Unit

6

Organic Compounds Containing Nitrogen

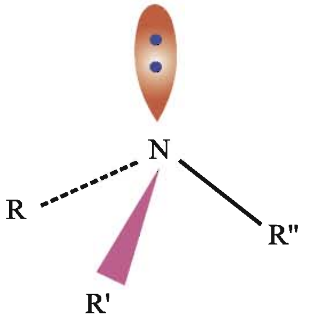
6.1 Introduction

In organic compounds the important functional groups containing nitrogen are amino, cyano or nitrile, isocyanide and nitro groups. If amino group is attached with carbon then an amino compound, is formed if cyano or nitrile group is attached then cyanide or nitrile compounds, the isocyanides group is attached then isocyanide compounds and if nitro group is attached then nitro compounds are made. In this unit, we shall study amine compounds, cyanide (nitrile) compounds, isocyanide compounds and nitro compounds.

6.2 Amines (Structure of Amine Compounds)

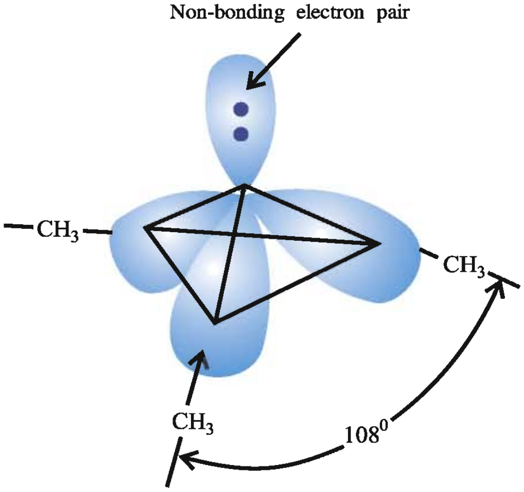
As the hydrogen present in water is replaced by hydrocarbon group, alcohol, phenol and ether are formed, similarly if hydrogen present in ammonia is replaced by hydrocarbon group then amine is formed. So, the structures of amine compounds are similar to structure of ammonia. **In the amine class of compounds, mainly carbon, hydrogen and nitrogen elements are present. One, two or all the three hydrogen atoms present in ammonia are displaced by alkyl or aryl groups.**

Like ammonia, in amine compounds, nitrogen atom is trivalent and possesses one nonbonding electron pair. Therefore the atomic orbital of nitrogen atom in amine compounds possess sp^3 hybridisation and the compounds possess pyramidal structure. Each sp^3 hybrid orbit of nitrogen gets overlapped with atomic orbital of carbon and forms amine compounds. The fourth orbital of nitrogen possesses nonbonding electron pair. Because of the presence of non-bonding electron pairs, C–N–R (where R is H or C) bond angle decreases slightly from 109^0 28'. As shown in the fig 6.1 the bond angle in trimethyl amine is 108^0.



Electronic structure of amines

N–R, N–R' and N–R" σ–bond
N sp^3 hybridisation
any R–N–R angle ≈ 109.5^0



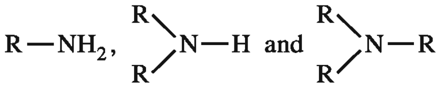
Pyramidal shape of tertiary amine

Fig. 6.1

6.3 Classification of Amine Compounds

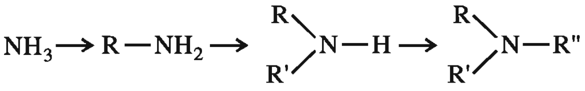
The classification of amine compounds is made on the basis of alkyl or aryl groups combined with nitrogen of amino group. If alkyl group is attached it is called alkyl amine and if aryl group is attached it is called aryl amine.

On replacement of hydrogen present in ammonia, if one alkyl or aryl group is attached with nitrogen, it is called primary (1^0) amine, if two groups are attached then secondary (2^0) and if three groups are joined, then tertiary (3^0) amine. The general formula of compounds in amino class is shown as :



$$R-NH_2,\ \ R_2N-H\ \text{and}\ R_2N-R$$

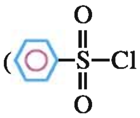
where R = alkyl or aryl group. If all the alkyl or aryl groups in amine compounds are same they are called simple amines and if different groups are there then, they are called mixed amines. Alkyl amines are called aliphatic amines and aryl amines are called aromatic amines.



$$NH_3 \longrightarrow R-NH_2 \longrightarrow RR'N-H \longrightarrow RR'N-R''$$

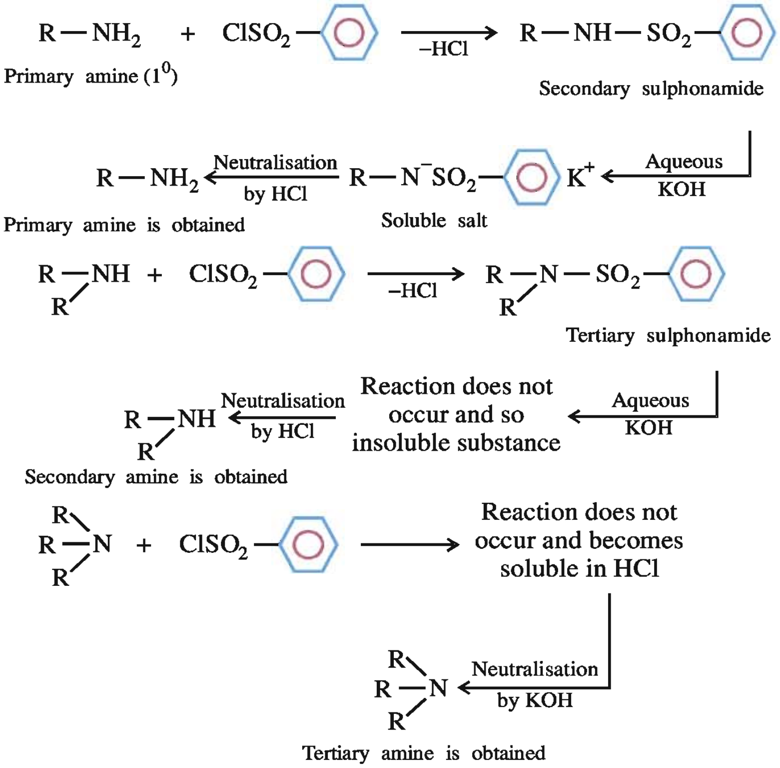
Primary (1^0) Secondary (2^0) Tertiary (3^0)

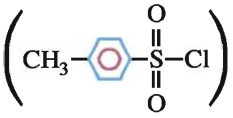
Separation of primary, secondary and tertiary amines : The separation of alkyl or aryl mixture of primary, secondary and tertiary amine can be carried out by the use of Hinsberg's reagent.

Benzene sulphonylchloride ( $C_6H_5-SO_2-Cl$ or $C_6H_5SO_2Cl$) is called Hinsberg's reagent.

In the mixture of primary, secondary and tertiary alkyl (aliphatic) and aryl (aromatic) amines, if benzene sulphonylchloride is added, then by the chemical reaction of primary, and secondary amine, secondary sulphonamide and tertiary sulphonamide are formed respectively; while tertiary amine does not react. To this mixture when dilute hydrochloric acid (HCl) is added the unreacted tertiary amine becomes soluble and the secondary sulphonamide and tertiary sulphonamide being insoluble in acid are obtained as residue by filtration. By neutralization of filtrate, tertiary amine is separated.

In the residue of secondary and tertiary sulphonamide, aqueous solution of potassium hydroxide (KOH) is added so that secondary sulphonamide becomes soluble. This reaction mixture is filtered and by neutralisation of the filtrate with acid, primary amine and secondary amine from residue gets separated by neutralisation.



Presently paratoluene sulphonylchloride  $\left(CH_3-C_6H_4-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-Cl\right)$ **is used of instead benzene sulphonylchloride.**

6.4 Nomenclature of Amine Compounds (IUPAC and Common)

For nomenclature of primary alkyl amine, after the alkyl group 'amine' word is placed viz. methylamine, ethylamine etc.

For common nomenclature of secondary alkyl amine, if two alkyl groups attached to nitrogen are the same then the prefix 'di' is placed before alkyl group followed by 'amine' viz dimethylamine, diethylamine etc. If the two alkyl groups attached to nitrogen are different then, the alkyl groups are arranged in the English alphabetical order and the word 'amine' is placed in the end. viz. ethylmethylamine, methylpropylamine etc.

For common nomenclature of tertiary amine if the three alkyl groups attached to nitrogen are same then the word tri is placed as the prefix before alkyl group and then the word 'amine' is placed in the end. Viz. trimethylamine, triethylamine etc. If two alkyl groups from the attached three alkyl groups are common, then the prefix di is placed before the two common alkyl groups and then the name of third alkyl group is attached and at the end the word 'amine' is placed viz. ethyldimethylamine, diethylmethylamine. If all the three alkyl groups attached to nitrogen are different then the alkyl groups are arranged in the English alphabetical order and then in the end word 'amine' is placed viz. ethylmethylpropylamine, butylethylmethylamine.

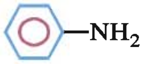
Amine compounds having more than one amine group according to the number of amino groups prefix di, tri, tetra etc. are attached. viz. $H_2N–CH_2–CH_2–NH_2$ is ethylenediamine, $H_2N–CH_2–CH(NH_2)–CH_2–NH_2$ is propylenetriamine.

IUPAC names :

(i) For IUPAC nomenclature of primary amine, the longest carbon chain of original hydrocarbon is determined and then 'e' is removed from the name of hydrocarbon and suffix amine is applied viz. methan + amine = Methanamine, ethan + amine = ethanamine, benzen + amine = benzenamine.

$CH_3–NH_2$ Methanamine

$CH_3\text{-}CH_2\text{-}NH_2$ Ethanamine

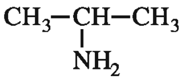


or $C_6H_5 \cdot NH_2$ Benzenamine

It is necessary to note here that the common name of benzenamine is aniline. It is also accepted as IUPAC name.

(ii) If there are more than two carbon in primary alkylamine then in the longest carbon chain at original hydrocarbon, the position of amino group showing lowest number, suffix amine is shown earlier to it. viz. propan-1-amine, propan-2-amine.

$CH_3–CH_2–CH_2–NH_2$ Propan-1-amine



$CH_3-\underset{\substack{| \\ NH_2}}{CH}-CH_3$ Propan-2-amine

(iii) For amine compounds having more than one carbon, in the number of amino group if it is two, three... etc. then di, tri, ... etc. are written as prefix before the 'amine' group, respectively **Here, the last letter 'e' is not removed** e.g.,

$H_2N–CH_2–CH_2–NH_2$ Ethane-1,2-diamine

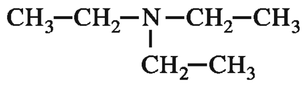
$H_2N–CH_2–CH(NH_2)–CH_2–NH_2$ Propane-1,2,3-triamine

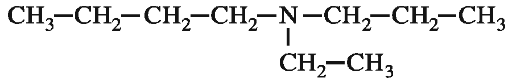
$H_2N-(CH_2)_6-NH_2$ Hexane-1,6-diamine

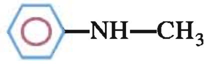

Benzene-1,4-diamine

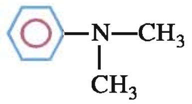
(iv) For the names of secondary and tertiary amines, the names are written according to rules (i), (ii) and (iii). Here symbol N is used to show the position of displacers of hydrogen in amine group e.g.

$CH_3-NH-CH_2-CH_3$ N-Methylethanamine


$CH_3-CH_2-\underset{\underset{\displaystyle CH_2-CH_3}{|}}{N}-CH_2-CH_3$ N, N-Diethylethanamine

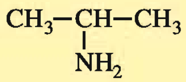

$CH_3-CH_2-CH_2-CH_2-\underset{\underset{\displaystyle CH_2-CH_3}{|}}{N}-CH_2-CH_2-CH_3$ N-Ethyl-N-propylbutanamine

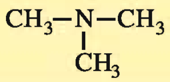
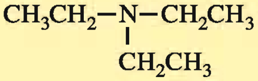
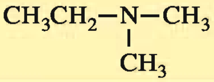
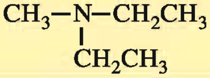
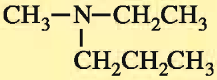
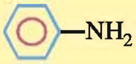
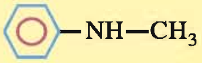
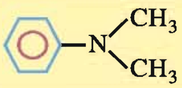

N-Methylbenzenamine


N, N-Dimethylbenzenamine

The structural formula, IUPAC name, common name, type and boiling points of certain amine compounds are given in table 6.1.

Table 6.1 Amine compounds

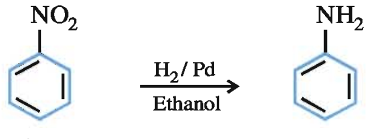
Sr.	Structural formula	Common name	IUPAC name	Type	Boiling point
1.	CH_3NH_2	Methylamine	Methanamine	1^0	280 K
2.	$CH_3CH_2NH_2$	Ethylamine	Ethanamine	1^0	290 K
3.	$CH_3CH_2CH_2NH_2$	Propylamine	Propan-1-amine	1^0	322 K
4.	 $CH_3-\underset{\underset{\displaystyle NH_2}{\vert}}{CH}-CH_3$	Isopropylamine	Propan-2-amine	1^0	306 K
5.	$CH_3-NH-CH_3$	Dimethylamine	N-Methylmethan-amine	2^0	280 K
6.	$CH_3CH_2-NH-CH_2CH_3$	Diethylamine	N-Ethylethanamine	2^0	329.K
7.	$CH_3CH_2CH_2-NH-CH_2CH_2CH_3$	Dipropylamine	N-Propylpropan-1-amine	2^0	383 K

8.	$CH_3-NH-CH_2CH_3$	Ethylmethylamine	N-Methylethanamine	2^0	309 K
9.	$CH_3-NH-CH_2CH_2CH_3$	Methylpropylamine	N-Methylpropan-1-amine	2^0	335 K
10.	 $CH_3-\underset{\underset{CH_3}{\vert}}{N}-CH_3$	Trimethylamine	N, N-Dimethyl methanamine	3^0	276 K
11.	 $CH_3CH_2-\underset{\underset{CH_2CH_3}{\vert}}{N}-CH_2CH_3$	Triethylamine	N, N-Diethyl ethanamine	3^0	363 K
12.	 $CH_3CH_2-\underset{\underset{CH_3}{\vert}}{N}-CH_3$	Ethyldimethylamine	N, N-Dimethyl ethanamine	3^0	310 K
13.	 $CH_3-\underset{\underset{CH_2CH_3}{\vert}}{N}-CH_2CH_3$	Diethylmethylamine	N-Ethyl-N-methyl ethanamine	3^0	339 K
14.	 $CH_3-\underset{\underset{CH_2CH_2CH_3}{\vert}}{N}-CH_2CH_3$	Ethylmethylpropyl-amine	N-Ethyl-N-methyl propan-1-amine	3^0	367 K
15.		Aniline	Benzenamine or aniline	1^0	475 K
16.		N-Methylaniline	N-Methylbenzenamine	2^0	469 K
17.		N, N-Dimethylaniline	N, N-Dimethyl benzenamine	3^0	467 K

6.5 Preparation of Amine Compounds

The methods for preparation of amine compounds are as follows :

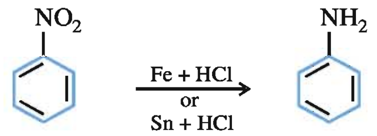
(i) Reduction of nitro compounds : Amine is produced by reduction reaction of nitro compounds by passing dihydrogen gas in presence of catalyst like nickel, palladium or platinum. Amine is also produced by their reduction in presence of metal in acidic medium. By reduction of nitroalkanes, alkanamines are formed. **In reduction of nitroalkane $LiAlH_4$ or $NaBH_4$ is also used.**



Nitrobenzene   Benzenamine or aniline

$$CH_3-CH_2-NO_2 \xrightarrow[\text{or } NaBH_4]{LiAlH_4} CH_3-CH_2-NH_2$$

Nitroethane   Ethanamine



Nitrobenzene

Benzenamine or Aniline

Presently time, iron scrap and hydrochloric acid is used in larger proportions.

(ii) Ammonolysis of halides : As studied earlier in semester III, the carbon-halogen bond which is present in alkyl or aryl halide is easily broken by nucleophilic reagent. Hence by reaction of ethanolic ammonia on alkyl or aryl halide, the nucleophilic reagent (NH_2) substitutes the halogen and amine is formed. **The C–X bond is broken by molecule of ammonia so the reaction is called ammonolysis.**

The ammonolysis reaction of alkyl halide is carried out in air tight tube at 373 K temperature. Primary amine is first obtained, then it reacts with alkyl halide by chain reaction and secondary and tertiary amines are formed. In the end quarternary ammonium salt is formed.

$$\ddot{N}H_3 + R-X \longrightarrow R-{}^{+}NH_3X^-$$

By the reaction of ammonium salt with strong base free amine is obtained.

$$R-\overset{+}{N}H_3\overset{-}{X} + NaOH \rightarrow R-NH_2 + H_2O + \overset{+}{Na}\overset{-}{X}$$

$$\underset{\substack{(1^0)\\ \text{Primary}}}{R-NH_2} \xrightarrow{RX} \underset{\substack{(2^0)\\ \text{Secondary}}}{R_2NH} \xrightarrow{RX} \underset{\substack{(3^0)\\ \text{Tertiary}}}{R_3N} \xrightarrow{RX} \underset{\substack{\text{Quarternary}\\ \text{ammonium salt}}}{R_4\overset{+}{N}-\overset{-}{X}}$$

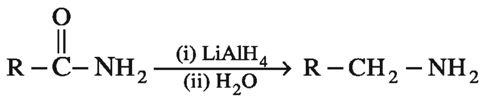
The disadvantage of ammonolysis is that the mixture of primary, secondary, tertiary and quarternary salt is obtained as product but by the use of ammonia in larger proportion primary amine can be obtained.

The order of reactivity of halide with amines is RI > RBr > RCl

(iii) Reduction of nitrile : By reaction of nitrile with lithium aluminium hydride ($LiAlH_4$) or by catalytic hydrogenation reaction, reduction takes place and primary amine is obtained. **This reaction is useful in increasing the number of carbons in the amine series i.e.** reaction of amine with one carbon can be started for preparation of amines.

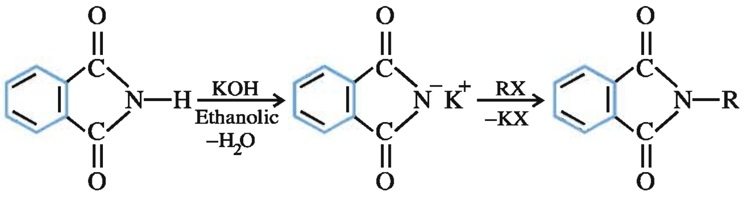
$$R-C\equiv N \xrightarrow[Na(Hg)\,/\,C_2H_5OH]{H_2/Ni} R-CH_2-NH_2$$

(iv) Reduction of amide : Amines are obtained by reduction of amide with lithium aluminium hydride.



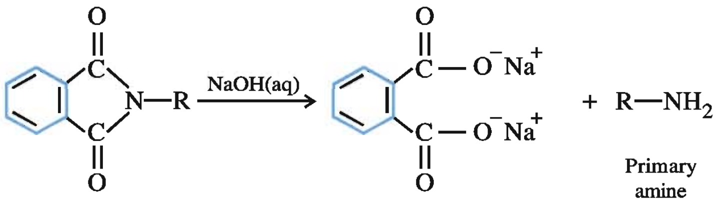
$$\underset{\text{Amide}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2} \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} \underset{\text{Amine}}{R-CH_2-NH_2}$$

(v) Gabriel pthalimide synthesis : Gabriel synthesis is used in the preparation of primary amines. By reaction of pthalimide with ethanolic potassium hydroxide, potassium salts of pthalimide are obtained which are when heated alkyl halide primary amines are obtained by alkaline aromatic hydrolysis. Primary aromatic amine can not be prepared by this method beacuse nucleophilic aryl halide, does not become favourable anion for phthalimide.

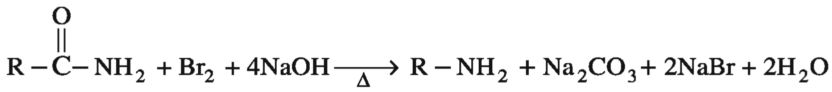


Pthalimide

N-Alkyl pthalimide



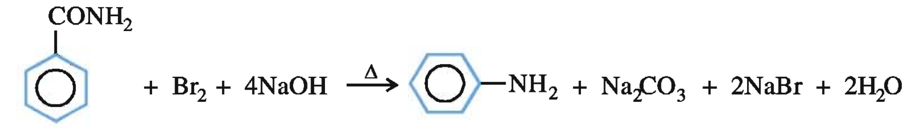
(vi) Hoffmann reaction : In Hoffmann reaction to prepare primary amine, the amide is heated with ethanolic solution of sodium hydroxide so that during the decomposition reaction, in place of carbonyl carbon in amide the nitrogen atom migrates to alkyl or aryl group. **Primary amine having one carbon less than amide is thus obtained.**



$$R-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \xrightarrow[\Delta]{} R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

$$CH_3CONH_2 + Br_2 + 4NaOH \xrightarrow{\Delta} CH_3-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

Ethanamide Methanamine

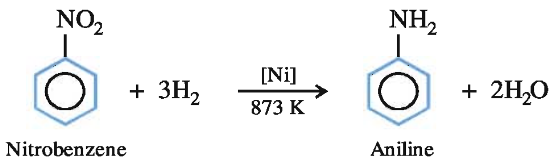


Benzenamide

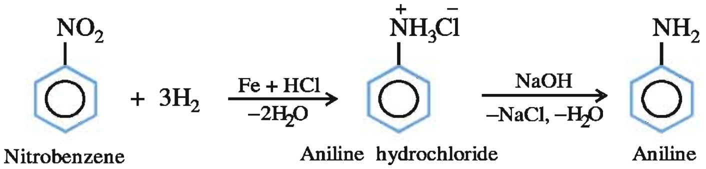
Aniline or Benzenamine

Industrial production of Aniline : As the use of aniline is widespread in chemical industry, its industrial production is carried out by reduction of nitrobenzene or by ammonolysis reaction with chlorobenzene.

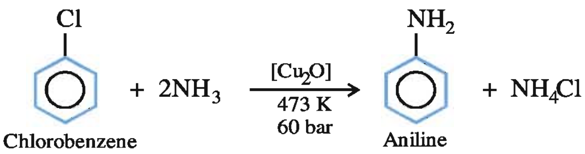
(a) The mixture of vapour of nitrobenzene and dihydrogen gas is heated at 873 K in presence of nickel catalyst, aniline is formed by reduction. Pure aniline is obtained by this method.



(b) By reduction of nitrobenzene with iron and hydrochloric acid, aniline hydrochloride is formed which is neutralised with sodium hydroxide and so aniline is separated.



When the mixture of chlorobenzene and two moles of ammonia are heated at 60 bar pressure and 473 K temperature in closed vessel in presence of Cu_2O catalyst, aniline is produced by ammonolysis reaction.



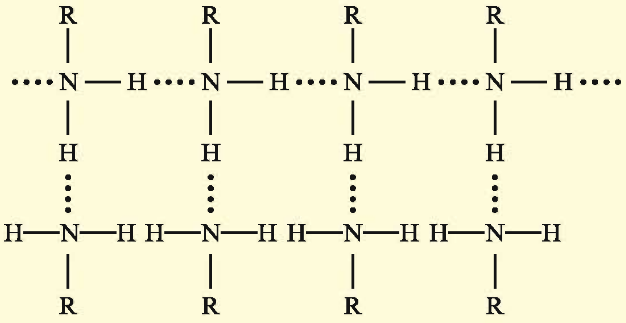
Pure aniline is almost colourless liquid having bad smell. It becomes dark red coloured when kept open in air for a long time because of oxidation. **The industrial use of aniline is in the manufacture of drugs, resin, varnish, as well as solvent and in vulcanisation of rubber.**

6.6 Physical Properties of Amines

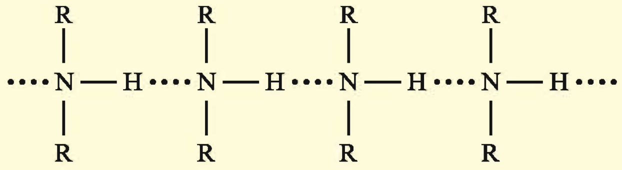
The boiling points of the primary amines having same number of carbon atoms containing alkane are higher; also the boiling points increases successively with the increase in number of carbon atoms in primary amine viz, in methanamine (boiling point 280 K), ethanamine (boiling point 290 K) propanamine (boiling point 322 K) increases successively with the increase in number of carbon atoms. In the isomeric alkyl amines having same molecular formula, the boiling point decreases from primary amine to tertiary amine, viz. (1^0) Propanamine (boiling point 322 K), (2^0) ethylmethyl amine (boiling point 309 K) and (3^0) trimethyl amine (boiling point 276 K) boiling points are decreasing.

As the electronegativity of nitrogen is less than that of oxygen, the $N^{-\delta}–H^{+\delta}$ bond in amines is less polar than the $O^{-\delta}–H^{+\delta}$ bond in alcohol. Hence, amine compounds are more polar than alkane but less polar than alcohol. Also, the intermolecular attraction in amine is less than that in alcohol. Hence, the boiling points of amine are higher than those of their corresponding alkanes and lower than those of their corresponding alcohols, viz ethanamine (boiling point 290 K) is more than ethane (boiling point 184 K) but lower than ethanol (boiling point 351 K).

There are intermolecular hydrogen bonds in primary and secondary amines while they are not there in tertiary amine. Hence, in isomeric primary alkyl amines having same molecular formula, it is highest, in secondary amine it is comparatively less and it is least in tertiary amine. viz. in (1^0) propanamine, (2^0) ethylmethylamine and (3^0) trimethylamine there is decrease in boiling point which is shown in fig 6.2.



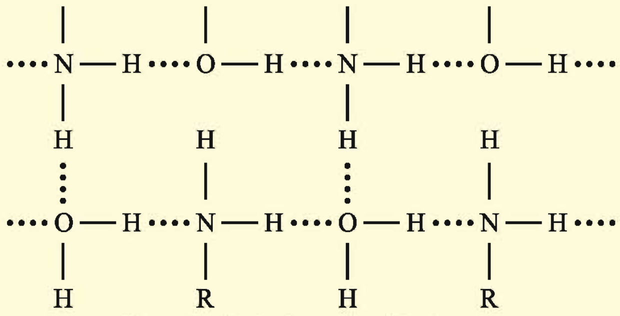
Intermolecular hydrogen bond between molecules of 1^0 amine



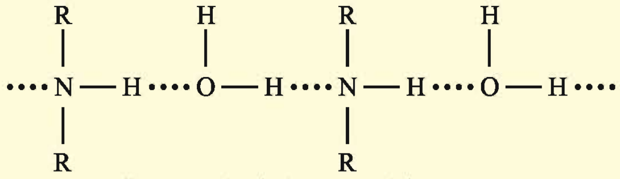
Intermolecular hydrogen bond between molecules of 2^0 amine

Fig. 6.2

In the aqueous solutions of primary and secondary amine compounds, water and amine molecules form hydrogen bond so the intermolecular attraction increases. In primary amines, there are two hydrogen atoms on the nitrogen and in secondary amine one hydrogen atom on nitrogen so the number of hydrogen bonds in primary amine becomes double. Hence, secondary amines corresponding to their primary amines having less molecular mass are less soluble in water as shown in the Fig 6.3.



Intermolecular hydrogen bond between molecules of 1^0 amine and water



Intermolecular hydrogen bond between molecules of 2^0 amine and water

Fig. 6.3

6.7 Chemical Reactions of Amine Compounds

(1) Basic characteristics of amine compounds : In amine compounds, the nitrogen atom has a non bonding electron pair, so amine compounds behave as Lewis base. **As amine compounds possess basic property, they react with acid and form salts.**

$$R-\overset{\bullet\bullet}{N}H_2+HX \rightleftarrows R-\overset{+}{N}H_3\overset{-}{X}\ \text{(Salt)}$$

These amine salts are soluble in water but insoluble in organic (non polar) solvents like ether. By reaction of amine salts with base like NaOH, the original amine compound is obtained back.

$$R-\overset{+}{N}H_3\overset{-}{X}+OH^- \rightarrow R-\overset{\bullet\bullet}{N}H_2+H_2O+\overset{-}{X}$$

The strength of amines as base can be explained easily as follows according to K_b or pK_b values.

$$R-NH_2+H_2O \rightleftharpoons R-\overset{+}{N}H_3+OH^-$$

$$K=\frac{[R-\overset{+}{N}H_3][OH^-]}{[R-NH_2][H_2O]}$$

$$K\,[H_2O]=\frac{[R-\overset{+}{N}H_3][OH^-]}{[R-NH_2]}$$

$$\therefore\ K_b=\frac{[R-\overset{+}{N}H_3][OH^-]}{[R-NH_2]}\quad \text{or}\quad pK_b=-\log K_b$$

Higher value of K_b (or lower value of pK_b) shows more basicity of amine. In table 6.2 the values of pK_b of some amine compounds are shown. For ammonia the value of pK_b is 4.75. The values of pK_b of aliphatic amines are between 3 to 4.22 and so they are a stronger base than ammonia; while the values of pK_b of aromatic amines are higher than 4.22, and so they are weak base.

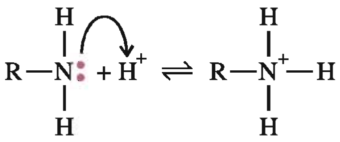
Table 6.2 pK_b values of aqueous solution of amines

Sr.	Name of amine	pK_b
1.	Methanamine	3.38
2.	N-Methylmethanamine	3.27
3.	N, N-dimethylmethanamine	4.22
4.	Ethanamine	3.29
5.	N-Ethylethanamine	3.00
6.	N, N-Diethylethanamine	3.25
7.	Benzenamine	9.38
8.	Phenylmethanamine	4.70
9.	N-Methylaniline	9.70
10.	N, N-Dimethylaniline	8.92

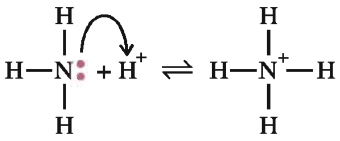
Relation between basicity of amines and structure : The basicity of amines is related with their structures. The basicity of amine depends on the tendency to form positive ion easily by receiving proton from acid. If the corresponding positive ion of amine is more stable then, amine is more basic.

(a) Basicity of aliphatic amine (alkanamine) :

(i) Comparison of alkanamine with ammonia : The basicing of alkanamies and ammonia are compared by taking into consideration their reaction with proton (H^+).



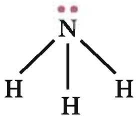
$$R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{N}}: + H^+ \rightleftharpoons R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{N^+}}-H$$



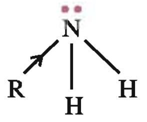
$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{N}}: + H^+ \rightleftharpoons H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{N^+}}-H$$

Because of the electron donating property of alkyl group, in alkanamine, alkyl group produces + I effect (You have studied + I effect in semester 1). Hence, in alkalanine the non-bonding electron pair is easily available for sharing with proton. In addition, they attain stability because of + I effect of alkyl group, the **displaced ammonium ion formed from amine by, spreading of positive charge. Hence, alkanamines are stronger base than ammonia.**

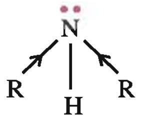
(ii) Comparison of primary, secondary and tertiary alkanamines : Going from tertiary amine to primary amine, the + I effect of alkyl group is decreasing because of the three groups attached with nitrogen atom in primary, secondary and tertiary amines having one, two and three alkyl groups are attached respectively.



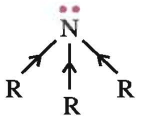
Ammonia



Primary Amine



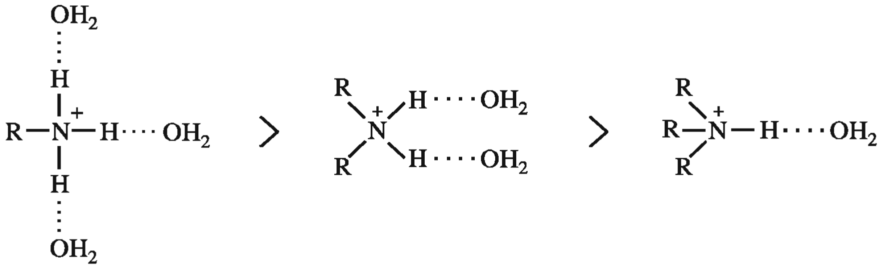
Secondary Amine



Tertiary Amine

Alkyl group is electron releasing group and so it sends the electrons of bond towards N. Thus the electron density of N-atom increases. As there are more number of alkyl group in tertiary amine, N atom will have more electron density in the compound. So such compounds can easily donate electron pair. **Hence, the order of basicity of ammonia, primary amine, secondary amine and tertiary amine gaseous phase is Tertiary amine > secondary amine > primary amine > ammonia.**

The strength of different types of alkanamines in aqueous medium are not observed in the above order, because in addition to + I effect of alkyl group due to the solvation (hydration) with molecule of water, the stability of displaced positive ion affect the stability. More the size of the positive ion less is the solvation. Hence the stability of positive ion is less. The order of stability of different positive ions in aqueous medium is as below :



So the order of basicity of alkanamines will be primary amine > secondary amine > tertiary amine.

Also, if the alkyl group is small (viz. $-CH_3$) then there is no steric hindrance for H–bond but for alkyl group bigger than $-CH_3$ (viz. $-C_2H_5$). If $-C_2H_5$ is present then the steric hindrance increases and so there is a difference in basic strength. Thus, +I effect, solvation effect and steric hindrance of alkyl group play an important role in determining the strength of alkanamine as base in aqueous medium.

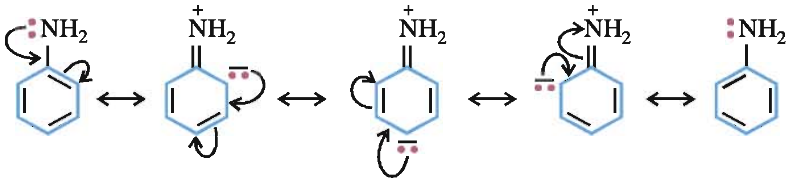
The order of strength as base in methyl displaced amines and ethyl displaced amines is respectively as follow :

$(C_2H_5)_2-NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$ and

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

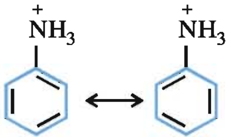
(b) Basicity of aromatic amine (Aryl amine) :

(i) The basicity of aryl amine is less than that of ammonia because of the resonance of aniline as follows : the non-bonding electron pair on N delocalises on benzene ring. Hence, the non-bonding electron pair is not easily available for protonation on N.



(I) (II) (III) (IV) (V)

Also, the anilinium ion that is obtained by protonation of aniline possesses two resonance structures.



So, the stability of aniline is more than anilinium ion. Hence, the tendency of aniline or aromatic amine to receive proton is less.

The resonance strctures are not available in ammonia and aliphatic amines compounds, like aniline, so the electron pair on their N atom is localised. Hence, these compounds can easily donate electron pairs so that their basicity is more than that of aniline. As discussed in the earlier points, keeping in mind the order of basicity of aliphatic amine and ammonia the order of basicity of amine compounds can be written as follows :

Tertiary amine > secondary amine > primary amine > ammonia > aniline.

(ii) In the case of substituted aniline, it is found that because of the presence of electron donating groups like $-OCH_3$, $-CH_3$ the strength as base increases. While because of the presence of electron attracting groups like $-NO_2$, $-SO_3H$, $-COOH$ its strength as a base decreases.

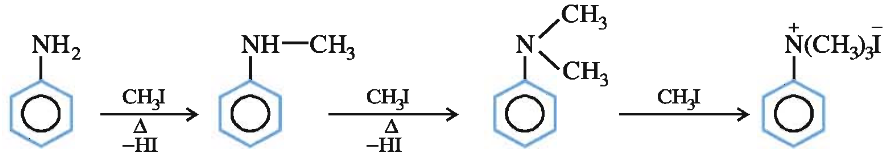
(2) Alkylation : By reaction of aliphatic and aromatic primary (1^0) amines with alkyl halide, secondary (2^0) amine is obtained. If it reacts with more amount of alkyl halide, then successively tertiary and then quarternary ammonium salt is obtained.

(a) On reacting ethanamine with ethyl iodide, N-ethylethanamide is obtained. By reacting this product with more amount of ethyl iodide, first N, N-diethylethanamine and then tetramethyl ammonium iodide salt is obtained

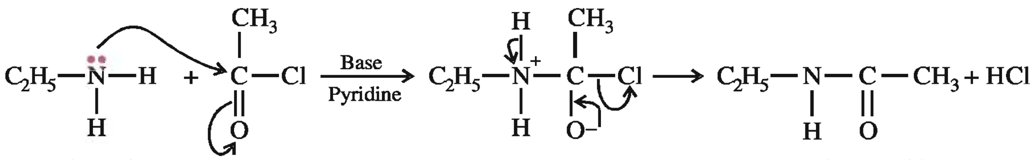
$$C_2H_5NH_2 + C_2H_5I \xrightarrow[-HI]{} (C_2H_5)_2NH \xrightarrow[-HI]{+C_2H_5I} (C_2H_5)_3N \xrightarrow{+C_2H_5I} (C_2H_5)_4\overset{+}{N}\overset{-}{I}$$

Ethanamine — N-Ethyl ethanamine — N, N-Diethyl ethanamine — Quaternary ethyl ammonium iodide (salt)

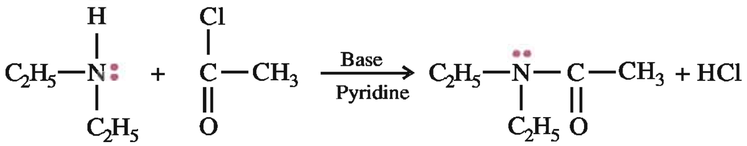
(b) Similarly, on heating aniline with methyl iodide N-Methylaniline is obtained. If methyl iodide is taken in excess proportion then tertiary amine and then quaternary ammonium salt is obtained.



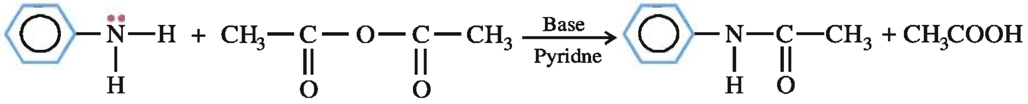
(3) Acylation : When aliphatic and aromatic primary and secondary amines react with acid chloride or acid anhydride, nucleophilic subtitution reaction takes place and amide product is obtained. This reaction is known as acylation. This reaction is carried out in pyridine which is a stronger base than amine.



Ethanamine — N-Ethylethanamide

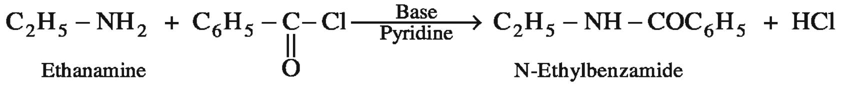


N-Ethylethanamine — N, N-Diethylethanamide



N-Phenylethanamine
(Acetanilide)

Primary and secondary amine react with benzoyl chloride. This reaction is called benzoylation.



$$C_2H_5-NH_2 + C_6H_5-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow[\text{Pyridine}]{\text{Base}} C_2H_5-NH-COC_6H_5 + HCl$$

Ethanamine N-Ethylbenzamide

$$C_6H_5-NH_2 + C_6H_5COCl \xrightarrow[\text{Pyridine}]{\text{Base}} C_6H_5-NH-CO-C_6H_5 + HCl$$

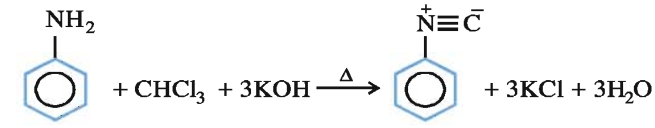
Aniline N-Phenylbenzamide

(4) Carbylamine reaction : On heating aliphatic or aromatic primary amine with chloroform ($CHCl_3$) and alcoholic potassium hydroxide (KOH) foul smell possessing poisonous isocyanide (carbylamine) is formed. This reaction is called carbylamine test or isocyanide identification. Secondary and tertiary amines do not give this test. **This test is used in laboratory for the identification of primary amine.**

$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} R-\overset{+}{N}\equiv\overset{-}{C} + 3KCl + 3H_2O$$

$$CH_3-CH_2-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} CH_3-CH_2-NC + 3KCl + 3H_2O$$

Ethanamine Ethyl isocyanide



Aniline or
Benzenamine

Phenyl isocyanide

(5) Reaction with nitrous acid : All the three types (1^0, 2^0 and 3^0) amine compounds react with nitrous acid (HNO_2) in different ways. Here, nitrous acid is prepared by the reaction of sodium nitrite ($NaNO_2$) and hydrochloric acid (HCl)

(a) Primary alkyl amine reacts with nitrous acid (HNO_2) and gives alkyldiazonium salt which is unstable and so this salt releases nitrogen and changes to alcohol.

$$R-NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [R-\overset{+}{N_2}\bullet\overset{-}{Cl}] \xrightarrow{H_2O} R-OH + N_2 + HCl$$

Alkanamine Unstable Alcohol

$$CH_3-CH_2-NH_2 + HNO_2 \xrightarrow[+ HCl]{NaNO_2} [CH_3-CH_2-\overset{+}{N_2}\overset{-}{Cl}] \xrightarrow{H_2O} CH_3-CH_2-OH + N_2 + HCl$$

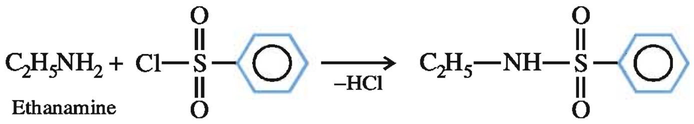
Ethanamine Unstable Ethanol

(b) Aromatic primary amine reacts with nitrous acid (HNO_2) at low temperature (273-278 K) and forms diazonium salt. The use of this salt in synthesis of aromatic compounds is very important which we shall study later on in this unit.

$$C_6H_5NH_2 \xrightarrow[\text{[HNO}_2\text{]}\ \ 273\text{-}278\ K]{NaNO_2 + HCl} C_6H_5 - \overset{+}{N}_2\overset{-}{Cl} + NaCl + 2H_2O$$

Benzenamine

(6) Reaction with Hinsberg reagent : Primary amine and secondary amine react with benzene sulphonyl chloride (Hinsberg reagent) and give sulphonamide product while in tertiary amine, because hydrogen is not attached with N, it does not undergo this reaction.

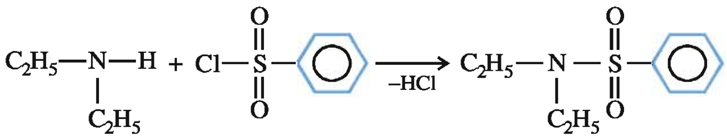


Ethanamine

Benzene sulphonyl chloride

N-Ethyl benzene sulphonamide (2^0)

In this compound, acidic hydrogen is combined with nitrogen, so it is soluble in alkali.



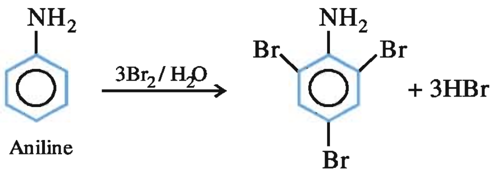
N-Ethylethanamine

N, N-Diethylbenzene sulphonamide (3^0)

In this compound, acidic hydrogen is not joined with N, and so it is insoluble in alkali.

(7) Electrophilic substitution reaction : Aromatic amines give electrophilic substitution reactions. **In case of $-NH_2$ group electron density is very high on o- and p- position so ortho and para substituted products are obtained.**

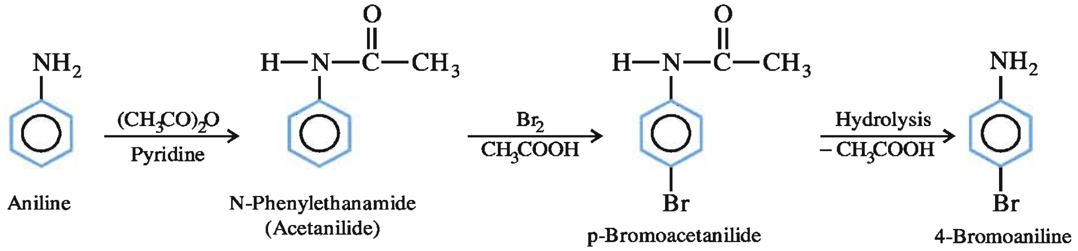
(a) Bromination : At room temperature aniline reacts with bromine water and gives white precipitates of 2,4,6-tribromoaniline.



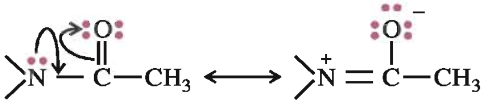
Aniline

2,4,6-Tribromoaniline

If only monosubstituted aniline derivative is desired then first, acetylation of $-NH_2$ group with acetic anhydride, (electrophilic substitution) is carried out. At the end of this reaction the amide product is hydrolysed so that monosubstituted aromatic amine is obtained.

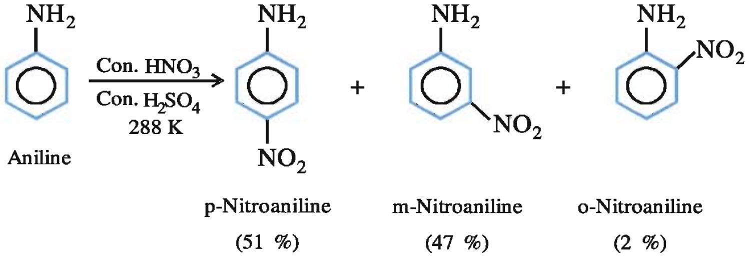


In the above reaction, in the formed acetanilide there is resonance and so the non-bonding electron pair interacts with oxygen atom.

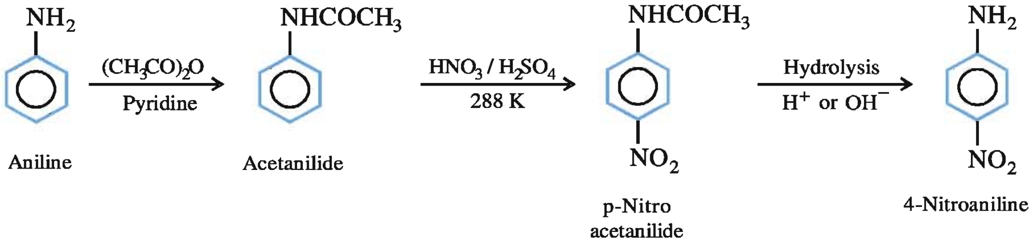


Hence, the electrons are not easily available to benzene for resonance. This functional effect of $-NHCOCH_3$ group decreases compared to $-NH_2$ group.

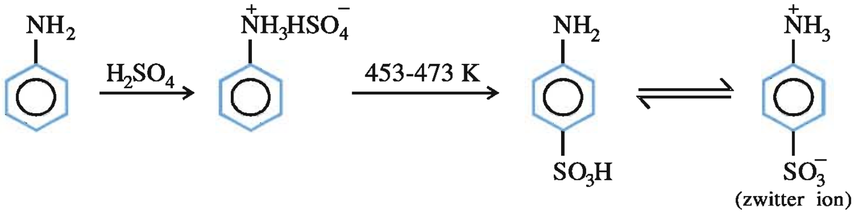
(b) Nitration : Aniline in presence of con. H_2SO_4 reacts with con. HNO_3 at 288 K temperature and mixture of p- and o- nitroaniline with m- nitroaniline are obtained by nitration because the **anilinium ion $-\overset{+}{N}H_3$ formed in acidic medium is m-directing group.**



Here also, to obtain monosubstituted derivative, first acetylation of $-NH_2$ group with acetic anhydride is carried out and then nitration is carried out.



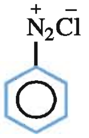
(c) Sulphonation : On reaction of aniline with con. H_2SO_4, anilinium hydrogen sulphate is obtained, which is if heated at 453-473 K temperature product, p-aminobenzene sulphonic acid (sulphanilic acid) is obtained as product.



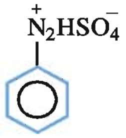
Aniline does not give Friedel-Crafts alkylation and acylation reactions because the catalyst anhydrous $AlCl_3$ used in the reaction is Lewis acid and so it forms salt by combining with aniline. Hence, **nitrogen in aniline attains positive electric charge so it acts as deactivating group for the further reaction.**

6.8 Diazonium Salt

Diazonium salt is shown by general formula as Ar $\overset{+}{N_2}\overset{-}{X}$ where $X^- = Cl^-$, Br^-, HSO_4^-, BF_4^- etc. $\overset{+}{N_2}$ $(-\overset{+}{N}\equiv N)$ group is called diazonium group. In their nomenclature diazonium suffix is applied to original hydrocarbon and then the name of negative ion is written. e.g.,



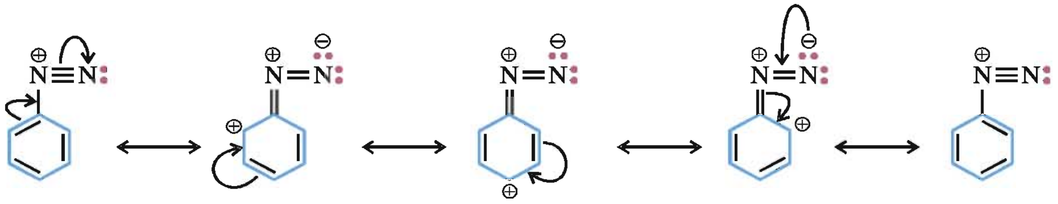
Benzenediazonium chloride



Benzenediazonium hydrogen sulphate

p-Toluenediazonium chloride

Primary aliphatic amine forms highly unstable alkyl diazonium salt while primary aromatic amine which forms arenediazonium salt, is stable due to resonance as shown below.

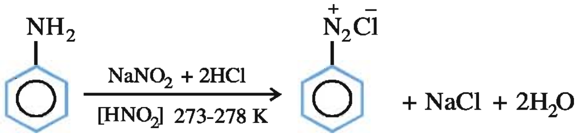


(a) Preparation of benzenediazonium chloride salt : In the reaction between primary aromatic amine and nitrous acid carried out at low temperature, diazonium salt is formed. This reaction is called diazotisation.

A solution of aniline in dilute hydrochloric acid is prepared and, it is cooled 273-278 K temperature; On adding sodium nitrite, nitrous acid is formed and benzene diazonium chloride (salt) is obtained. As benzenediazonium salt is unstable at higher temperature, it is necessary to keep the temperature 273-278 K.

$$Ar-NH_2 \xrightarrow[\text{[HNO}_2\text{] 273-278 K}]{NaNO_2 + 2HCl} Ar-\overset{+}{N}\equiv N\cdot\overset{-}{Cl} + NaCl + 2H_2O$$

As diazonium salt is unstable, it is used immediately.



Aniline

Benzenediazonium-chloride

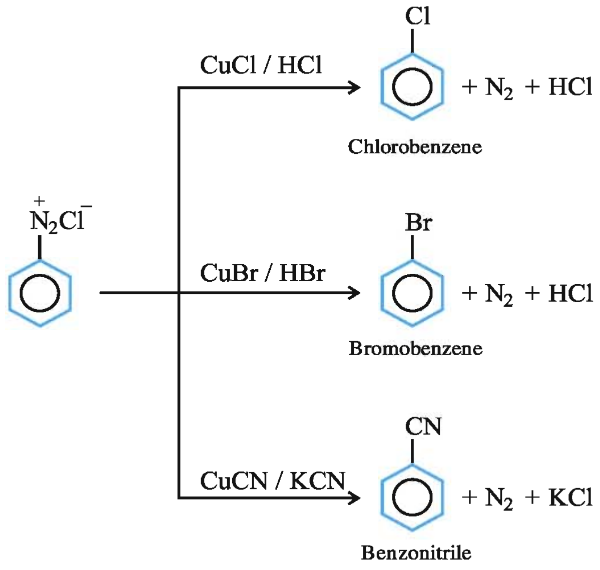
(b) Physical properties : Benzenediazonium chloride is colourless, crystalline solid. It is easily soluble in water and at low temperature becomes stable in solution; but on heating it reacts with water. It easily decomposes in dry state. Benzenediazonium fluoroborate $(C_6H_5\overset{+}{N}_2\overset{-}{BF_4})$ named diazonium salt is insoluble in water and is stable at room temperature.

(c) Chemical reactions :

(A) Displacement of nitrogen : Diazonium group $(-\overset{+}{N}\equiv N)$ can be substitute by groups like Cl^-, Br^-, I^-, CN^-, OH^- and dinitrogen (N_2) is removed in the form of gas because of substitution reaction.

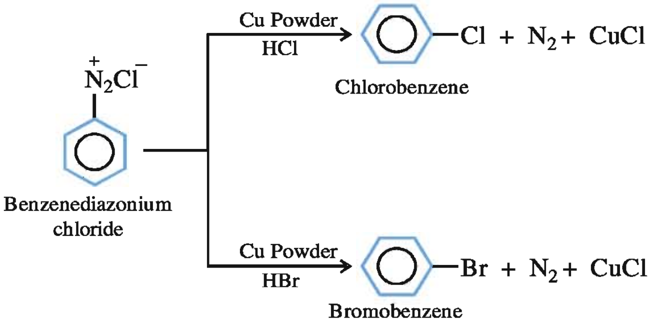
(i) Diazonium salt reacting with cuprous chloride in HCl gives chlorobenzene, with cuprous bromide in HBr gives bromobenzene and with cuprous cyanide in KCN gives benzonitrile (cyanobenzene). These reactions are called **Sandmeyer reactions.**

$$Ar-\overset{+}{N}_2\overset{-}{Cl}\xrightarrow{CuX\,/\,HX\,(X=Cl^-,\,Br^-,\,CN^-)}Ar-X+N_2+HCl$$



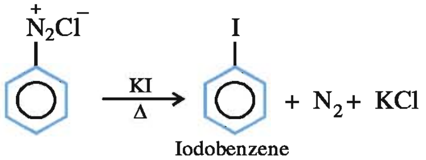
(ii) On reaction of diazonium salt in presence of copper powder with HCl or HBr, chlorobenzene or bromobenzene are respectively obtained. This reaction is called Gatterman reaction.

$$Ar-\overset{+}{N}_2\overset{-}{Cl}\xrightarrow[HX\,(X=Cl,\,Br)]{Cu\ powder}Ar-X+N_2+CuCl$$



(iii) On heating diazonium salt with potassium iodide, iodobenzene is formed.

$$Ar-\overset{+}{N}_2\overset{-}{Cl}\xrightarrow[\Delta]{KI}Ar-I+N_2+KCl$$

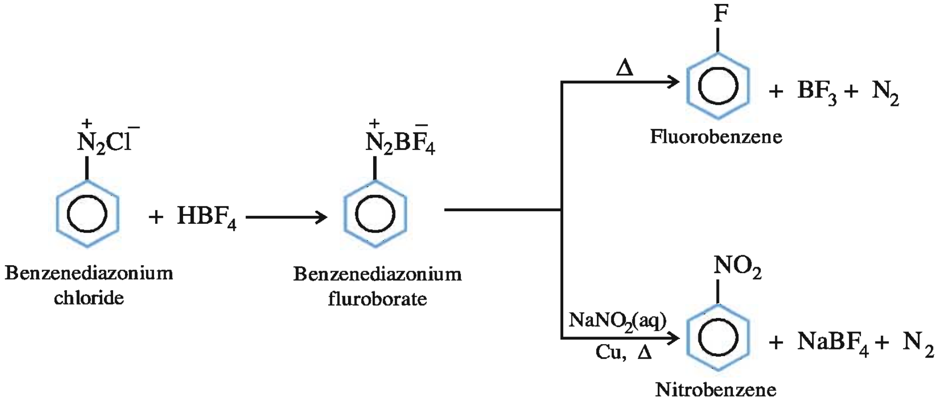


(iv) Precipitates of diazonium fluoroborate are obtained by reaction of diazonium salt with fluoroboric acid (HBF_4). On heating, it decomposes and gives fluorobenzene.

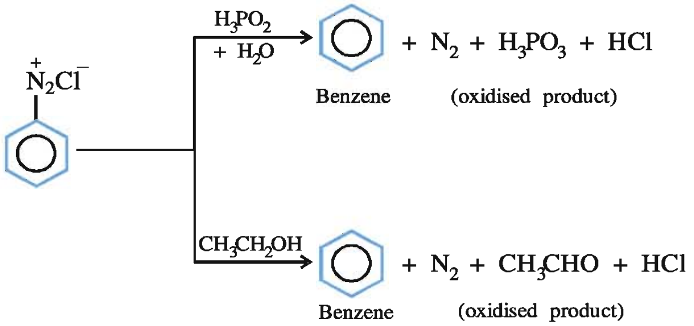
In addition, nitrobenzene is obtained by heating diazonium fluoroborate with aqueous solution of sodium nitrite ($NaNO_2$) in presence of copper metal.

$$Ar\overset{+}{N}_2\overset{-}{Cl}+HBF_4\rightarrow Ar\overset{+}{N}_2BF_4^-\xrightarrow{\Delta}ArF+BF_3+N_2$$

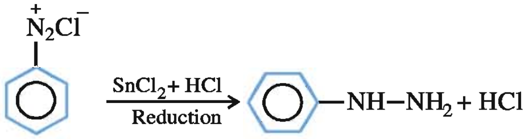
$$Ar\overset{+}{N}_2\overset{-}{Cl}+HBF_4\rightarrow Ar\overset{+}{N}_2BF_4^-\xrightarrow[Cu,\ \Delta]{NaNO_2(aq)}ArNO_2+NaBF_4+N_2$$



(v) Benzene is obtained by reduction of diazonium salt with weak reducing agent like hypophosphorus acid (Phosphinic acid, H_3PO_2) or ethanol.



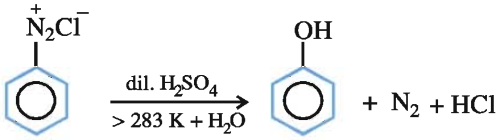
When diazonium salt is reduced with stannous chloride and hydrochloric acid, it gives phenyl hydrazine (Here diazonium group is not substituted).



Phenyl hydrazine

(vi) Phenol is obtained by heating diazonium salt with dil. H_2SO_4 at temperature higher than 283 K.

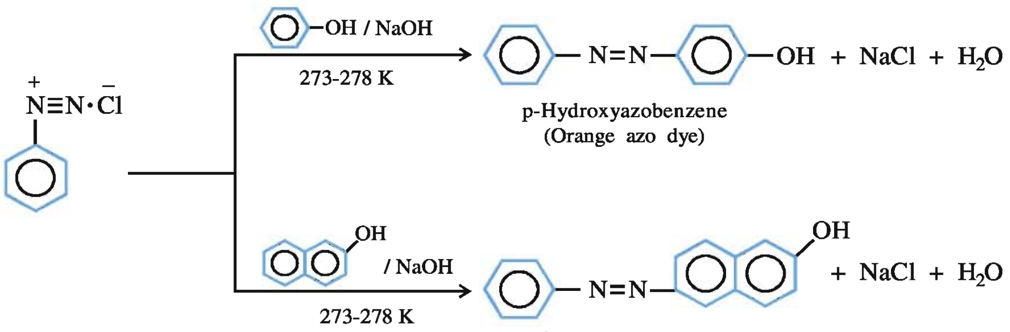
$$Ar\overset{+}{N}_2\overset{-}{X} \xrightarrow[283\ K + H_2O]{H_2SO_4} Ar-OH + N_2 + HCl$$



Benzendiazonium chloride

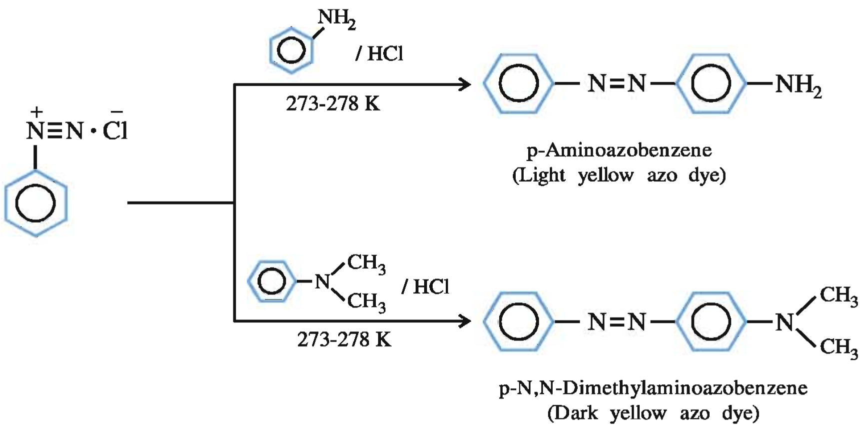
Phenol

(B) Azo coupling reaction : Solution of phenol or beta naphthol (β-naphthol) in sodium hydroxide when reacts with benzene diazonium chloride at 273-278 K temperature, orange and red colour azo dyes are obtained. Also, light yellow and dark yellow coloured azo dyes are respectively obtained when solutions of aniline or N,N-dimethyl aniline in hydrochloric acid react with benzene diazonium chloride.



p-Hydroxyazobenzene
(Orange azo dye)

β-Naphthylazobenzene
(Red azo dye)



(d) Importance of Diazonium salts in synthesis of Aromatic compounds : From the above reactions, it can be said that to introduce –F, –Cl, –Br, –I, –CN, –OH, –NO$_2$ groups in aromatic (benzene) ring, diazonium salt is an important intermediate compound.

From aromatic (benzene) compounds, aromatic (aryl) fluoride and aromatic (aryl) iodide can not be obtained by direct halogenation reaction. **Similary benzonitrile can not be prepared by nucleophilic substitution of benzene but these compounds can be easily prepared via diazonium salt.**

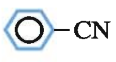
6.9 Cyanide or Nitrile Compounds

If cyano or nitrile group is present in organic compounds they are called cyanide or nitrile compounds. Carbon, hydrogen and nitrogen elements are mainly present in nitrile compounds. Its general formula is shown as $R - C \equiv N$ in which R = alkyl or aryl group.

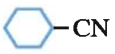
IUPAC Nomenclature of nitrile compounds : For common nomenclature, "Cyanide" word is placed at the end of the name of hydrocarbon. Viz. $CH_3–C{\equiv}N$ methyl cyanide, $CH_3–CH_2–C{\equiv}N$ ethyl cyanide etc.

For IUPAC nomenclature of nitrile compounds, the longest carbon series of original hydrocarbon is determined and then with carbon of nitrile group the longest carbon series of original hydrocarbon is determined and then at the end the word "nitrile' is attached, viz. $CH_3–C{\equiv}N$ ethane nitrile; $CH_3–CH_2–C{\equiv}N$ propane nitrile. **If –CN group is attached with cyclic system, then for their IUPAC name the suffix "carbonitrile" is joined.**

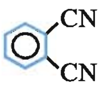
Viz.,



Benzenecarbonitrile



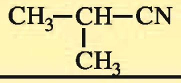
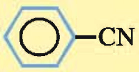
Cyclohexanecarbonitrile



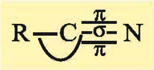
Benzene-1,2-dicarbonitrile

Structural formulas, common name, IUPAC name and boiling points of some cyanide compounds are given in table 6.3

Tabel 6.3 Structural formula, common name IUPAC name and boiling points of some cyanide compounds

Sr.	Structural formula	Common name	IUPAC name	Boiling point
1.	CH_3-CN	Methyl cyanide	Ethanenitrile	355 K
2.	CH_3-CH_2-CN	Ethyl cyanide	Propanenitrile	370 K
3.	$CH_2=CH-CN$	Vinyl cyanide (Acrylonitrile)	Prop-2-enenitrile	351 K
4.	$CH_3-CH_2-CH_2-CN$	Propyl cyanide	Butane nitrile	391 K
5.	 $CH_3-\underset{\underset{CH_3}{\mid}}{CH}-CN$	Isopropyl cyanide	2-Methyl propane nitrile	377 K
6.		Phenyl cyanide (Benzonitrile)	Benzene carbonitrile or Benzonitrile	464 K

Electronic structure of Cyanide :



C–N one σ and two π bonds

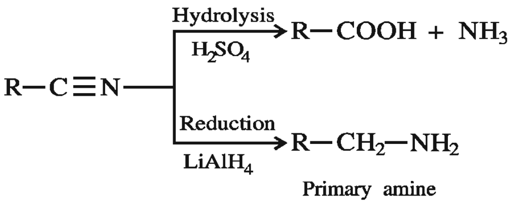
C and N sp hybridisation

R–C–N bond angle 180^0.

Physical properties of cyanides : In alkyl cyanide compounds $-C^{+\delta}\equiv N^{-\delta}$ bond being polar and absence of intermolecular hydrogen bond, the boiling points of alkyl cyanides are less than their corresponding carboxylic acids, viz. The boiling points of ethane nitrile (boiling points 355 K) and propane nitrile (boiling point 370 K) are lower than the boiling points of ethanoic acid (boiling point 391 K) and propanoic acid (boiling point 414 K) respectively

Alkyl cyanides are very weak basic compounds, having fine fragrant smell and are non-poisonous compounds. The alkyl cyanides having less molecular masses are soluble in water as well as is many other organic solvents. Ethane nitrile (acetonitrile) is the most dipolar and so it makes many types of organic reagents soluble in it. Its boiling point being normal, it can be easily removed so that it can be used again and it being inert it is useful as solvent in many most of the organic reactions.

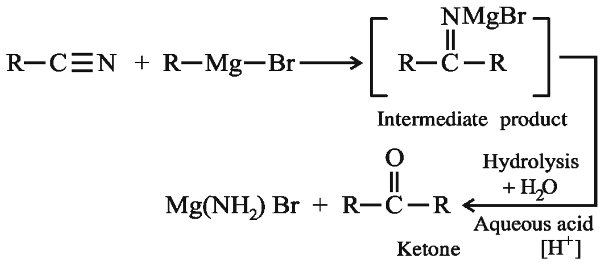
Chemical properties of cyanides : Carboxylic acids are obtained by hydrolysis of cyanide compounds in presence of sulphuric acid and ammonia is liberated. Primary amine is obtained by reduction with $LiAlH_4$.

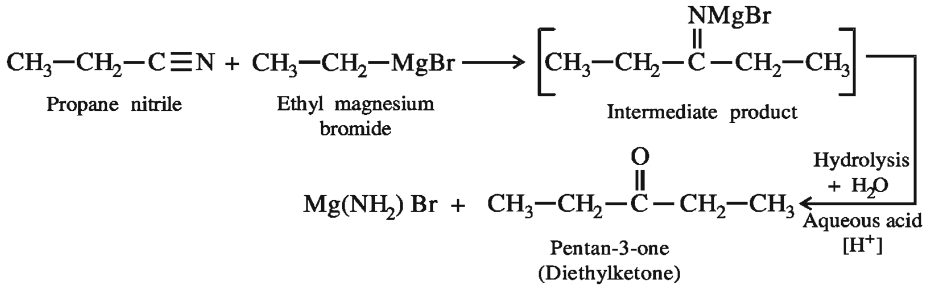


(i) Ethylethanoate (ethyl acetate) is formed when ethane nitrile and ethanol are heated in presence of concentrated sulphuric acid.

$$\underset{\text{Ethane nitrile}}{CH_3-C\equiv N}+\underset{\text{Ethanol}}{CH_3-CH_2-OH}+H_2O\xrightarrow[\Delta]{\text{Con. }[H_2SO_4]}\underset{\text{Ethylethanoate}}{CH_3COOCH_2CH_3}+NH_3$$

(ii) Ketone is obtained by hydrolysis of the intermediate product in presence of aqueous acid; the intermediate product is obtained by addition reaction of cyanide compounds with Grignard reagent (R–Mg–X) (X = Br, I)





6.10 Isocyanide Compounds

If isocyanide group is present in organic compounds, they are called isocyanide compounds. These compounds are also called isonitrile or carbylamine compounds. In isocyanide compounds, mainly carbon, hydrogen and nitrogen elements are present. **Their general formula can be shown as $R-\overset{+}{N}\equiv\overset{-}{C}$ where R = alkyl group or aryl group.** Isocyanide group is dipolar in which nitrogen possesses positive charge and carbon possesses negative charge. The characteristic of cyanide groups are opposite to those of isocyanides.

The naming of isocyanide compounds is done by placing the prefix "iso" before the name of cyanide compounds. In other method of nomeclature, carbylamine word is placed at the end of the alkyl group, viz **CH_3–NC is methylisocyanide and according to IUPAC it is called ethan isonitrile or methylcarbylamine.**

The boiling points of alkyl isocyanides are lower than their isomeric alkyl cyanides because isocyanide group is dipolar. These compounds possess very foul smell and are very poisonous and sparingly soluble in water.

When isocynide compounds are reduced with $LiAlH_4$, secondary amine is obtained as product.

$$R-\overset{+}{N}\equiv\overset{-}{C}\xrightarrow[\text{LiAlH}_4]{\text{Reduction}}R-NH-CH_3$$

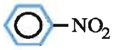
(2^0) Secondary amine

$$CH_3-\overset{+}{N}\equiv\overset{-}{C}\xrightarrow[\text{LiAlH}_4]{\text{Reduction}}CH_3-NH-CH_3$$

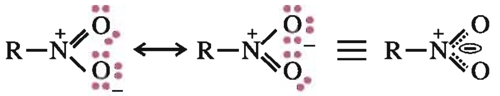
Ethanisonitrile N-Methylmethanamine (Dimethyl amine)

6.11 Nitro Compounds

If nitro group is present in organic compounds, they are called nitro compounds. In nitro compounds mainly carbon, hydrogen, nitrogen and oxygen atoms are present. Their general formula is shown as **$R–NO_2$ where R = alkyl or aryl group.**

For IUPAC nomenclature of alkyl nitro compounds, the longest carbon series of the original alkane is determined and the prefix nitro is added. viz. $CH_3–NO_2$ nitromethane, $CH_3–CH_2–NO_2$ nitroethane etc. The nomenclature of aryl nitro compounds is done as for alkyl nitro compounds, viz.  nitrobenzene.

Nitro compounds are colourless, having odour, neutral and sparingly soluble in water. The resonance forms of alkyl nitro compounds :



The mixture of alkyl nitro compounds is obtained by nitration reaction of alkane hydrocarbon and heating with fuming nitric acid in vapour state at 673 K temperature, viz. By nitration of propane, nitro methane, nitroethane and 1-nitropropane are obtained. The industrial production of alkyl nitro compounds is carried out by this method.

$$2CH_3-CH_2-CH_3\xrightarrow[673\text{ K}]{\text{Fuming HNO}_3}CH_3-NO_2+CH_3-CH_2-NO_2+CH_3-CH_2-CH_2-NO_2$$

Propane Nitromethane Nitroethane 1-Nitropropane

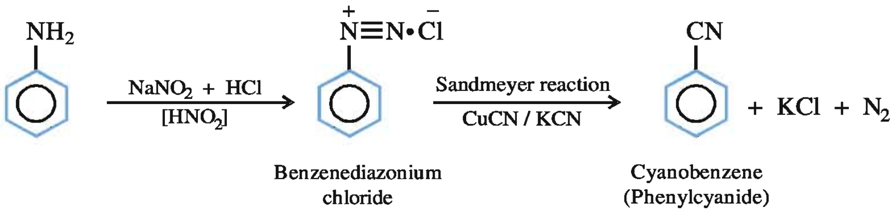
Primary alkyl amines are obtained by carrying out reduction of nitroalkane with lithium aluminium hydride ($LiAlH_4$) or with hydrogen in presence of nickel catalyst.

$$CH_3-CH_2-NO_2+3H_2\xrightarrow[\text{or [Ni]}]{\text{LiAlH}_4}CH_3-CH_2-NH_2+2H_2O$$

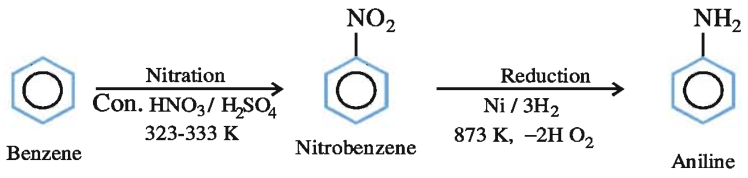
Nitroethane Ethanamine

Some Organic Conversions :

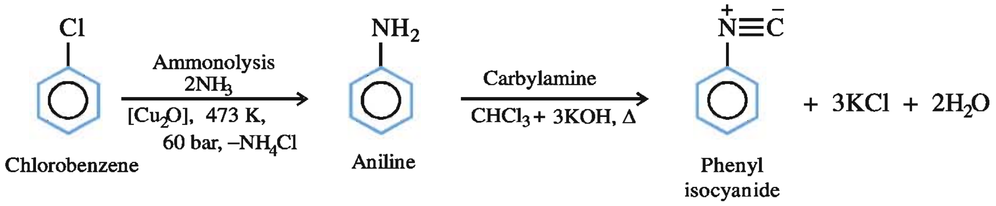
(i) Cyanobenzene from aniline :



(ii) Aniline from benzene :



(iii) Phenyl isocyanide from chlorobenzene :



(iv) Diethylamine from methylcyanide :

$$CH_3-C\equiv N \xrightarrow[LiAlH_4]{Reduction} CH_3-CH_2-NH_2 \xrightarrow[-HI]{Alkylation,\ C_2H_5I} C_2H_5-NH-C_2H_5$$

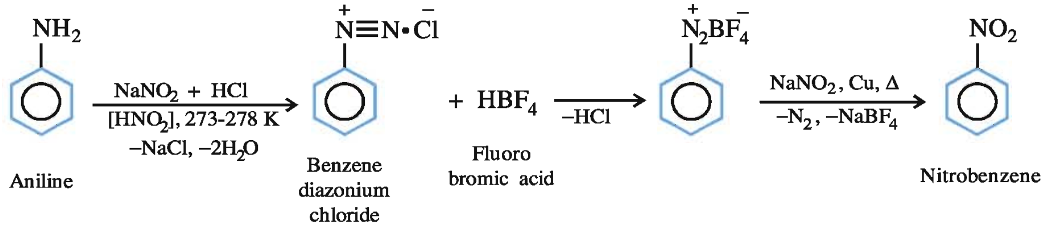
Methylcyanide Ethanamine Diethylamine

(v) N-acetyl ethylamine from acetamide :

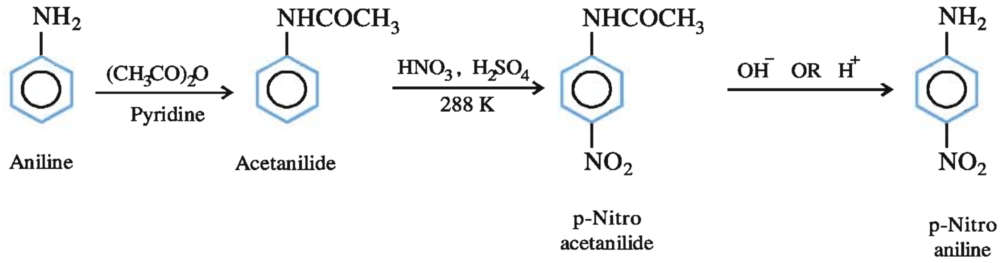
$$CH_3CONH_2 \xrightarrow[(i)\ LiAlH_4\ (ii)\ H_2O]{Reduction} CH_3-CH_2-NH_2 \xrightarrow[\substack{or\ (CH_3CO)_2O,\ -HCl\\ or\ -CH_3COOH}]{Acetylation,\ CH_3COCl} CH_3-CH_2NHCOCH_3$$

Acetamide Ethanamine N-Acetylethyle amine

(vi) Nitrobenzene from aniline :



(vii) p-Nitroaniline from aniline :

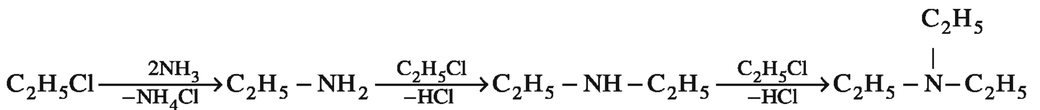


(viii) Dimethyl amine from methylchloride

$$CH_3Cl \xrightarrow[-NH_4Cl]{\substack{2NH_3\\ \text{Ammonolysis}}} CH_3-NH_2 \xrightarrow[\substack{CHCl_3 + 3KOH,\\ -3KCl,\ -3H_2O}]{\text{Carbylamine}} CH_3-N\equiv C \xrightarrow[Ni/2H_2]{\text{Reduction}} CH_3-NH-CH_3$$

Methylchloride Methanamine Methyl isocyanide Dimethyl amine

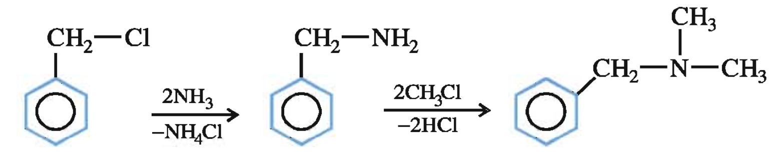
(ix) N,N-Diethylethanamine from chloroethane



$$C_2H_5Cl \xrightarrow[-NH_4Cl]{2NH_3} C_2H_5-NH_2 \xrightarrow[-HCl]{C_2H_5Cl} C_2H_5-NH-C_2H_5 \xrightarrow[-HCl]{C_2H_5Cl} C_2H_5-\overset{\displaystyle C_2H_5 \atop |}{N}-C_2H_5$$

Chloroethane Ethanamine N-Ethylethanamine N, N-Diethylethanamine

(x) N, N-Dimethylphenylmethanamine from benzyl chloride



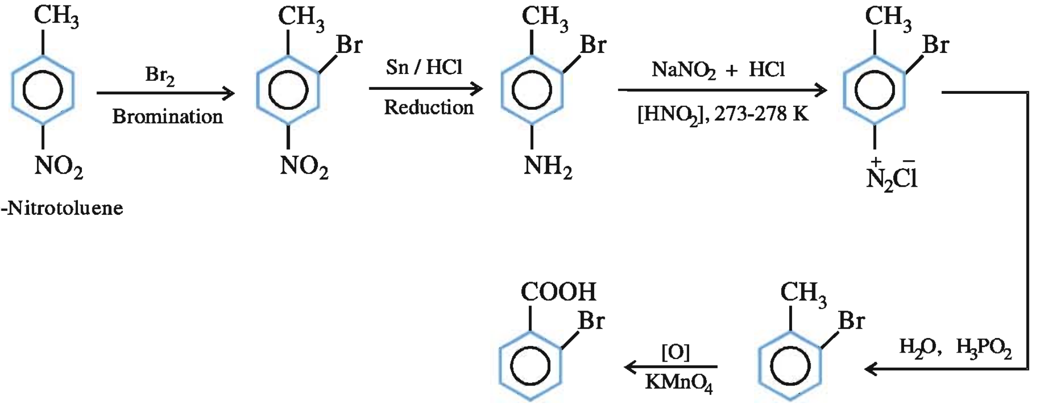
Benzylchloride Benzylamine N, N-Dimethyl phenyl methanamine

(xi) Propan-1-amine from chloroethane :

$$CH_3-CH_2-Cl \xrightarrow[KCN,\ -KCl]{\text{Ethanolic}} CH_3-CH_2-C\equiv N \xrightarrow[2H_2/Ni]{\text{Reduction}} CH_3-CH_2-CH_2-NH_2$$

Chloroethane Propanenitrile Propan-1-amine

(xii) 2-Bromobenzoic acid from p-nitrotoluene



p-Nitrotoluene

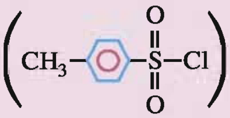
2-Bromo benzoic acid

(xiii) Ethanol from acetyl chloride

$$CH_3-COCl \xrightarrow[-NH_4Cl]{2NH_3} CH_3-CONH_2 \xrightarrow[\substack{\text{(i) } LiAlH_4\\ \text{(ii) } H_2O}]{\text{Reduction}} CH_3-CH_2-NH_2 \xrightarrow[\substack{NaNO_2\\ +HCl}]{\substack{\text{Nitrous}\\ \text{acid}}} CH_3-CH_2-OH$$

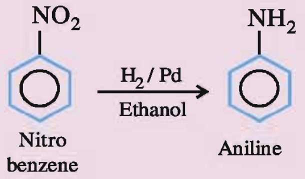
Acetyl chloride Ethanamine Ethanol

SUMMARY

- In nitrogen containing organic compounds there are amino ($-NH_2$), cyano or nitrile ($-CN$), isocyanide ($-NC$), and nitro ($-NO_2$) functional groups.
- If amino, cyano, isocyanide and nitro groups are attached to carbon in hydrocarbon series then they are called amine compounds, cyanide compounds, isocyanide compounds and nitro compounds, respectively.
- Amine is formed by substitution of hydrogen in ammonia by hydrocarbon. Like ammonia, in amine compounds, nitrogen atom is trivalent and posseses non-bonding electron pair.
- In amine compounds, the atomic orbitals of nitrogen atom possesses sp^3 hybridisation and these compounds possess pyramidal structure. The four orbitals of nitrogen possess non-bonding electron pair.
- Because of the presence of non bonding election pair, C–N–R (where R is H or C) the angle decreases slightly from $109^0\ 28'$. In trimethyl amine the bond angle is 108^0.
- If one alkyl or aryl group is attached with nitrogen atom then it is called primary (1^0) amine, two groups are attached then secondary (2^0) amine and three groups are attached then tertiary (3^0) amine.
- The separation of primary, secondary and tertiary amines can be carried out by Hinsberg reagent- benzene sulphonylchloride (). In the present time instead of benzene sulphonyl chloride, paratoludine sulphonyl chloride () is used.
- For common nomenclature of primary amine compounds, at the end of the alkyl group attached to nitrogen, the word amine is placed. In secondary alkyl amines, if two alkyl groups attached to nitrogen are same then the prefix di is added and then at the end amine word is placed. If the two alkyl groups are different then they are written in alphabetical order and then the word amine is placed at the end. In tertiary amine if three alkyl groups are common then the prefix tri is placed before the name of alkyl group and then word amine is placed at the end. If two alkyl groups out of three are same then the prefix di is placed before the name of that alkyl group and then the name of third alkyl group is combined and the word amine is placed at the end. If the three alkyl groups attached to nitrogen are different, then they are shown in alphabetical order and then the word amino is placed at the end. In amino compounds having more than one amine group corresponding to the number of amine groups, the words di, tri, tetra etc. are added as prefix and the position of amino group is mentioned.

- In IUPAC nomenclature of primary amine from the end of the hydrocabon attached to nitrogen the last letter 'e' is removed and the suffix 'amine' is attached. If there are more than two carbon atoms then in the longest chain of hydrocarbon the minimum number of amino group showing position is shown before the suffix amine. If there are more than two amine groups then the prefix di, tri, tetra etc. are mentioned corresponding to numbers 2, 3, 4 etc. Here the last letter 'e' is not removed from the name of hydrocarbon.
- For nomenclature of secondary and tertiary amines, symbol N is used to show the position of substituent of hydrogen of amine group.
- For preparation of amine compounds

(i) Reduction of nitro group



$$CH_3{-}CH_2{-}NO_2 \xrightarrow[\text{or NaBH}_4]{\text{LiAlH}_4} CH_3{-}CH_2{-}NH_2$$

Nitro ethane   Ethanamine

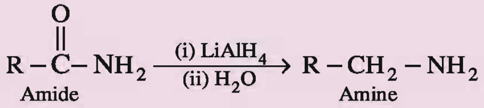
(ii) Ammonolysis of halide :

$$R{-}X + NH_3 \rightarrow R{-}NH_3{-}X \xrightarrow[-NH_4Cl]{NH_3} R{-}NH_2$$

(iii) Reduction of nitrile :

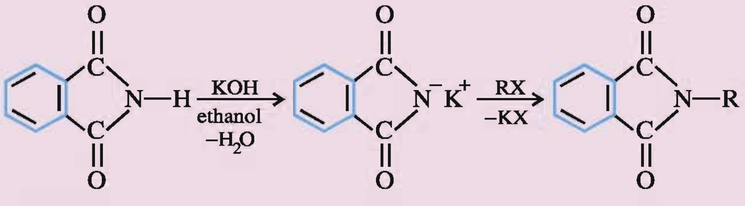
$$R{-}C{\equiv}N \xrightarrow[\text{Na(Hg)} / C_2H_5OH]{H_2 / \text{Ni}} R{-}CH_2{-}NH_2$$

(iv) Reduction of amide :

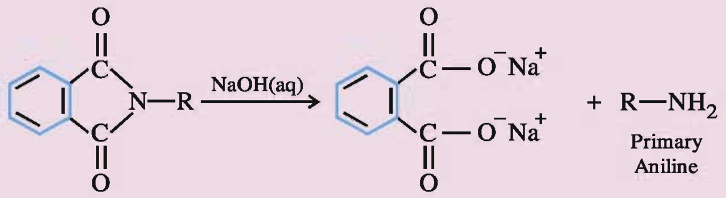


$$\underset{\text{Amide}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2} \xrightarrow[\text{(ii) } H_2O]{\text{(i) LiAlH}_4} \underset{\text{Amine}}{R-CH_2-NH_2}$$

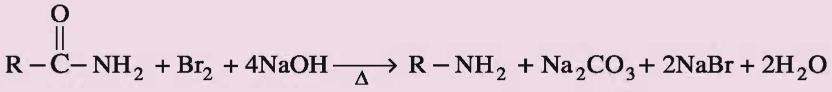
(v) Gabriel phthalimide:



Phthalimide   N-Alkylphthalimide

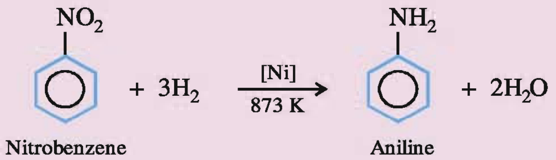


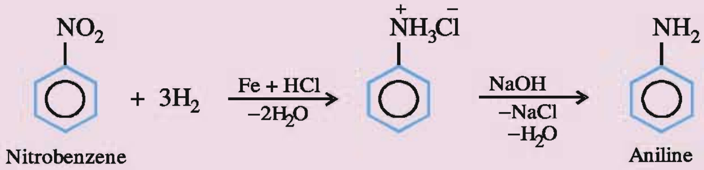
(vi) Hoffmann reaction :

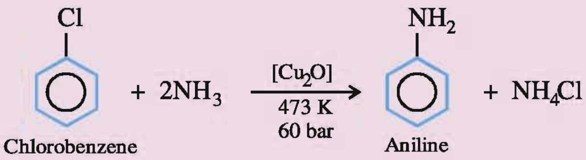


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \xrightarrow[\Delta]{} R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

- **Industrial production of aniline :**







- The boiling points of primary alkylamines are higher than those of corresponding hydrocarbons. With the increase in number of carbon in primary alkylamine, the boiling point increases. In isomeric alkylamines having same molecular formula, the boiling point decreases on going from primary to tertiary.

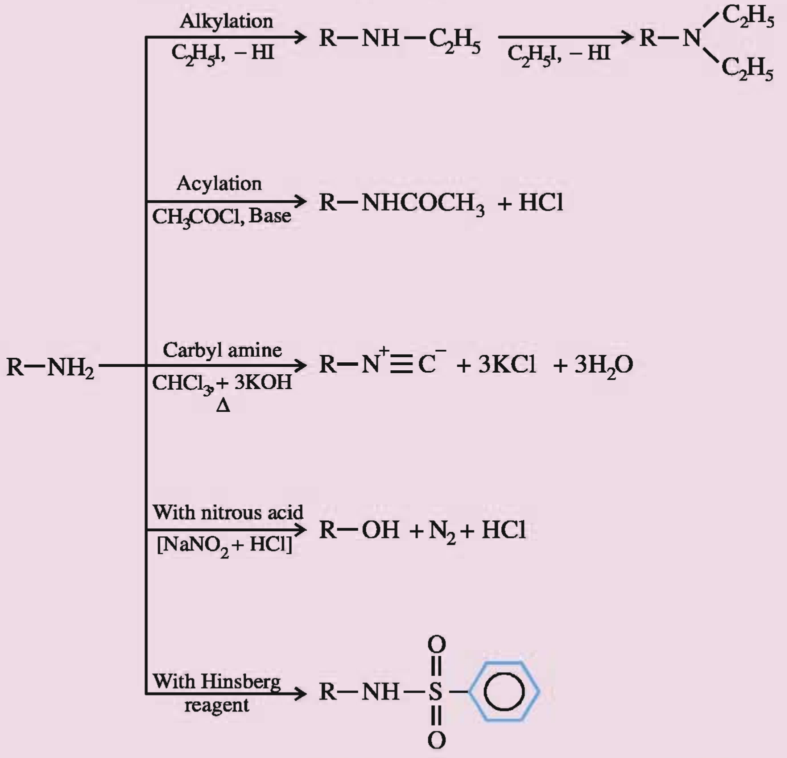
- In aqueous solutions of primary and tertiary amine compounds, hydrogen bonds are formed between molecules of amine and water and so the intermolecular attraction increases. The secondary amines are less soluble in water than the corresponding primary amines.

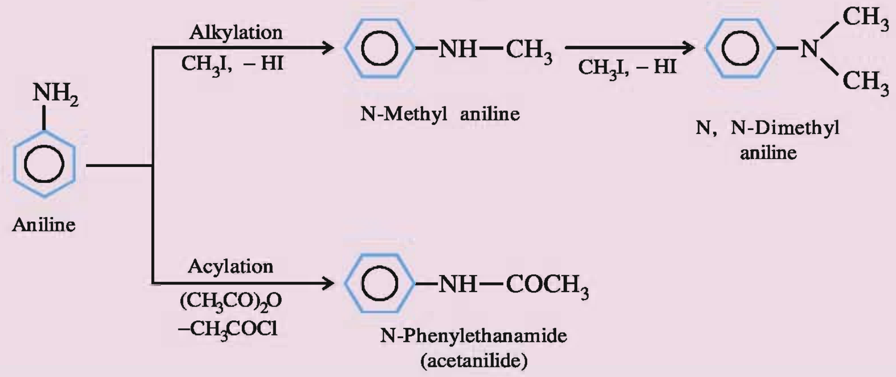
- Amines act as Lewis base because the nonbonding electron pair is on nitrogen atom of amine compounds and forms salt by reaction with acid.

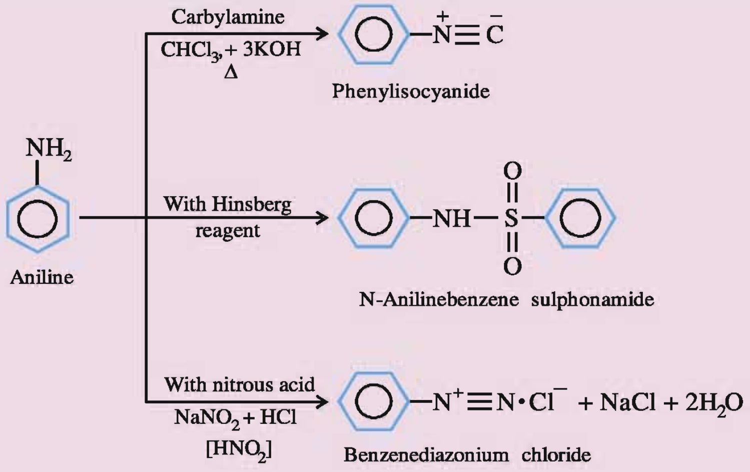
$$R-\ddot{N}H_2 + HX \rightleftharpoons R-\overset{+}{N}H_3\overset{-}{X} \text{ (salt)}$$

Amine compounds are soluble in water but insoluble in organic solvent like ether.

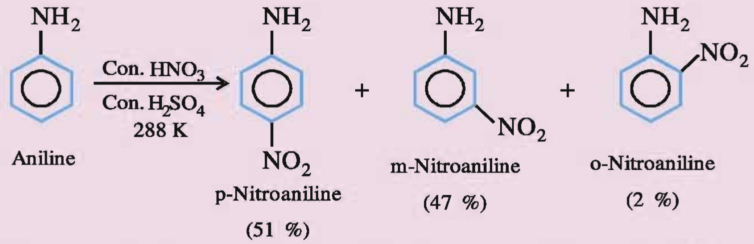
- The order of basicity of ammonia, primary amine, secondary amine and tertiary amines in gaseous state is tertiary amine > secondary amine > primary amine > ammonia.
- Order of basicity in aqueous medium : primary amine > secondary amine > tertiary amine.
- The order of strength as a base in methyl substituted amine and ethyl substituted amine is respectively $(C_2H_5)_2$–NH > $(C_2H_5)_3N$ > $C_2H_5NH_2$ > NH_3 and $(CH_3)_2NH$ > CH_3NH_2 > $(CH_3)_3N$ > NH_3
- The basicity of aryl amine is less than ammonia because, in aniline there is resonance. In substituted aniline, due to the presence of electron donor groups $-OCH_3$, $-CH_3$, its strength as base increases while the strength as base decreases because of the presence of electron attracting groups like $-NO_2$, $-SO_3H$, –COOH, –X.



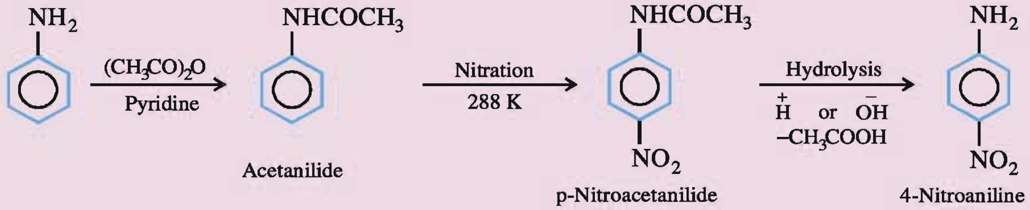




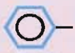
- **Nitration :**

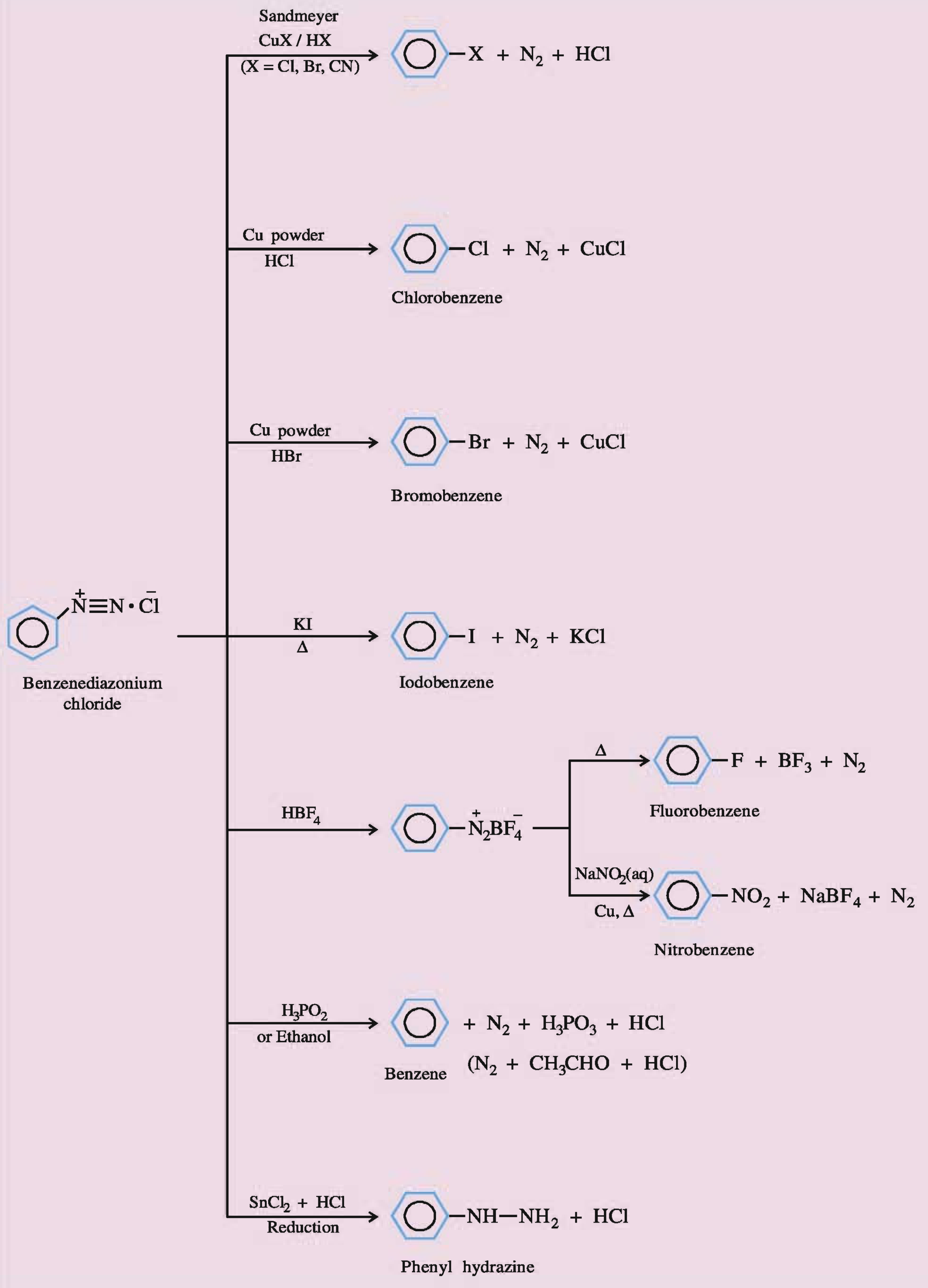


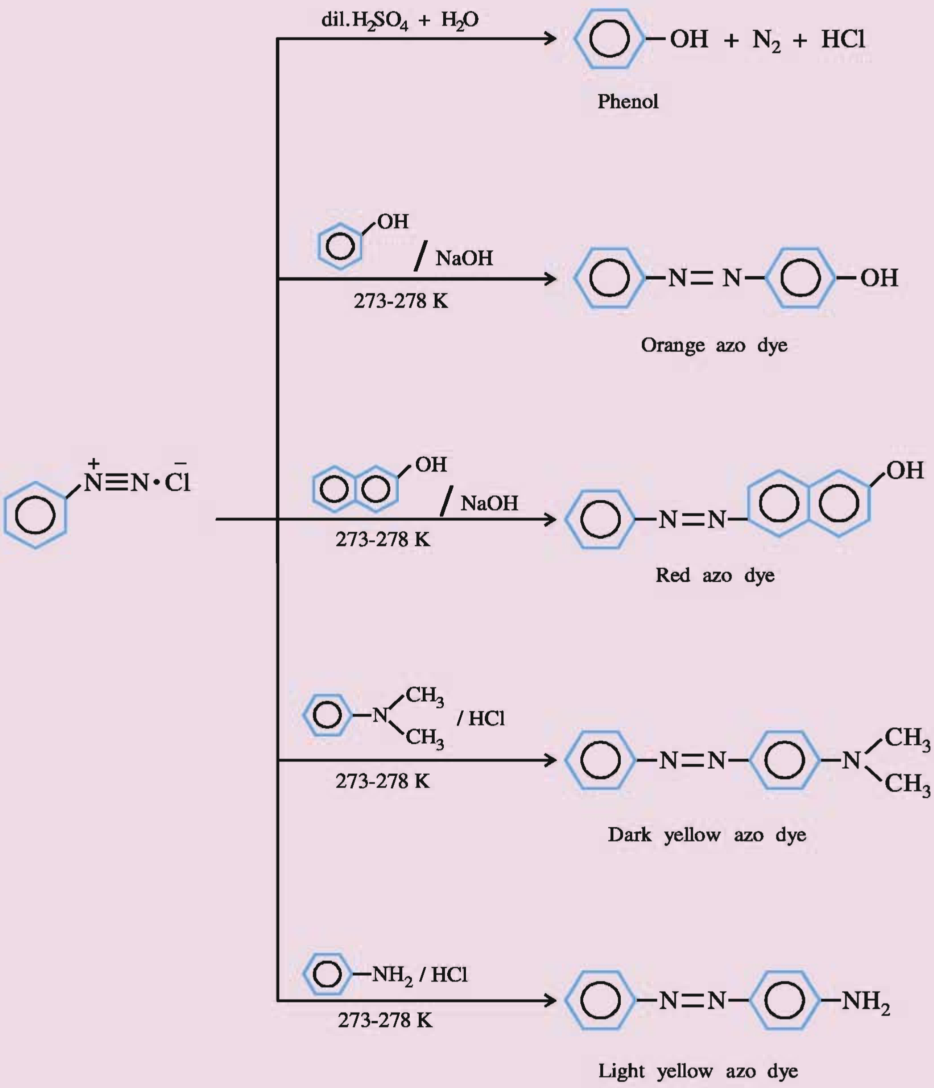
- Here, to obtain monosubstituted derivative acetylation of $-NH_2$ group is done with acetic anhydride and then nitration is carried out.



- **Sulphonation :**

- **Diazonium salt :** $-\overset{+}{N}\equiv N\cdot\overset{-}{Cl}$ $(Ar-\overset{+}{N_2}\cdot\overset{-}{Cl})$ is colourless, crystalline solid and easily soluble in water. At low temperature it becomes stable in water. In dry state it decomposes easily. Benzene diazonium fluoroborate salt is insoluble in water and is stable at room temperature. The chemical reactions are as follows :


Sandmeyer
CuX / HX
(X = Cl, Br, CN)
—X + N2 + HCl
Cu powder
HCl
—Cl + N2 + CuCl
Chlorobenzene
Cu powder
HBr
—Br + N2 + CuCl
Bromobenzene
N≡N·Cl
Benzenediazonium chloride
KI
Δ
—I + N2 + KCl
Iodobenzene
HBF4
—N2BF4
Δ
—F + BF3 + N2
Fluorobenzene
NaNO2(aq)
Cu, Δ
—NO2 + NaBF4 + N2
Nitrobenzene
H3PO2
or Ethanol
+ N2 + H3PO3 + HCl
(N2 + CH3CHO + HCl)
Benzene
SnCl2 + HCl
Reduction
—NH—NH2 + HCl
Phenyl hydrazine

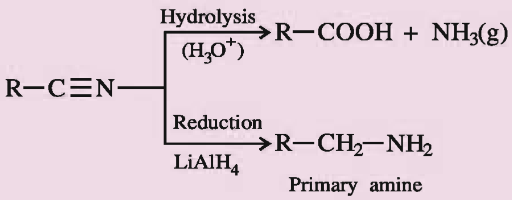


- From the reactions given above, it can be said that diazonium salt is important intermediate compound to introduce groups such as –F, –Cl, –Br, –I, –CN, –OH, $-NO_2$.

- If cyano or nitrile group is present in organic compounds then they are called cyanide or nitrile compounds. Their general formula is R–C≡N for common nomenclature, at the end of the hydrocarbon, the word cyanide is placed. For IUPAC nomenclature, after the longest series of carbon the word nitrile is joined with end of the name of hydrocarbon. If –CN group is attached with cyclic system, then carbonitrile suffix is attached.

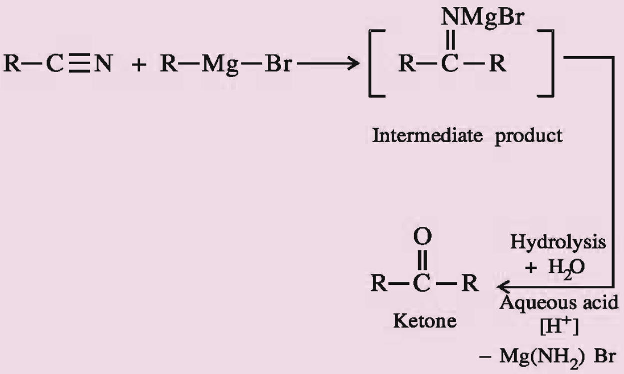
- In the electronic configuration of C–N one σ- and two π-bonds, C and N possess sp hybridisation and R–C–N bond angle is 180^0.

- In alkyl cyanide compounds the $-C^{+\delta}\equiv N^{-\delta}$ bond is polar and intermolecular hydrogen bond being not possible their boiling points are less than corresponding carboxylic acids. These compounds possess low molecular masses, and so are soluble in water and many organic solvents. Ethane nitrile (acetonitrile) being most polar it dissolves many types of organic substances.



$$CH_3-C\equiv N+CH_3-CH_2-OH+H_2O\xrightarrow[\text{Con. }[H_2SO_4]]{\Delta}CH_3COOCH_2CH_3+NH_3$$

Ethanenitrile Ethanol Ethylethanoate



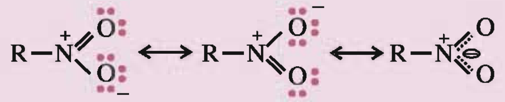
- If isocyanide group is present in organic compounds, they are called isocyanide compounds. These compounds are called isonitrile or carbylamine compounds.
- Before names of cyanide compounds, the prefix 'iso' is attached for the nomenclatures of isocyanide compounds.
- The boiling points of alkyl isocyanides are lower than their isomeric alkyl cyanides.

$$R-\overset{+}{N}\equiv\overset{-}{C}\xrightarrow[\text{LiAlH}_4]{\text{Reduction}}R-NH-CH_3$$

(2^0) Secondary amine

- In organic compounds if nitro group is present then they are called nitro compounds. They are shown as $R–NO_2$, R = alkyl or aryl group. In IUPAC nomenclature of alkyl nitro compounds, the longest original carbon series is selected and the word nitro is placed as prefix first with alkane compounds.

- The resonance forms of alkyl nitro compounds :



$$2CH_3-CH_2-CH_3 \xrightarrow[673\ K]{\text{Fuming } HNO_3} CH_3-NO_2 + CH_2-CH_2-NO_2 + CH_3-CH_2-CH_2-NO_2$$

Propane　　Nitromethane　　Nitroethane　　1-Nitropropane

$$CH_3-CH_2-NO_2 \xrightarrow[\text{or } [Ni] / 3H_2]{LiAlH_4} CH_3-CH_2-NH_2 + 2H_2O$$

Nitroethane　　Ethanamine

EXERCISE

1. Select the proper choice from the given multiple choices :

(1) Which of the following will give secondary amine on reduction ?

(A) Ethane nitrile (B) Ethyl cyanide (C) Nitro ethane (D) Ethane isonitrile

(2) Which of the following compounds gives alcohol with $NaNO_2$ / HCl ?

(A) CH_3-NH_2 (B) $(CH_3)_2NH$ (C) $C_6H_5NH_2$ (D) $C_6H_5-NH-CH_3$

(3) Which of the following compounds will not give diazotisation reaction ?

(A) Benzenamine (B) Phenylmethanamine

(C) p-Aminophenol (D) o-Amino phenol

(4) Which of the following reactions will not give primary amine ?

(A) $CH_3CONH_2 \xrightarrow{Br_2 / NaOH}$ (B) $CH_3-\overset{+}{N}\equiv\overset{-}{C} \xrightarrow{LiAlH_4}$

(C) $CH_3-C\equiv N \xrightarrow{LiAlH_4}$ (D) $CH_3CONH_2 \xrightarrow{LiAlH_4}$

(5) Substance A + $CHCl_3$ + 3KOH $\xrightarrow{\Delta}$ isocyanide + 3KCl + $3H_2O$.

What can be A in the reaction ?

(A) Aniline (B) Dimethylamine

(C) N-Methylaniline (D) All the given

(6) Which of the following substances gives reaction with benzene sulphonyl chloride ?

(A) N, N-Dimethyl ethanamine (B) Trimethylamine

(C) Methylethyl amine (D) Dimethylethyl amine

(7) Which product will be obtained by the hydrolysis of the product obtained by reaction of ethyl cyanide with methyl magnesium bromide ?

(A) Diethylether (B) Methyl ethyl ketone

(C) Dimethyl ketone (D) Methyl ethanoate

(8) In which of the following reagents aminobenzene is soluble ?

(A) HCl (B) NaOH (C) NH_3 (D) $NaHCO_3$

(9) Mention the IUPAC name of the product obtained by reaction of ethanol and concentrated H_2SO_4 with aqueous solution of methyl cyanide.

(A) Methylethanoate (B) Ethylmethanoate

(C) Ethyl acetate (D) Ethyl ethanoate.

(10) What is the correct order of basicity of different types of amines having C_3H_9N molecular formula in non-aqueous solvent ?

(A) $CH_3–NH–CH_2–CH_3 > (CH_3)_3N > CH_3–CH_2–CH_2–NH_2$

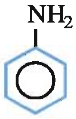
(B) $CH_3–CH_2–CH_2–NH_2 > CH_3–NH–CH_2–CH_3 > (CH_3)_3N$

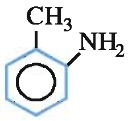
(C) $(CH_3)_3N > CH_3–NH–CH_2–CH_3 > CH_3–CH_2–CH_2–NH_2$

(D) $(CH_3)_3N > CH_3–CH_2–CH_2–NH_2 > CH_3–NH–CH_2–CH_3$

(11) Which of the following substances will give diazotisation reaction ?

(A) 

(B) 

(C) 

(D) All the given

(12) Which of the following compounds is not prepared by Sandmeyer's reaction?

(A) Chlorobenzene (B) Iodobenzene (C) Benzene nitrile (D) Bromobenzene.

(13) Which of the following is a tertiary amine ?

(A) $CH_3–NH–CH_2–CH_3$ (B) $CH_3–CH_2–NH–CH_3$

(C) $CH_3CH_2–NH–CH_2CH_3$ (D) $(CH_3)_2–N–CH_2–CH_3$

(14) Which of the following statements is in correct ?

(A) Some amines possess hydrogen bond

(B) Methylamine is more basic than ammonia

(C) Diethylamine is less basic than methylamine

(D) The boiling point of ethane is lower than that of ethylamine

(15) Which of the following amines gives alcohol or phenol by reaction with $NaNO_2$ and HCl at 273-278 K ?

(A) $C_6H_5CH_2NH\text{–}CH_3$ (B) $(CH_3)_2NH$

(C) $C_6H_5CH_2\text{–}NH_2$ (D) $C_2H_5\text{–}NH_2$

2. Answer the following questions in brief :

(1) Give structural formula and IUPAC names :

(a) Isopropyl amine (h) N, N-Dimethyl aniline

(b) Benzylamine (i) Methylpropyl amine

(c) Propyl amine (j) Diethyl methyl amine

(d) Dimethyl amine (k) N, N-Diethyl aminobenzene

(e) Ethyl methyl amine (l) Methyl isocyanide

(f) Phenylcyanide (m) Phenyl isocyanide

(g) p-Nitroaniline (n) Isopropyl cyanide

(2) Write shape and bond angle of tertiary amine.

(3) Give name and structural formula of Hinsberg reagent.

(4) What is used at present for the separation of amines ?

(5) Write equation of ammonolysis of halides.

(6) Write Hoffmann reaction.

(7) Write reaction of nitrous acid with alkyl amine.

(8) Write bromination of aniline.

(9) Explain giving scientific reasons for the following :

(a) The boiling points of primary amine are higher than those of alkanes.

(b) The boiling points of primary amines are less than those of their corresponding alcohols.

(c) The boiling point of isomeric secondary amine is more than that of tertiary amine and that of primary amine is the highest.

(d) Amine compounds are basic in aqueous solutions.

(e) Aniline is less basic than methylamine.

(f) The boiling points of alkyl cyanides are lower than their corresponding carboxylic acids.

(g) The aqueous solubility of primary amine is more than that of secondary amine.

(10) Explain the following reactions giving reason :

(a) With ethanamine :

(i) Methyl iodide (ii) Ethyl chloride (iii) Nitrous acid

(iv) Hinsberg reaction (v) Acetic anhydride

(b) With aniline :

(i) Acetyl chloride (ii) Nitrous acid (iii) Ethyl iodide

(iv) $CHCl_3$ / KOH

(c) Reaction of methyl cyanide with ethanol.

(d) Ethyl cyanide with ethyl magnesium bromide.

3. Write the answers of the following questions :

(1) Write classification of amines giving examples.

(2) Write electronic configuration of amine (with figure).

(3) Explain reduction of nitrile compounds.

(4) Write Gabriel phthalimide synthesis.

(5) Explain Hoffmann reaction with example.

(6) Explain physical properties of amines.

(7) Explain alkylation of methanamine and aniline.

(8) Explain giving example the reaction to obtain monosubstituted aniline.

(9) Explain nitration of aniline.

(10) Explain preparation of benzene diazonium chloride.

(11) Explain azo coupling reactions.

(12) Write electronic structure and physical properties of cyanide.

(13) Write chemical reactions of cyanide compounds.

(14) Mention the physical properties and resonance structures of nitro compounds.

(15) Explain preparation of nitro compounds and their reduction.

4. Write the answers of the following questions in detail :

(1) Explain separation of 1^0, 2^0 and 3^0 amines.

(2) Write a note on the industrial production of amine.

(3) Explain basicity of aliphatic amines.

(4) Explain basicity of aromatic amines.

(5) Explain chemical reaction of benzene diazonium chloride.

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