** In substitution or replacement reactions, nitrogen of diazonium salts is lost as N_2 and different groups are introduced in its place.

(a) *Replacement by –OH group*



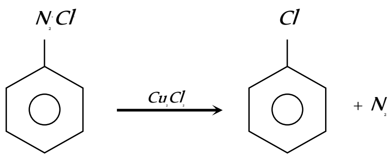
Benzene diazonium chloride Phenol

(b) *Replacement by hydrogen*



Benzene diazonium chloride Benzene

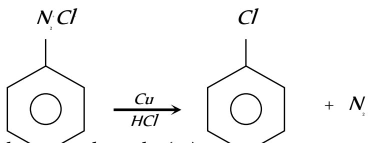
(c) *Replacement by–Cl group*



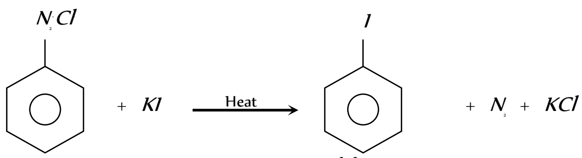
Chlorobenzene

This reaction is called ***Sandmeyer reaction.***

When the diazonium salt solution is warmed with copper powder and the corresponding halogen acid, the respective halogen is introduced. The reaction is a modified form of Sandmeyer reaction and is known as ***Gattermann reaction.***

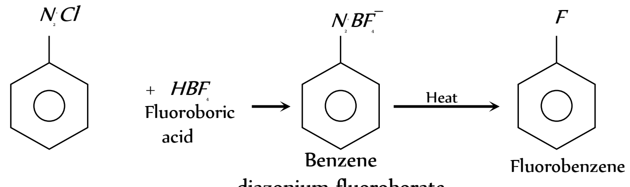


(d) *Replacement by iodo (–I) group*



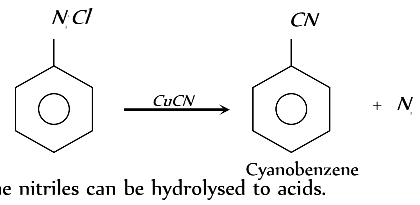
Iodobenzene

(e) *Replacement by – F group*

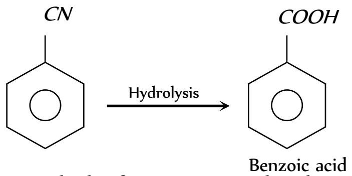


This reaction is called **Balz Schiemann reaction.**

(f) *Replacement by Cyano (– CN) group*

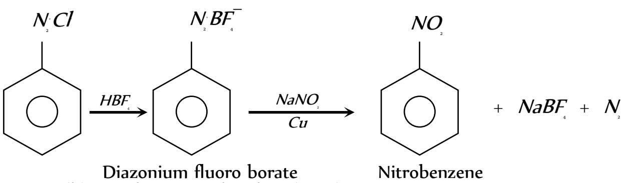


The nitriles can be hydrolysed to acids.

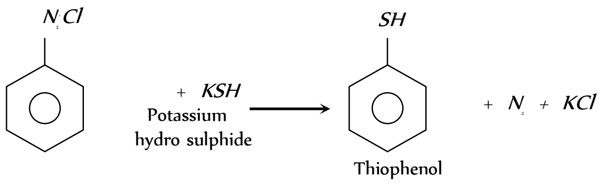


This method of preparing carboxylic acids is more useful than carbonation of Grignard reagents.

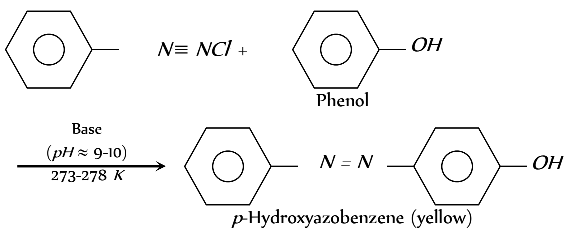
(g) *Replacement by – NO_2 group*

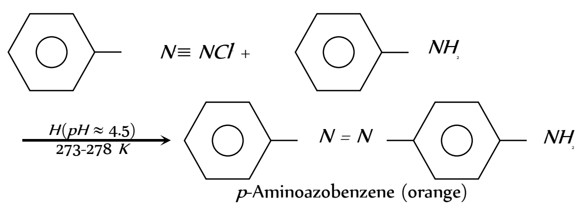


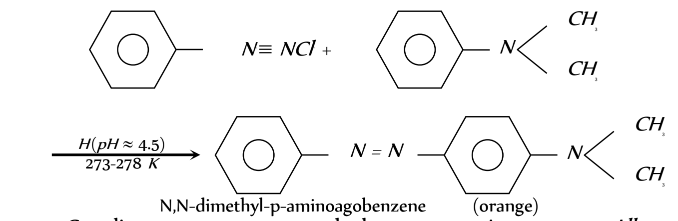
(h) *Replacement by thio (–SH) group*



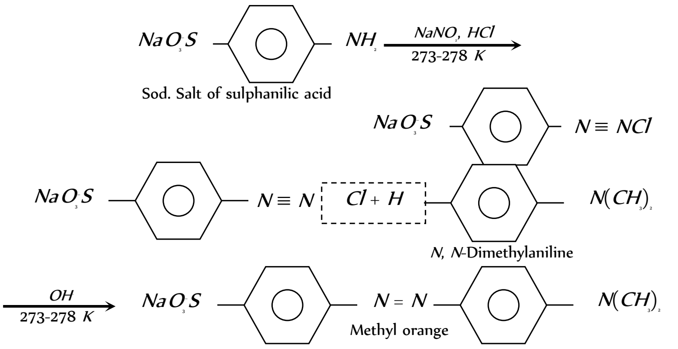
(ii) ***Coupling reactions*** **:** The diazonium ion acts as an electrophile because there is positive charge on terminal nitrogen. It can react with nucleophilic aromatic compounds (*Ar–H*) activated by electron donating groups (– *OH* and – NH_2), which as strong nucleophiles react with aromatic diazonium salts. Therefore, benzene diazonium chloride couples with electron rich aromatic compounds like phenols and anilines to give azo compounds. The azo compounds contain $-N=N-$ bond and the reaction is called **coupling reaction.**



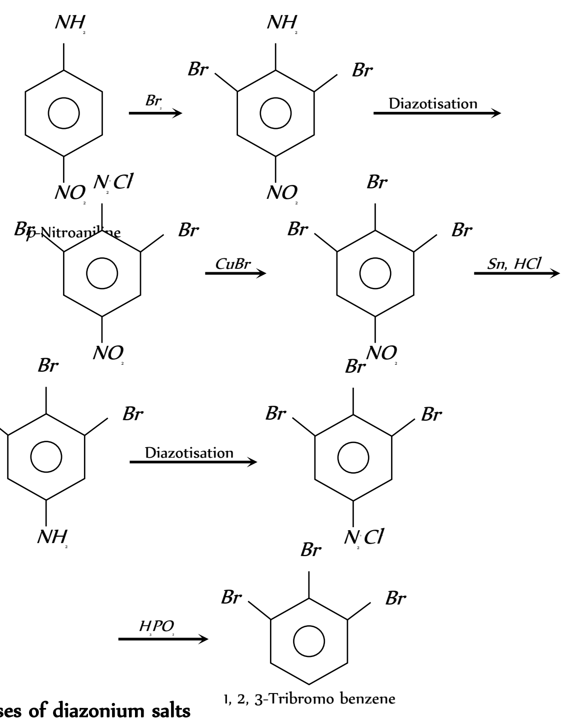




Coupling occurs para to hydroxy or amino group. *All azo compounds are strongly coloured and are used as dyes.* Methyl orange is an important dye obtained by coupling the diazonium salt of sulphanilic acid with *N, N*-dimethylaniline.



❑ *Diazonium salts are highly **useful intermediates** in the synthesis of large variety of aromatic compounds. These can be used to prepare many classes of organic compounds especially aryl halides in pure state. For example,. 1, 2, 3-tribromo benzene is not formed in the pure state by direct bromination of benzene. However, it can be prepared by the following sequence of reaction starting from p-nitroaniline through the formation of diazonium salts as :*



(5) **Uses of diazonium salts**

(i) For the manufacture of azo dyes.

(ii) For the industrial preparation of important organic compounds like *m*-bromotoluene, *m*-bromophenol, etc.

(iii) For the preparation of a variety of useful halogen substituted arenes.

Tips & Tricks

- Alkyl nitrites are the esters of nitrous acid.

- Nitroparaffins are used as solvents for oils, fats, resins, esters, rubbers and cellulose etc. nitromethane is used as high power fuel in racing automobiles.

- Nitrobenzene is good solvent in friedel crafts reaction because it dissolves $AlCl_3$

- All amines have basic properties. The basic property, that is, the tendency of primary, secondary and tertiary amines to bind a proton, is due to the unshared pair of electrons on the nitrogen. When a proton is bound, positive ion is formed and originally electrically neutral amine takes on the charge of the proton. When ions are formed in this way, they are called onium ions. The ion formed in case of amines are substituted ammonium ions. The hydronium ion, H_3O is also the onium ion, which belongs to the class of oxonium ions.

- Some derivatives of ammonia arranged in order of deecreasing basicity are $(CH_3)_4NOH$, $(CH_3)_2NH$, CH_3NH_2, $(CH_3)_3N$, NH_3, $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5NH_2$, $(C_6H_5)_2NH$, CH_3CONH_2.

- In water the basicity follows the order : Primary < Tertiary < Secondary amine, with reference to hydronium ion, H_3O. In this case solvation factor and steric effect alter, to some extent, the order of basicity because of inductive effect alone.

- In a non-polar solvent such as benzene, using trichloroacetic acid as the reference acid, the basicity follows the order Tertiary < Secondary < Primary amines. The solvation factor is absent but steric effect upsets the inductive effect of alkyl groups.

- Carylamine test is specific for primary amines.