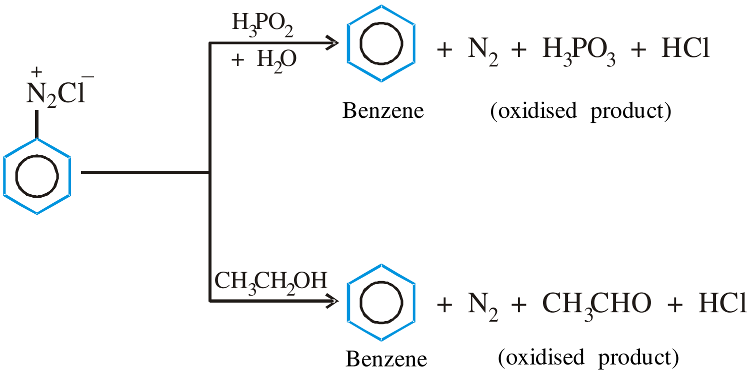
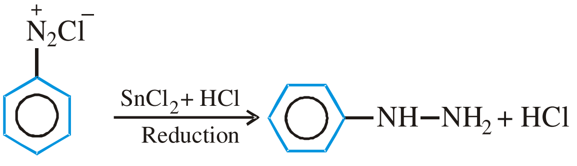


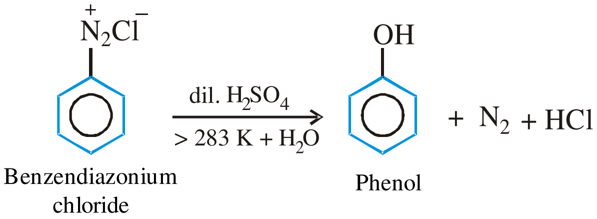
When diazonium salt is reduced with stannous chloride and hydrochloric acid, it gives phenyl hydrazine (Here diazonium group is not substituted).



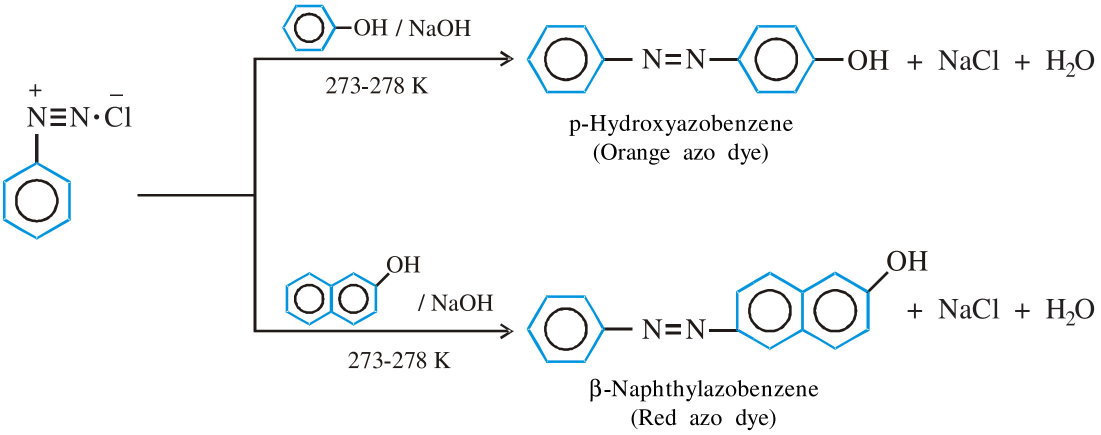
Phenyl hydrazine

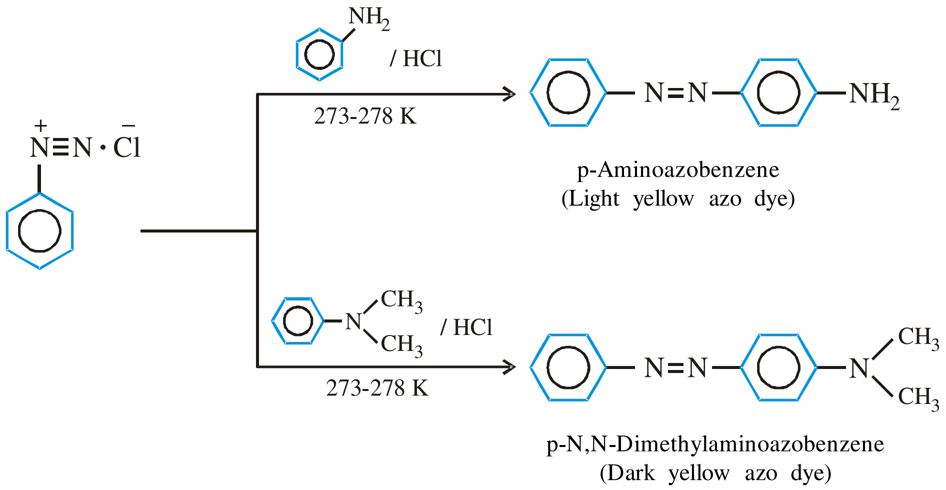
(vi) Phenol is obtained by heating diazonium salt with dil. H_2SO_4 at temperature higher than 283 K.

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



(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.





(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.**

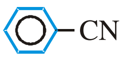
6.9 Cyanide or Nitrile Compounds

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.

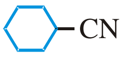
IUPAC Nomenclature of nitrile compounds : For common nomenclature, “Cyanide” word is placed at the end of the name of hydrocarbon. Viz. $CH_3–C\equiv N$ methyl cyanide, $CH_3–CH_2–C\equiv N$ ethyl cyanide etc.

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.**

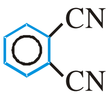
Viz.,



Benzenecarbonitrile



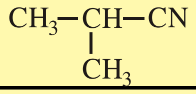
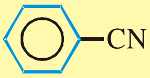
Cyclohexanecarbonitrile



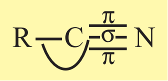
Benzene-1,2-dicarbonitrile

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.	 $CH_3-\underset{\underset{\displaystyle CH_3}{\vert}}{CH}-CN$	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

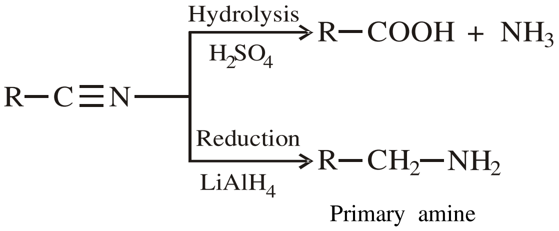
C and N sp hybridisation

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.

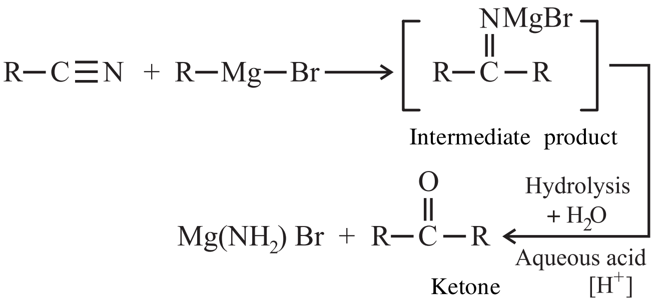
Chemical properties of cyanides : Carboxylic acids are obtained by hydrolysis of cyanide compounds in presence of sulphuric acid and ammonia is liberated. Primary amine is obtained by reduction with $LiAlH_4$.

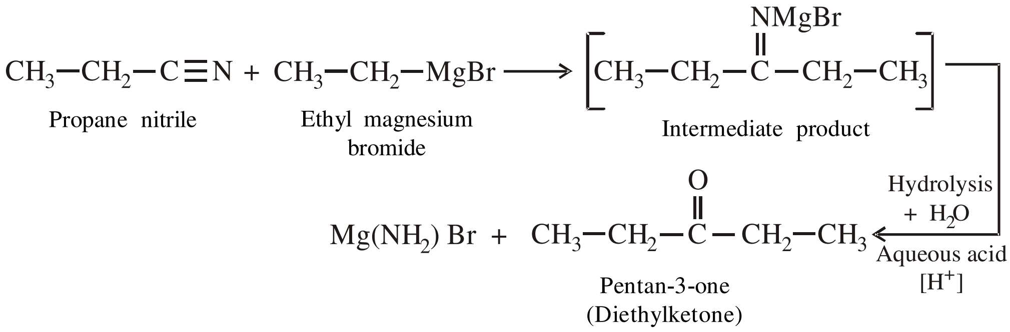


(i) Ethylethanoate (ethyl acetate) is formed when ethane nitrile and ethanol are heated in presence of concentrated sulphuric acid.

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

(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.

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

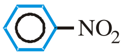
(2⁰) Secondary amine

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

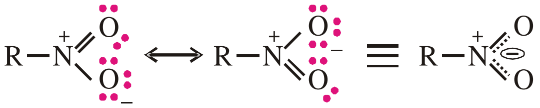
Ethanisonitrile — N-Methylmethanamine (Dimethyl amine)

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.

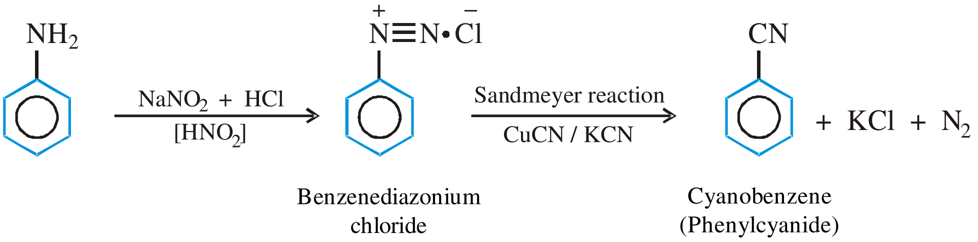
$$\underset{\text{Propane}}{2CH_3-CH_2-CH_3}\xrightarrow[\text{673 K}]{\text{Fuming HNO}_3}\underset{\text{Nitromethane}}{CH_3-NO_2}+\underset{\text{Nitroethane}}{CH_3-CH_2-NO_2}+\underset{\text{1-Nitropropane}}{CH_3-CH_2-CH_2-NO_2}$$

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.

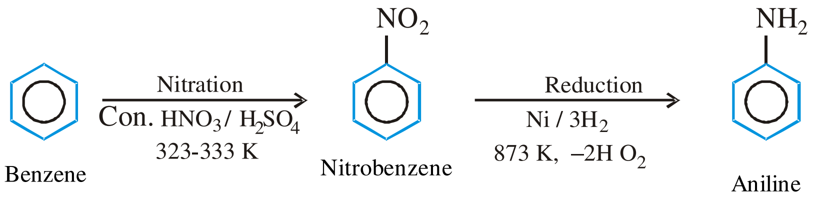
$$\underset{\text{Nitroethane}}{CH_3-CH_2-NO_2}+3H_2\xrightarrow[\text{or [Ni]}]{\text{LiAlH}_4}\underset{\text{Ethanamine}}{CH_3-CH_2-NH_2}+2H_2O$$

Some Organic Conversions :

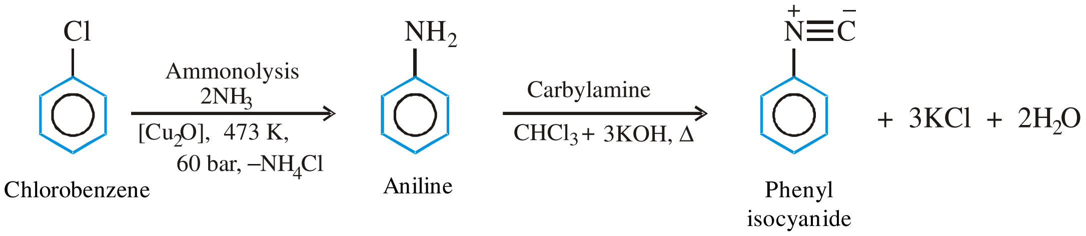
(i) Cyanobenzene from aniline :



(ii) Aniline from benzene :



(iii) Phenyl isocyanide from chlorobenzene :



(iv) Diethylamine from methylcyanide :

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

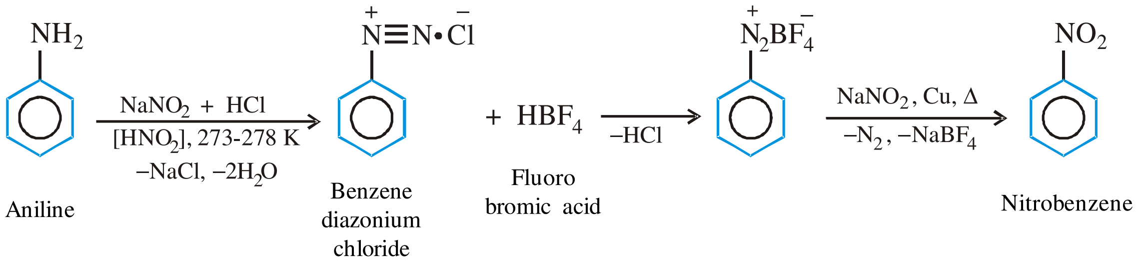
Methylcyanide Ethanamine Diethylamine

(v) N-acetyl ethylamine from acetamide :

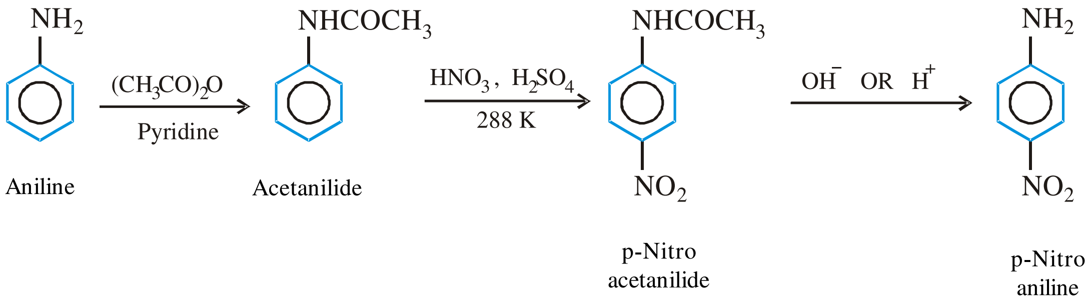
$$CH_3CONH_2 \xrightarrow[(i)\ LiAlH_4\ \ (ii)\ H_2O]{Reduction} CH_3-CH_2-NH_2 \xrightarrow[\substack{or\ (CH_3CO)_2O,\ -HCl\\ or\ -CH_3COOH}]{Acetylation,\ CH_3COCl} CH_3-CH_2NHCOCH_3$$

Acetamide Ethanamine N-Acetylethyle amine

(vi) Nitrobenzene from aniline :



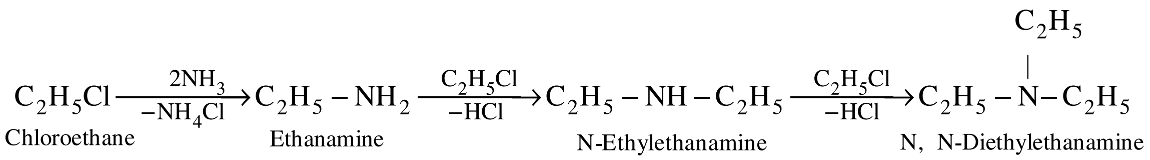
(vii) p-Nitroaniline from aniline :



(viii) Dimethyl amine from methylchloride

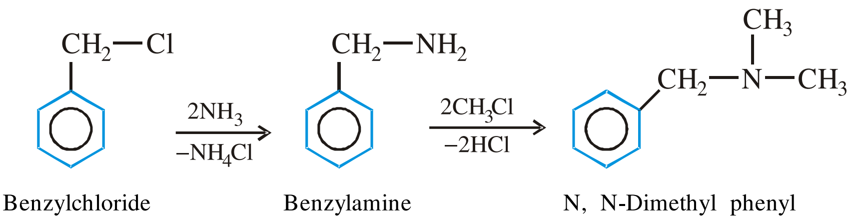
$$\underset{\text{Methylchloride}}{CH_3Cl} \xrightarrow[-NH_4Cl]{\substack{2NH_3 \\ \text{Ammonolysis}}} \underset{\text{Methanamine}}{CH_3-NH_2} \xrightarrow[\substack{CHCl_3\ +3KOH, \\ -3KCl,\ -3H_2O}]{\text{Carbylamine}} \underset{\substack{\text{Methyl} \\ \text{isocyanide}}}{CH_3-N\equiv C} \xrightarrow[Ni\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

(ix) N,N-Diethylethanamine from chloroethane



$$\underset{\text{Chloroethane}}{C_2H_5Cl} \xrightarrow[-NH_4Cl]{2NH_3} \underset{\text{Ethanamine}}{C_2H_5-NH_2} \xrightarrow[-HCl]{C_2H_5Cl} \underset{\text{N-Ethylethanamine}}{C_2H_5-NH-C_2H_5} \xrightarrow[-HCl]{C_2H_5Cl} \underset{\text{N, N-Diethylethanamine}}{C_2H_5-\overset{\overset{\displaystyle C_2H_5}{|}}{N}-C_2H_5}$$

(x) N, N-Dimethylphenylmethanamine from benzyl chloride

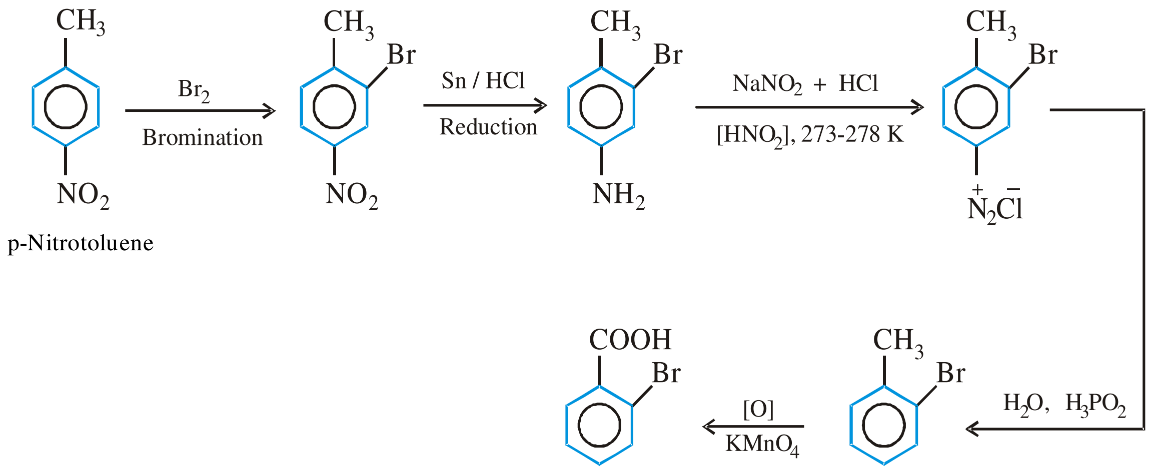


Benzylchloride Benzylamine N, N-Dimethyl phenyl methanamine

(xi) Propan-1-amine from chloroethane :

$$\underset{\text{Chloroethane}}{CH_3-CH_2-Cl} \xrightarrow[KCN,\ -KCl]{\text{Ethanolic}} \underset{\text{Propanenitrile}}{CH_3-CH_2-C\equiv N} \xrightarrow[2H_2\ /\ Ni]{\text{Reduction}} \underset{\text{Propan-1-amine}}{CH_3-CH_2-CH_2-NH_2}$$

(xii) 2-Bromobenzoic acid from p-nitrotoluene



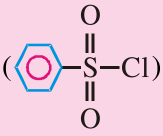
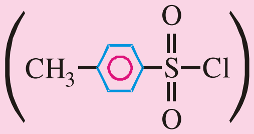
p-Nitrotoluene

2-Bromo benzoic acid

(xiii) Ethanol from acetyl chloride

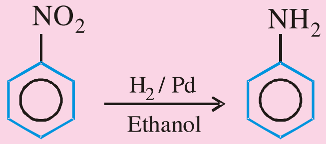
$$\underset{\text{Acetyl chloride}}{CH_3-COCl} \xrightarrow[-NH_4Cl]{2NH_3} CH_3-CONH_2 \xrightarrow[\substack{(i)\ LiAlH_4 \\ (ii)\ H_2O}]{\text{Reduction}} \underset{\text{Ethanamine}}{CH_3-CH_2-NH_2} \xrightarrow[\substack{NaNO_2 \\ +HCl}]{\substack{\text{Nitrous} \\ \text{acid}}} \underset{\text{Ethanol}}{CH_3-CH_2-OH}$$

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 ( $-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-Cl$). In the present time instead of benzene sulphonyl chloride, paratoludine sulphonyl chloride  $\left(CH_3-\ -\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-Cl\right)$ 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



Nitro benzene

Aniline

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

Nitro ethane

Ethanamine

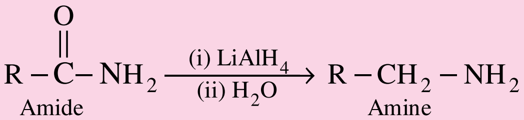
(ii) Ammonolysis of halide :

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

(iii) Reduction of nitrile :

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

(iv) Reduction of amide :

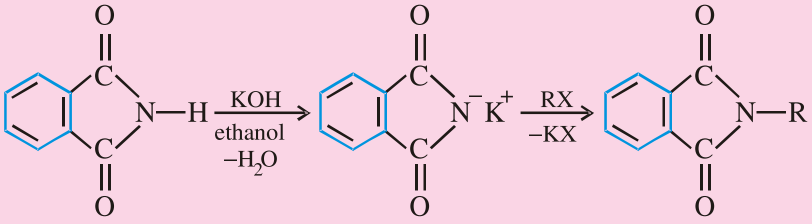


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} R-CH_2-NH_2$$

Amide

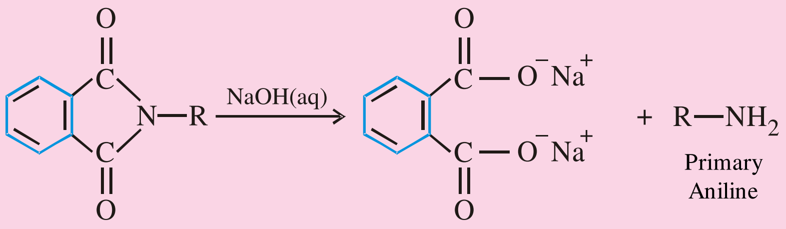
Amine

(v) Gabriel phthalimide :

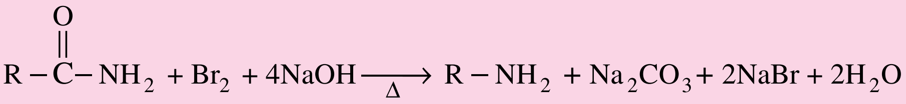


Phthalimide

N-Alkylphthalimide

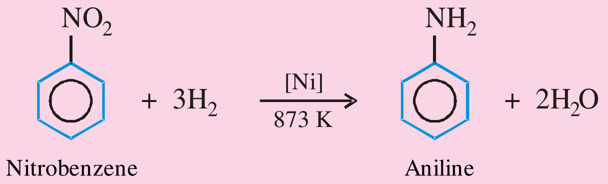


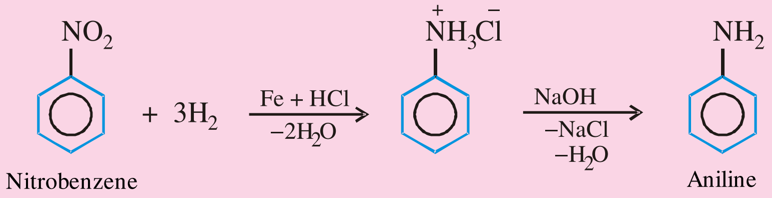
(vi) Hoffmann reaction :

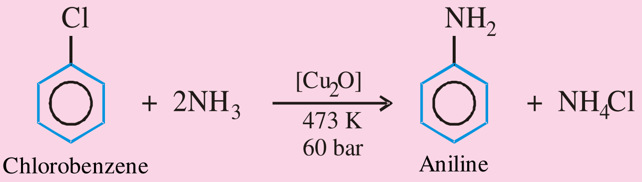


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \xrightarrow[\Delta]{} R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

- **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.

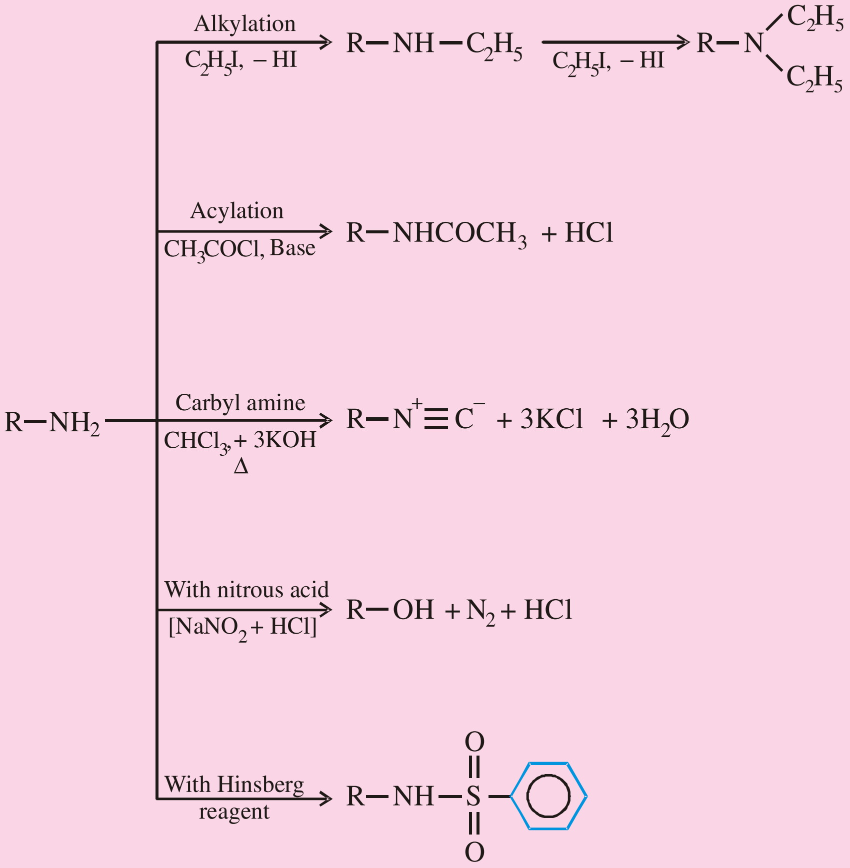
- In aqueous solutions of primary and tertiary amine compounds, hydrogen bonds are formed between molecules of amine and water and so the intermolecular attraction increases. The secondary amines are less soluble in water than the corresponding primary amines.

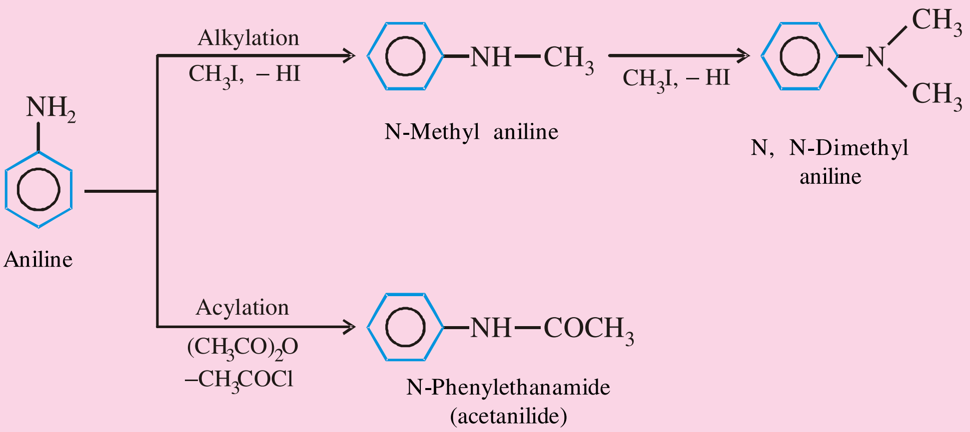
- Amines act as Lewis base because the nonbonding electron pair is on nitrogen atom of amine compounds and forms salt by reaction with acid.

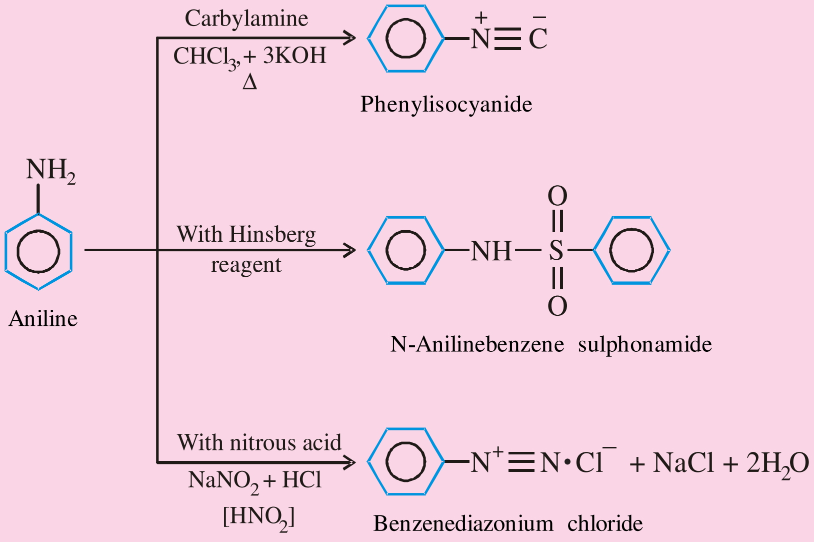
$$R-\ddot{N}H_2 + HX \rightleftharpoons R-\overset{+}{N}H_3\overset{-}{X} \text{ (salt)}$$

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

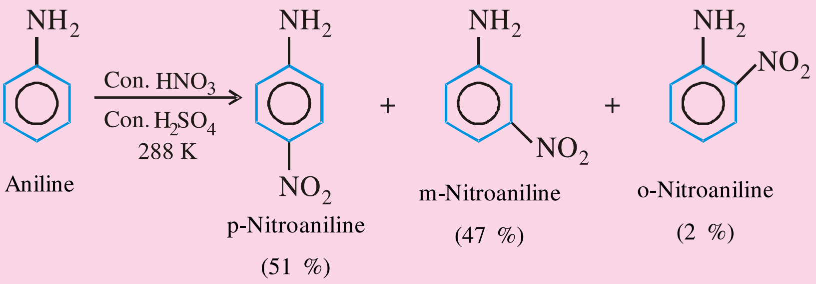
- The order of basicity of ammonia, primary amine, secondary amine and tertiary amines in gaseous state is tertiary amine > secondary amine > primary amine > ammonia.
- Order of basicity in aqueous medium : primary amine > secondary amine > tertiary amine.
- The order of strength as a base in methyl 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 $-NO_2$, $-SO_3H$, $-COOH$, $-X$.



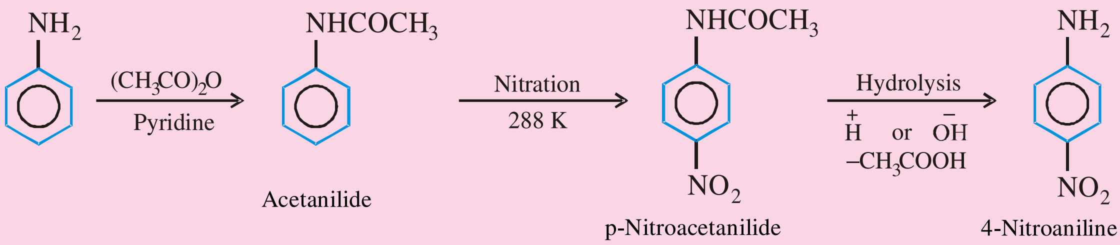




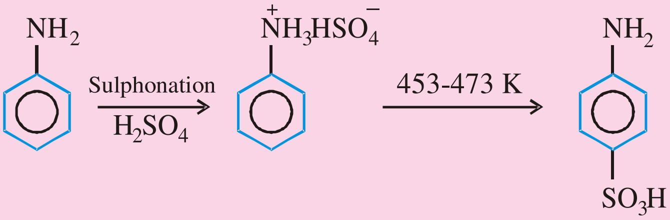
- **Nitration :**

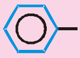


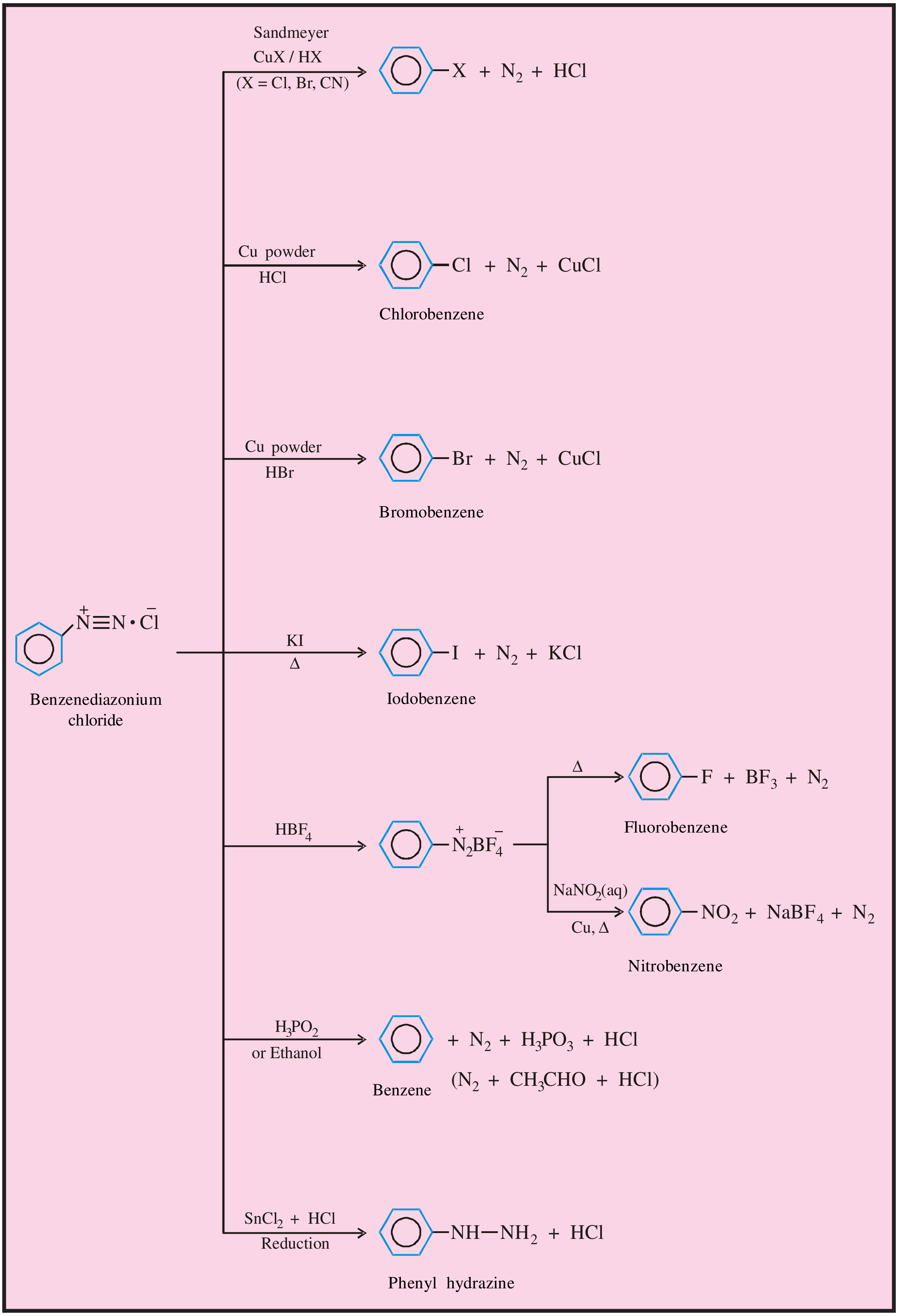
- Here, to obtain monosubstituted derivative acetylation of $-NH_2$ group is done with acetic anhydride and then nitration is carried out.

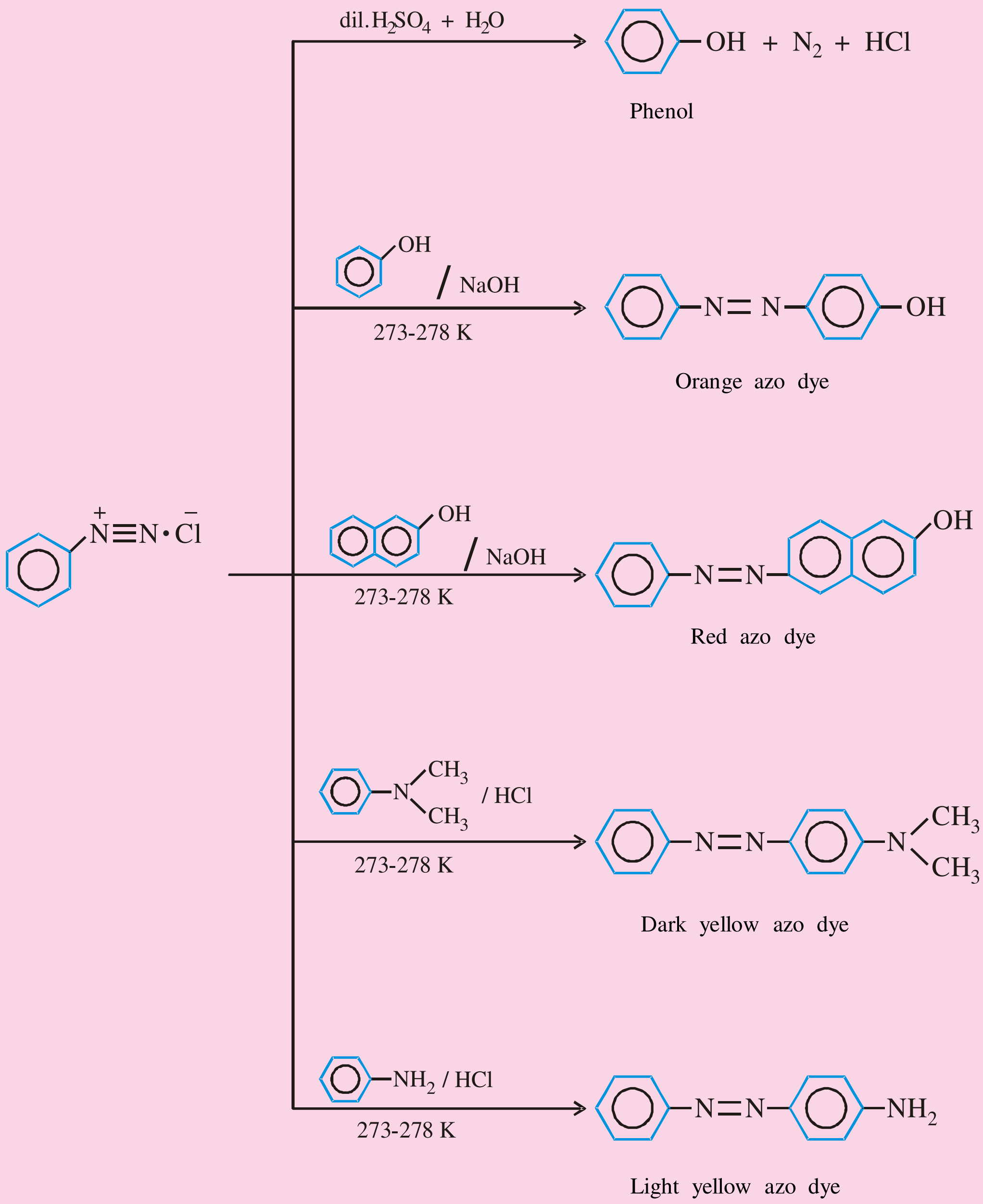


- **Sulphonation :**



- **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

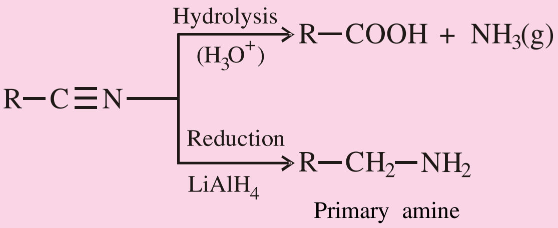


- From the reactions given above, it can be said that diazonium salt is important intermediate compound to introduce groups such as –F, –Cl, –Br, –I, –CN, –OH, $–NO_2$.

- 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.

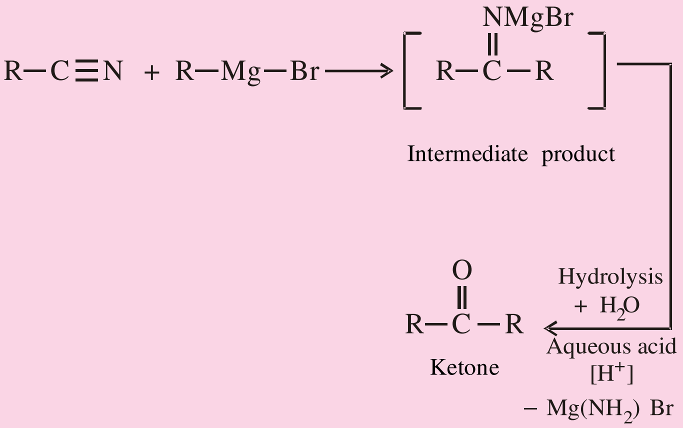
- In the electronic configuration of C–N one σ- and two π-bonds, C and N possess sp hybridisation and R–C–N bond angle is 180^0.

- 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.

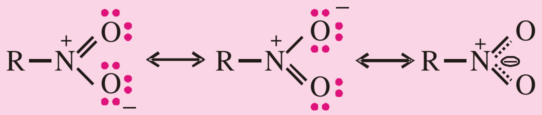
- The boiling points of alkyl isocyanides are lower than their isomeric alkyl cyanides.

$$R-\overset{+}{N}\equiv\overset{-}{C}\xrightarrow[LiAlH_4]{\text{Reduction}}R-NH-CH_3$$

(2^0) Secondary amine

- In organic compounds if nitro group is present then they are called nitro compounds. They are shown as $R\text{–}NO_2$, 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 :



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

Propane Nitromethane Nitroethane 1-Nitropropane

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

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) $CH_3–\overset{+}{N}≡C^{-} \xrightarrow{LiAlH_4}$

(C) $CH_3–C≡N \xrightarrow{LiAlH_4}$ (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 ?

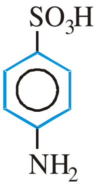
(A) $CH_3–NH–CH_2–CH_3 > (CH_3)_3N > CH_3–CH_2–CH_2–NH_2$

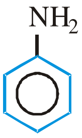
(B) $CH_3–CH_2–CH_2–NH_2 > CH_3–NH–CH_2–CH_3 > (CH_3)_3N$

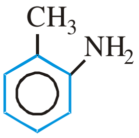
(C) $(CH_3)_3N > CH_3–NH–CH_2–CH_3 > CH_3–CH_2–CH_2–NH_2$

(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) $C_6H_5CH_2NH–CH_3$ (B) $(CH_3)_2NH$

(C) $C_6H_5CH_2–NH_2$ (D) $C_2H_5–NH_2$

2. Answer the following questions in brief :

(1) Give structural formula and IUPAC names :

(a) Isopropyl amine

(b) Benzylamine

(c) Propyl amine

(d) Dimethyl amine

(e) Ethyl methyl amine

(f) Phenylcyanide

(g) p-Nitroaniline

(h) N, N-Dimethyl aniline

(i) Methylpropyl amine

(j) Diethyl methyl amine

(k) N, N-Diethyl aminobenzene

(l) Methyl isocyanide

(m) Phenyl isocyanide

(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 reagent (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.

●

Unit

7

Biomolecules

7.1 Introduction

Chemical compounds present in living systems are known as **biomolecules.** Carbohydrates, proteins, vitamins, nucleic acids, enzymes and lipids are biomolecules. These molecules mainly contain carbon, hydrogen, oxygen, nitrogen, phosphorus and sulphur elements. Biomolecules play the important role in living systems so they are called basic constituents of living systems. We have general information about these biomolecules from the study during previous standards. In this unit we will study about classification, different structures and importance of biomolecules such as carbohydrates, proteins, vitamins, enzymes and nucleic acids.

7.2 Carbohydrates

Carbohydrates are the most important class of organic compounds. Generally they are obtained from plants. They fulfil basic requirements of human life, like foods, clothes and abode. **Carbohydrates are chemically polyhydroxy aldehydes or polyhydroxy ketones or such compounds which can be hydrolysed to these compounds.** Carbohydrates contain carbon, hydrogen and oxygen elements. In formulae of these compounds, the proportion of hydrogen and oxygen elements is 2 : 1. This proportion is equal to proportion of hydrogen and oxygen elements (2 : 1) in water molecule. Therefore, initially these compounds are known as hydrates of carbon. e.g.,

Carbohydrates	**Molecular formula**
(1) Glucose	$C_6H_{12}O_6$ OR $C_6(H_2O)_6$
(2) Sucrose	$C_{12}H_{22}O_{11}$ OR $C_{12}(H_2O)_{11}$
(3) Starch	$(C_6H_{10}O_5)_n$ OR $[C_6(H_2O)_5]_n$

Thus, **general formula of carbohydrates can be written as $C_x(H_2O)_y$ but it is not utterly true.** Some members of carbohydrate class do not possess 2:1 proportion of hydrogen and oxygen in their molecule. e.g., Rhamnose ($C_6H_{12}O_5$). Moreover, some compounds are not members of carbohydrate class but their molecules contain 2 : 1 proportion of hydrogen and oxygen. e.g., formaldehyde (CH_2O), acetic acid ($C_2H_4O_2$), lactic acid ($C_3H_6O_3$) etc. Thus, molecules of some members of carbohydrate class having 2:1 proportion of hydrogen and oxygen elements is like an accidental coincidence. All types of sugars, starch, cellulose etc. compounds are known as carbohydrates. Carbohydrates are often referred to as saccharides because of the sweet taste of the simpler members of the family, the sugars (sugar means saccharum in Latin and sakcharon in Greek)

7.2.1 Classification of Carbohydrates :

Carbohydrates are classified as monosaccharide, oligosaccharide or polysaccharide on the basis of hydrolysis of their molecules.

(1) Monosaccharide : Simplest carbohydrates are included in this class. A carbohydrate that cannot be further hydrolyzed to simpler carbohydrate is called **monosaccharide.** Carbohydrates containing two to ten carbon atoms are included in this class. Their general formula is $C_nH_{2n}O_n$. Glucose ($C_6H_{12}O_6$) and fructose ($C_6H_{12}O_6$) are six carbon atoms containing monosaccharide. They occur in nature.

(2) Oligosaccharide : Oligosaccharide is sugar containing two to four monosaccharide units. Oligosaccharide can be classified as disaccharide, trisaccharide or tetrasaccharide.

(A) Disaccharide : A carbohydrate that can be hydrolyzed to two monosaccharide molecules is called a **disaccharide.**

$$\text{Disaccharide} + \text{Water} \xrightarrow{H^+ \text{ or enzymes}} \text{Two monosaccharides}$$

Carbohydrates containing ten to twelve carbon atoms are included in this class. Their general formula is $C_nH_{2n-2}O_{n-1}$. Sucrose ($C_{12}H_{22}O_{11}$), maltose ($C_{12}H_{22}O_{11}$), lactose ($C_{12}H_{22}O_{11}$), cellobiose ($C_{12}H_{22}O_{11}$) etc. are disaccharides.

(B) Trisaccharide : A carbohydrate that can be hydrolyzed to three monosaccharide molecules is called a **trisaccharide.**

$$\text{Trisaccharide} + \text{Water} \xrightarrow{H^+ \text{ or enzymes}} \text{Three monosaccharides}$$

General formula of trisaccharides is $C_nH_{2n-4}O_{n-2}$. Raffinose ($C_{18}H_{32}O_{16}$) is an example of trisaccharides. Raffinose is also known as melitriose.

(C) Tetrasaccharide : A carbohydrate that can be hydrolyzed to four monosaccharide molecules is called **tetrasaccharide.**

$$\text{Tetrasaccharide} + \text{Water} \xrightarrow{H^+ \text{ or enzymes}} \text{Four monosaccharides.}$$

General formula of tetrasaccharide is $C_nH_{2n-6}O_{n-3}$. Stachyose is an example of tetrasaccharide.

(3) Polysaccharide : Polysaccharides are macromolecular substances. A carbohydrate that can be hydrolyzed to many monosaccharide molecules is called a **polysaccharide.**

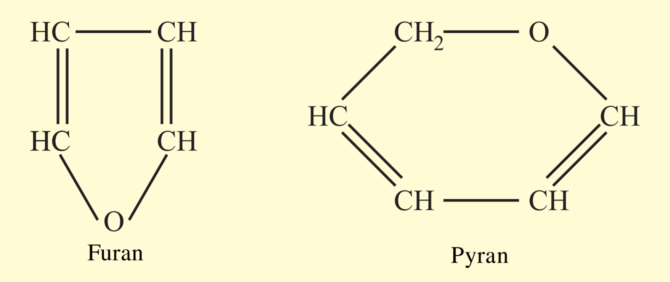
$$\text{Polysaccharide} + \text{Water} \xrightarrow{H^+ \text{ or enzymes}} \text{Many monosaccharide molecules}$$

Starch, cellulose, glycogen, dextrin etc. are common examples of polysaccharides. Starch and cellulose occur in nature.

Generally monosaccharides and oligosaccharides are crystalline, water soluble and sweet in taste. They are known as sugar. Polysaccharides are amorphous, water insoluble and tasteless. They are known as nonsugar.

7.2.2 Nomenclature of Carbohydrates :

Generally the compounds of carbohydrate class contain 'ose' suffix in their names. e.g., Glucose, fructose, lactose, sucrose, maltose, cellobiose, rhamnose, raffinose, stachyose. If carbohydrate compound contains an aldehyde group it is called an aldose and that containing a keto group is called a ketose. Moreover, the number of carbon atoms present in these compounds are indicated by addition of Greek word like tri, tetra, penta and hexa before suffix 'ose' in the name of carbohydrate for three, four, five and six carbon atoms, respectively. e.g., Three carbon atoms and aldehyde group containing carbohydrate compound is called an aldotriose. Three carbon atoms and ketone group containing carbohydrate compound is called ketotriose. Glucose contains six carbon atoms and aldehyde group, so it is known as aldohexose. In the same manner fructose contains six carbon atoms and ketone group so it is known as ketohexose. Moreover, after detailed study of carbohydrate compounds we will know that they generally exist in cyclic form. Many times a proper word is used to mention the five membered or six membered cyclic compounds. e.g., **Pyranose** word is six membered (five carbon atoms and one oxygen atom) cyclic compound. **Furanose** word is used for five membered (four carbon atoms and one oxygen atom) cyclic compound.



Cyclic structure of glucose contains six membered ring so it is known as glucopyranose. Cyclic structure of fructose contains five membered ring so it is known as fructofuranose.

7.3 Monosaccharides

As seen earlier, glucose and fructose are common examples of monosaccharide. So, in this unit, we will study about preparation and different types of structures of glucose as a representative member of monosaccharide class.

7.3.1 Glucose :

Glucose is present in ripe fruits and honey. Grapes contain 20 to 25 % glucose, so glucose is also known as grape sugar. It is also present in human blood and urine in fixed amount.

Preparation of glucose :

(1) From cane sugar : Mixture of glucose and fructose can be obtained by hydrolysis of alcoholic solution of cane sugar (sucrose) with the help of dilute hydrochloric acid or sulphuric acid as catalyst.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

After completion of this reaction, excess amount of alcohol is added to this mixture. Glucose is insoluble in alcohol so it settles down at the bottom of the vessel as precipitate and fructose is soluble in alcohol so it is present in solution. Therefore, glucose separates out easily by filtration.

(2) From starch : In industry, glucose is obtained by hydrolysis of starch with help of dilute H_2SO_4 at 393 K under 2-3 bar pressure.

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow[398\text{ K, 2-3 bar}]{H^+} nC_6H_{12}O_6$$

Starch　　　　　　　　　　Glucose

After completion of hydrolysis, excess sulphuric acid is neutralised by calcium carbonate. Due to this reaction insoluble calcium sulphate is formed. It is removed by filtration. Filtrate is made colourless by adsorption with charcoal. After concentrating this filtrate in absence of air, the crystals of glucose are formed.

Structure of Glucose : Structure of glucose and other aldose compounds are decided by following methods and reactions.

Open chain structure of glucose :

(1) From the analysis of glucose following results are obtained:

Empirical formula : CH_2O

Molecular mass : 180 gram mol^{-1}

Molecular formula : $C_6H_{12}O_6$

(2) When glucose is heated for a long time with hydrogen iodide results in formation of n-hexane. It indicates that all six carbon atoms of glucose are linked in linear chain.

$$C_6H_{12}O_6 \xrightarrow[\Delta]{HI} CH_3–CH_2–CH_2–CH_2–CH_2–CH_3$$

Glucose　　　　　　　　n-Hexane

Thus, C–C–C–C–C–C chain is present in the structure of glucose.

(3) Glucose gives typical reactions with reagents for carbonyl group. e.g., Glucose forms cyanohydrin with hydrogen cyanide (HCN); glucose forms oxime with hydroxylamine (NH_2OH); glucose forms phenylhydrazone with phenylhydrazine ($C_6H_5NHNH_2$). These reactions suggest that carbonyl group ($>C=O$) is definitely present in glucose molecule, because these reactions are specific reactions of carbonyl group.

(4) Oxidation of glucose by bromine water forms equal carbon containing acid-gluconic acid. Solution of ammonical silver nitrate (Tollens' reagent) is reduced to silver by glucose. Glucose can reduce Fehling's solution to cuprous oxide (precipitate) and will be self oxidized to acid. These three reactions prove the presence of aldehyde group in glucose, because all these reactions are specific tests for aldehyde functional group. As per general rule aldehyde group is attached to the end of the carbon chain.

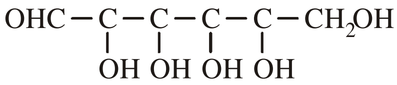
Thus, OHC–C–C–C–C–C chain is present in the structure of glucose.

(5) Glucose is oxidized by strong oxidizing agent nitric acid to equal number of carbon atoms containing dicarboxylic acid-saccharic acid. It suggests that aldehyde group is attached at one end of carbon chain of glucose and primary alcohol ($–CH_2OH$) group is attached at the other end of carbon chain of glucose.

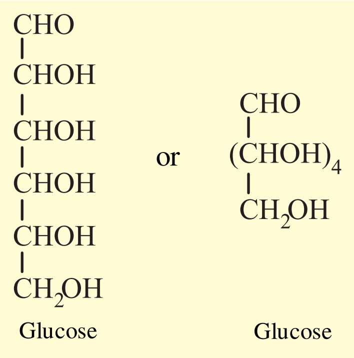
Thus, $OHC–C–C–C–C–CH_2OH$ chain is present in the structure of glucose.

(6) Glucose forms five acetyl groups containing penta acetyl glucose with acetic anhydride in presence of anhydrous zinc chloride or pyridine. It suggests that five hydroxyl groups are present in glucose molecule. Moreover these five hydroxyl groups are attached at

different carbon atoms because if two or more hydroxyl groups are attached at the same carbon atom then that compound is unstable and it loses water molecule easily. But glucose molecule does not lose water molecule and it is a stable compound.

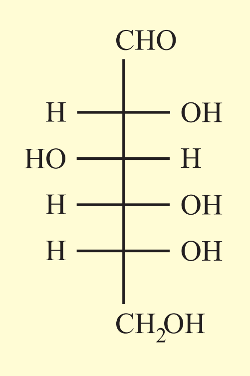
Thus,  $OHC-\underset{OH}{\underset{|}{C}}-\underset{OH}{\underset{|}{C}}-\underset{OH}{\underset{|}{C}}-\underset{OH}{\underset{|}{C}}-CH_2OH$ chain is present in the structure of glucose.

(7) In deciding the chain at point-6, the valency of second to fourth carbon atoms are satisfied by hydrogen atom, as a result structure of glucose obtained is as follows :



Now for understanding the structure of glucose molecule we will study about arrangement of its atoms and groups in space.

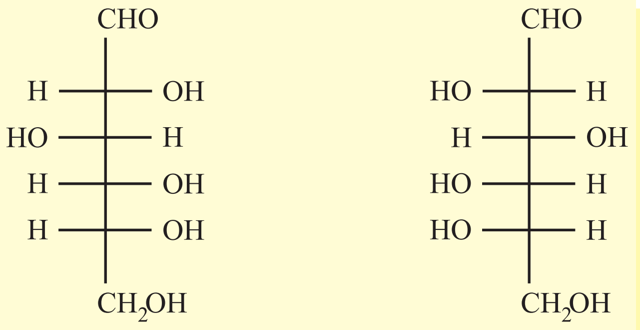
Configuration of Glucose : An arrangement of atoms or groups of molecule in space is called the configuration of that compound. Scientist Emil Fischer determined the configuration of glucose after studying many reactions. It is as following :



D-(+)-Glucose

Scientist Emil Fischer determined the configuration of almost all aldopentose and aldohexose in a period of only four years (1888-1891). In 1902, the Nobel prize was awarded to him for his research works in chemistry. We have learnt about D, L, d or (+), *l* or (–) in unit 6 of semester III.

In Fischer projection of carbohydrate compounds, if the –OH group is attached to the bottom most chiral carbon atom on the right side, the compound possesses D-configuration. If –OH group is attached on the left-side, the compound possesses L-configuration. D- and L-compounds are enantiomers. Optically active organic compound rotates the plane of polarized light. This value of rotation (in degree) is known as angle of rotation (α) shown by that compound. This rotation is measured by **polarimeter instrument.** If only optically active organic compound shows this rotation in a clockwise direction or on a right side direction then (+) sign is put before its rotation value. This compound is called **dextrorotatory.** It is mentioned with d or (+) sign. If any optically active organic compound shows this rotation in an anticlockwise direction or on left side direction then (–) sign is put before its rotation value. This compound is called **levorotatory.** It is mentioned with *l* or (–) sign. d or (+) (dextrorotatory) and l or (–) (levorotatory) compounds are also enantiomers. There is no direct relation of D and L with d or *l*.



D-(+)-Glucose L-(−)-Glucose

The specific rotation $[\alpha]_{\lambda}^{T}$ can be calculated from the value of angle of rotation (α) of optically active compound. The specific rotation is required for the comparison of optical activities of two compounds.

$$[\alpha]_{\lambda}^{T} = \frac{\alpha}{l \times C}$$

where, $[\alpha]$ = specific rotation

T = Temperature (K)

λ = Wavelength of the incident light

(D symbol is used for wavelength of sodium light)

α = Observed angle of rotation (by polarimeter)

l = Length of tube (in decimeter) (10 cm = 1 dm)

C = Concentration of compound (gram ml^{-1})

Example 1 : The observed angle of rotation of 2.0g of sucrose in 10 ml of aqueous solution in a polarimeter tube 10 cm long is $+13.3^{0}$. What is the specific rotation of the solution of sucrose ?

Solution : Here $C = 2.0$ g/10 ml $= 0.2$ gml^{-1}

l = 10 cm = 1 dm

$\alpha = +\ 13.3^{0}$

$$\text{Now, } [\alpha]_{\lambda}^{T} = \frac{\alpha}{l \times C}$$

$$= \frac{+\ 13.3}{1 \times 0.2}$$

$$= +\ 66.5^{0}$$

Thus, specific rotation of sucrose is $+\ 66.5^{0}$

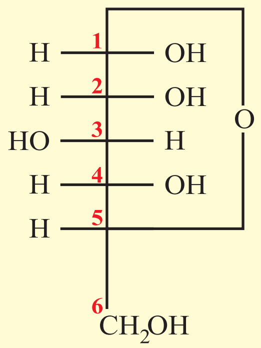
Cyclic structure of glucose : –CHO group is present in configuration of glucose, but glucose does not give some reactions of aldehyde. Moreover glucose also gives some reactions which are not given by an aldehyde.

(1) Glucose does not form addition product with sodium bisulphite ($NaHSO_3$). Generally aldehyde group containing compounds form addition product with sodium bisulphite.

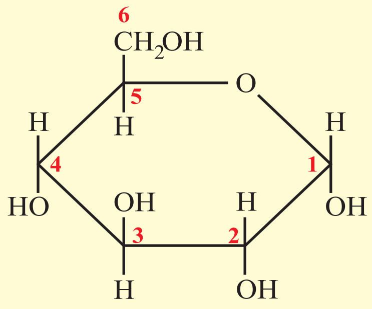
(2) An aldehyde reduces Tollens' reagent and Fehling's solutions. It also gives violet colour with Schiff's reagent. Glucose gives first two reactions but does not give violet colour with Schiff's reagent.

(3) An aldehyde does not show mutarotation property (process of changes in specific rotation) while glucose shows this property.

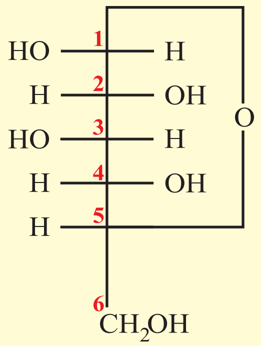
Thus, these reactions create doubt about the open chain structure of glucose. Experimental results have decided that glucose exists in two configurations α and β. Existence of these two configurations of glucose cannot be explained by its open chain structure. In 1895 scientists Fischer, Tollens and Tanret have suggested that structure of glucose should not be an open chain but it is a cyclic form. In 1925, Haworth and Hirst from experimental evidences suggested that glucose molecule may contain pyranose ring (ring contains five carbon atoms and one oxygen atom). Study of X-rays also supported this point. Thus, glucose consists of pyranose ring containing cyclic structure. It can be shown as below :



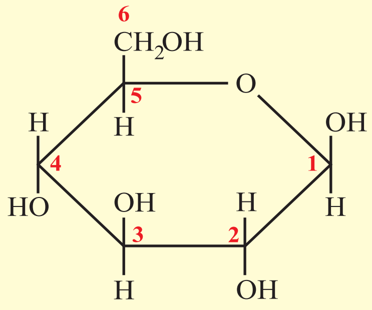
α-D-(+)-glucose
(Fischer projection)



α-D-(+)-glucose
(Haworth projection)

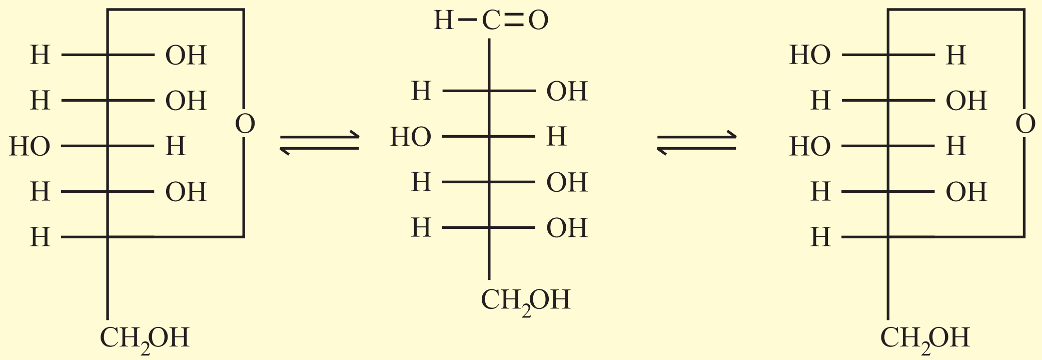


β-D-(+)-glucose
(Fischer projection)



β-D-(+)-glucose
(Haworth projection)

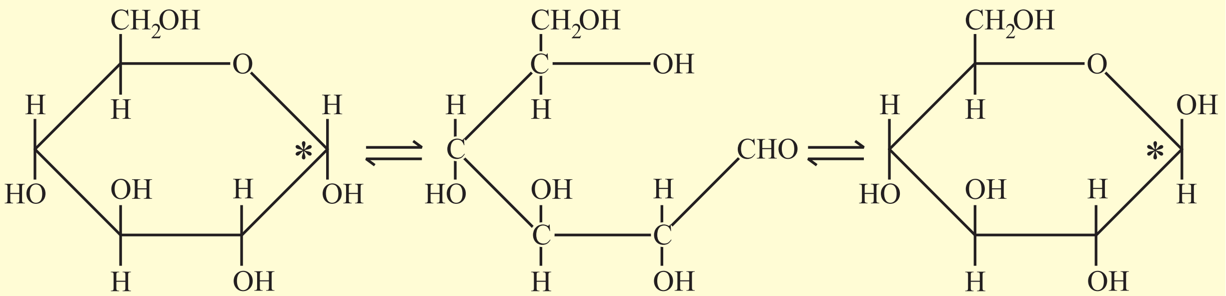
Generally the carbon of cyclic structure which is carbonyl carbon in open chain structure is called **anomeric carbon.** The first carbon atom of cyclic structure of glucose is anomeric carbon because it is a carbonyl carbon in open chain structure of glucose. The isomers differ in configuration at anomeric carbon and are called **anomers.** α-D-(+)-glucose and β-D-(+)-glucose are anomers, because the –OH group is attached at right side to anomeric carbon (C1) of Fischer projection of α-D-(+)-glucose, while the –OH group is attached at left side to anomeric carbon (C1) of Fischer projection of β-D-(+)-glucose. Atom or group on the right side in Fisher projection is below in Haworth projection. α-D-(+)-glucose can be obtained by crystallization from water at 303 K. It can also be obtained by crystallization from ethyl alcohol or glacial acetic acid. The crystals obtained in this way are dissolved in water and the specific rotation of this freshly prepared solution of glucose is $+112^0$. After some time it decreases to $+52.5^0$. β-D-(+)-glucose can be obtained by crystallization from water at 371 K. It can also be obtained by crystallization from pyridine. The crystals obtained this way are dissolved in water and the specific rotation of this freshly prepared solution of glucose is $+19^0$. After some time it increases to $+ 52.5^0$. This process of change in specific rotation is called **mutarotation.** This mutarotation is shown by glucose and it should be due to conversion of α-form to β-from and β-form to α-form. If the solution of glucose shows a specific rotation of $+52.5^0$ then mixture of α-D-(+)-glucose (36 %) and β-D-(+) glucose (64 %) is present in it. This conversion can be explained as follows :



α-D-(+)-glucose
(36 %)

β-D-(+)-glucose
(64 %)

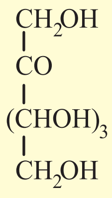
It can be easily understood by Haworth projections also.



α-D-(+)-glucose

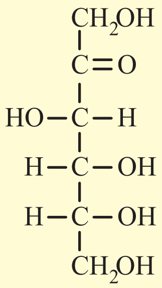
β-D-(+)-glucose

7.3.2 Fructose :



Fructose

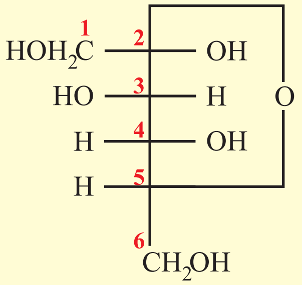
(Open chain structure)



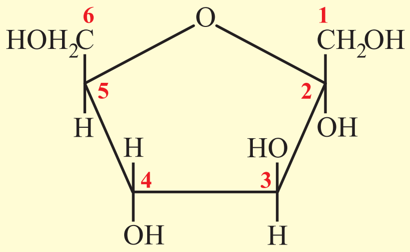
D-(–)-Fructose
(Configuration of fructose)

Fructose is a white crystalline substance. It is soluble in water, partially soluble in alcohol and insoluble in ether. It is levo rotatory optically active compound. It is sweet in taste. Its sweetness is higher compared to glucose, table sugar and also all other sugars. Molecular formula of fructose is $C_6H_{12}O_6$. It contains ketone group and six carbon atoms, so it is known as ketohexose. Experimentally established structures of fructose are mentioned below :

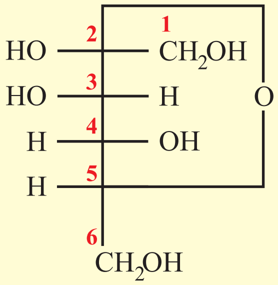
Experimental results have proved that fructose exists in two configurations α-and β-and consists of furanose ring containing cyclic structure. C2 is anomeric carbon in fructose. Fructose shows mutarotation property. Cyclic structure of fructose is as follows :



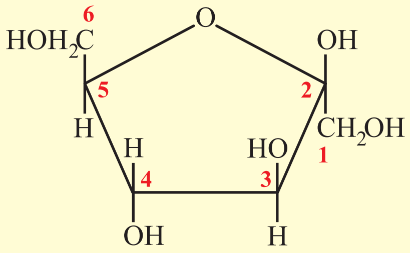
α-D-(–)-Fructose
(Fischer projection)



α-D-(–)-Fructose
(Haworth projection)



β-D-(–)-Fructose
(Fischer projection)



β-D-(–)-Fructose
(Haworth projection)

7.4 Disaccharides

Disaccharide molecule is formed by two monosaccharide units. Hydrolysis of disaccharide by diluted acid or enzyme gives same type or two different types of monosaccharides. Molecular formula of disaccharide is $C_{12}H_{22}O_{11}$.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} \xrightarrow[H_2O]{\text{Hydrolysis}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} \xrightarrow[H_2O]{\text{Hydrolysis}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

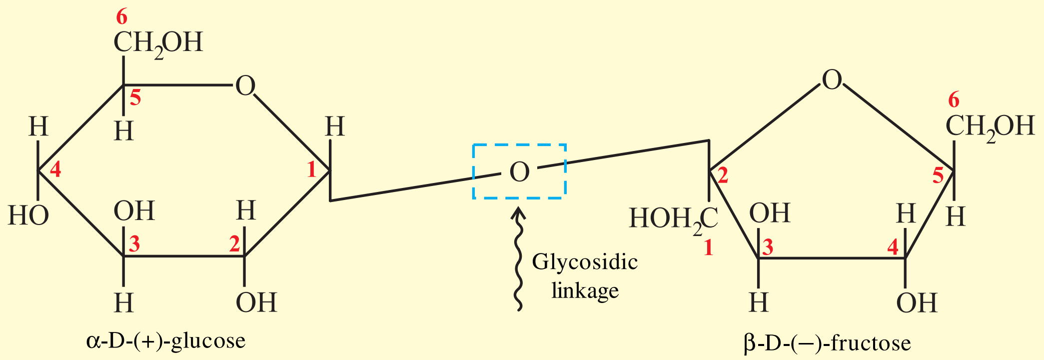
$$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} \xrightarrow[H_2O]{\text{Hydrolysis}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Galactose}}{C_6H_{12}O_6}$$

In disaccharide, the linkage of two monosaccharides joined with each other by linkage of oxygen atom is called glycosidic linkage. Disaccharides are sweet in taste, crystalline and soluble in water.

(1) Sucrose : Sucrose is table sugar used in our daily life. It is mostly found in sugar cane and beets. Therefore it is called cane sugar. Sucrose is colourless, crystalline, sweet in taste and water soluble. This sugar is dextrorotatory (+). Specific rotation of its aqueous solution is $+66.5^0$. Mutarotation does not occur in it. If sucrose is boiled with dilute acid (HCl or H_2SO_4) or hydrolyzed by invertase enzyme then mixture of D-(+)-glucose and D-(–)-fructose in equal proportion (1 : 1) is obtained.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{invertase}]{\text{dilute acid or}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

The aqueous solution of sucrose is dextrorotatory (+) before hydrolysis, but at the end of hydrolysis, produces aqueous solution of glucose and fructose mixture is found as levorotatory (–). The specific rotation of this solution observed is -20^0. The process of change in sign of rotation of sucrose solution is called inversion. The mixture of glucose and fructose obtained at the end of hydrolysis is called invert sugar. The specific rotation in inverted sugar during hydrolysis due to specific rotation of glucose solution is $+ 52.5^0$ and specific rotation of fructose solution is (-92^0). In this, the specific rotation of fructose is higher than that of glucose; as a result final mixture formed is levorotatory (–). Experimental results have proved that the glycosidic linkage is formed between C1 of α-D-(+)-glucose and C2 of β-D-(–)-fructose in structure of sucrose. Thus, **in sucrose, two monosaccharide units are joined to each other by C1–O–C2 linkage.**



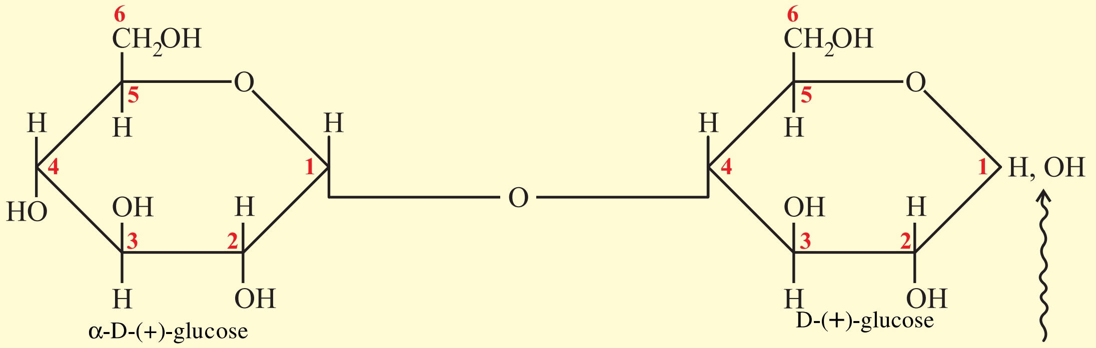
(+) Sucrose

In sucrose both monosaccharide units viz. glucose and fructose are reducing sugars. The –OH group attached to C1 in cyclic structure of glucose and to C2 in cyclic structure of fructose acts as reducing agent group. In sucrose, the reducing agent groups of two monosaccharide units are involved in glycosidic bond, because of which they are not free. Therefore sucrose does not reduce the Fehling's solution and does not form phenylhydrazone with phenylhydrazine. Thus, **sucrose is non-reducing sugar.** Sucrose is taken as a standard for comparison of sweetness of other sugars. Its sweetness index is considered as 100. As per this, glucose, fructose and lactose possess sweetness index as 74, 173 and 16, respectively. When sucrose is heated to 483 K it loses water and forms a brown amorphous substance called **caramal.** This caramal is used as a colouring agent in preparation of sweets and ice-creams.

(2) Maltose : Barley contains malt. Maltose is the main constituent of malt. Therefore maltose is known as malt sugar. Maltose is formed before alcohol is formed from the starch containing compounds. Maltose is colourless and has needle shaped crystals. It is very soluble in water but insoluble in alcohol. Maltose is dextrorotatory (+) and shows mutarotation. Its hydrolysis occurs by dilute acid or maltase enzyme and as a result D-(+)-glucose is formed.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{maltase}]{\text{dilute acid or}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$

Experimental results have proved that in structure of maltose, the glycosidic linkage is formed between C1 of α-D-(+)-glucose and C4 of another D-(+)-glucose unit. Thus, **in maltose two monosaccharide units are joined by C1–O–C4 linkage.**

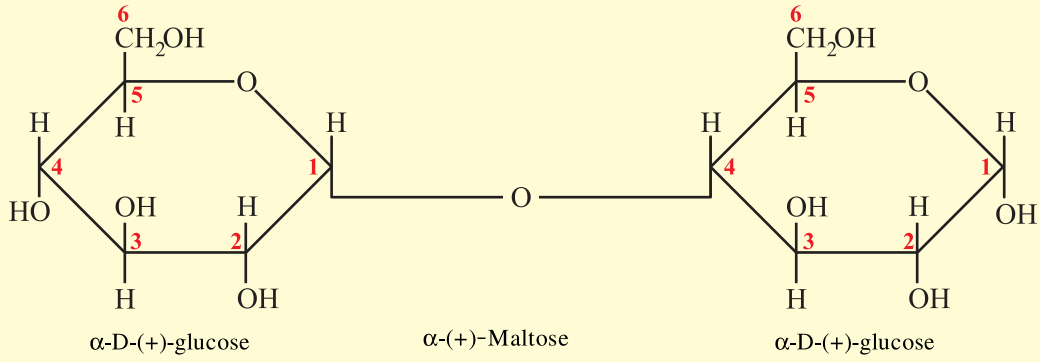


(+)-Maltose

This anomeric carbon (C1) does not have a definite configuration

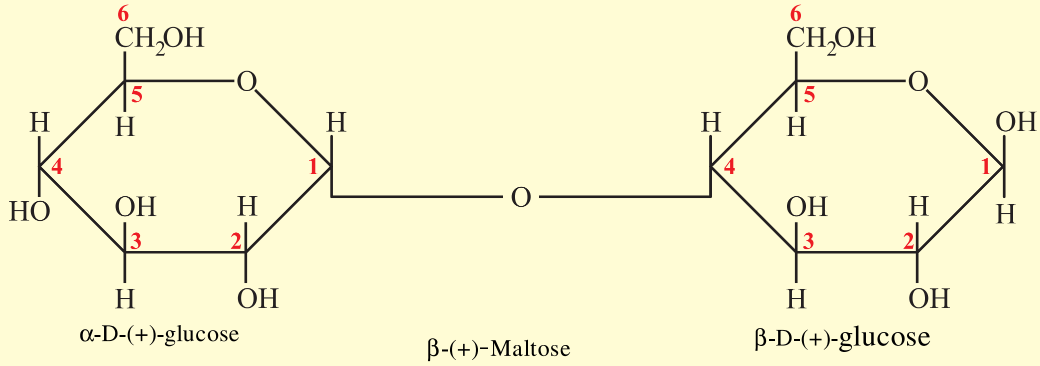
Here, anomeric carbon of one glucose unit, out of two glucose units is not involved in formation of glycosidic bond. The configuration of this anomeric carbon is changed and two forms of maltose are formed. They are called anomers of maltose. If the configuration of this anomeric carbon is similar to α-D-(+)-glucose then it is called α-maltose and if it is similar to β-D-(+)-glucose then it is called β-maltose. Thus,

α-(+)-Maltose = α-D-(+)-glucose + α-D-(+)-glucose



α-(+)-Maltose

β-(+)-Maltose = α-D-(+)-glucose + β-D-(+)-glucose



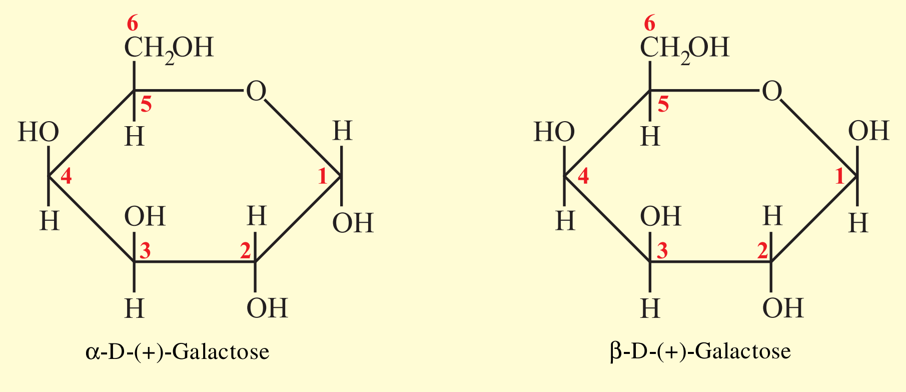
β-(+)-Maltose

In maltose, both the monosaccharide units viz. glucose are reducing sugars. In cyclic structure of glucose, –OH group attached to C1 act as reducing agent. Two glucose units are joined by C1–O–C4 linkage. Thus, reducing agent group of one glucose unit is involved in formation of glycosidic bond but reducing agent group of another glucose unit is free. Therefore maltose reduces Fehling's solution and forms phenylhydrazone with phenylhydrazine. Thus, **maltose is reducing sugar.**

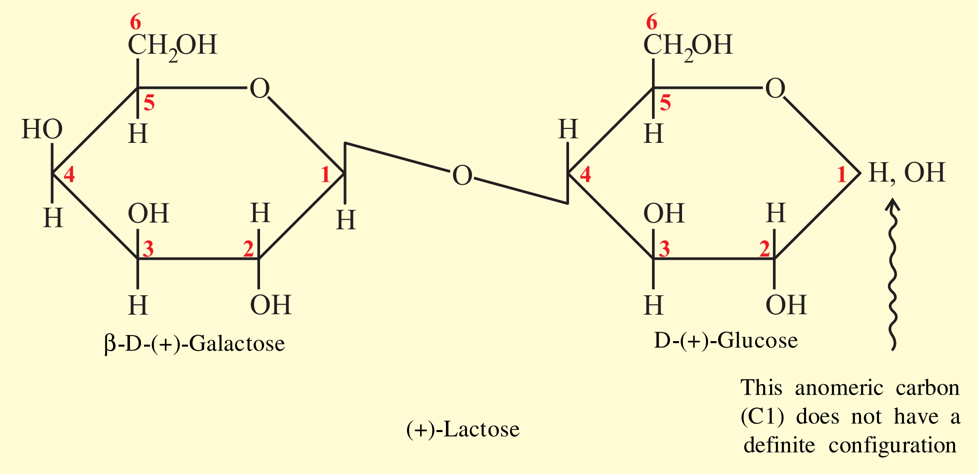
(3) Lactose : Lactose is present in the milk of animals, so it is known as milk sugar. This sugar in not present in plants. Casein is separated from milk; then after this fats are also taken out of it. Remaining milk contains lactose. Lactose sugar can be obtained by concentrating this milk in evacuated vessel. Lactose is soluble in water but insoluble in alcohol. It is dextrorotatory (+) and shows mutarotation. Its hydrolysis occurs by dilute acid or emulsin enzyme and as a result mixture of D-(+) -galactose and D-(+)-glucose in equal proportion (1:1) is formed.

$$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{emulsin}]{\text{dilute acid or}} \underset{\text{Galactose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$

It is necessary to know the structure of galactose before knowing the structure of lactose. Experimental results have proved the cyclic structure of galactose ($C_6H_{12}O_6$) as follows :

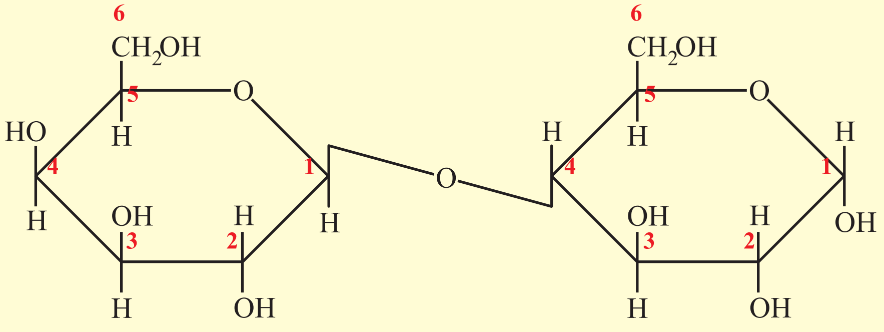


Experimental results have proved that in structure of lactose, the glycosidic linkage is formed between C1 of β-D-(+)- galactose and C4 of D-(+)-glucose. Thus **in lactose two monosaccharide units are joined by C1–O–C4 linkage.**



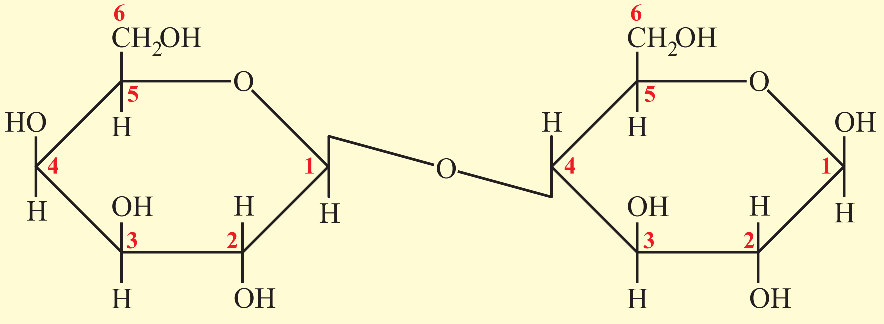
Here, anomeric carbon of D-(+)-glucose unit out of two monosaccharides is not involved in formation of glycosidic bond. The configuration of this anomeric carbon is changed and two forms of lactose are formed. They are called anomers of lactose. If configuration of this anomeric carbon is similar to α-D-(+)-glucose, then it is called α-lactose and if it is similar to β-D-(+)-glucose then it is called β-lactose. Thus,

α-(+)-lactose = β-D-(+)-galactose + α-D-(+)-glucose



β-D-(+)-galactose α-(+)-Lactose α-D-(+)-glucose

β-(+)-lactose = β-D-(+)-galactose + β-D-(+)-glucose



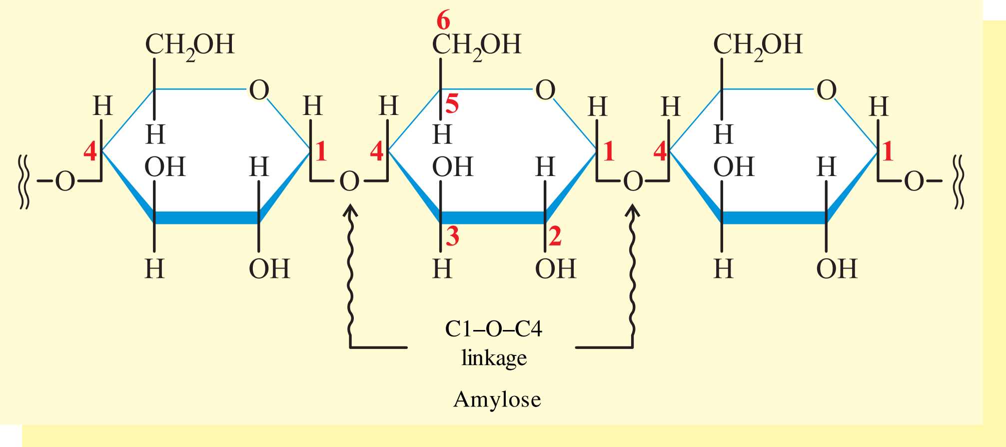
β-D-(+)-galactose β-(+)-Lactose β-D-(+)-glucose

In lactose, both the monosaccharides viz. galactose and glucose, are reducing sugars. In cyclic structures of glucose and galactose, –OH group attached to C1 acts as reducing agent. Galactose and glucose units are joined by C1–O–C4 linkage in lactose. Thus, reducing agent group of glucose unit is free. Therefore lactose reduces Fehling's solution and forms phenylhydrazone with phenylhydrazine. Thus, **lactose is a reducing sugar.**

7.5 Polysaccharides

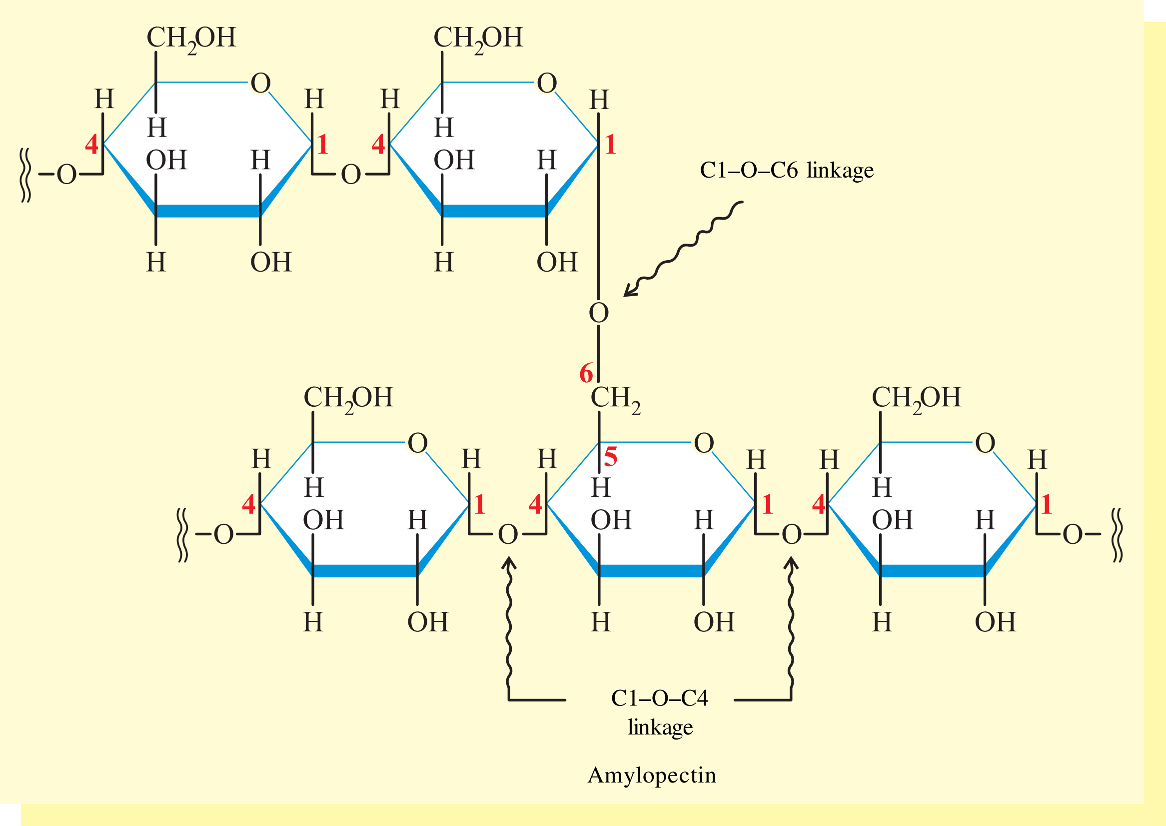
Many monosaccharide molecules are joined with one another in polysaccharide molecule. Starch, cellulose, glycogen and dextrin are examples of polysaccharide. Polysaccharide compounds possess very high molecular mass. Molecular mass of starch may be as high as 8 lakh to 10 lakh. Determination of exact molecular mass of polysaccharide compound is difficult. Therefore, their general formula of them can be written as $(C_6H_{10}O_5)_n$. These compounds are tasteless and amorphous. They are also insoluble in hot water. Hydrolysis of polysaccharide compounds by dilute acid or enzyme form disaccharide and in the end hexose and pentose are formed.

(1) Starch : In nature, the starch is found in all green plants, roots and seeds. Its main sources are wheat, rice, potatoes, maize and sorghum. They occur in the form of granules which vary in size and shape. Starch is colourless, odourless and solid insoluble compound in water. Starch is a mixture of amylose (about 20%) and amylopectin (about 80%) polysaccharides. Amylose structure consists of a long unbranched chain with 200 to 1000 glucose molecules. In this chain α-D-(+)-glucose units are joined by C1–O–C4 linkage.



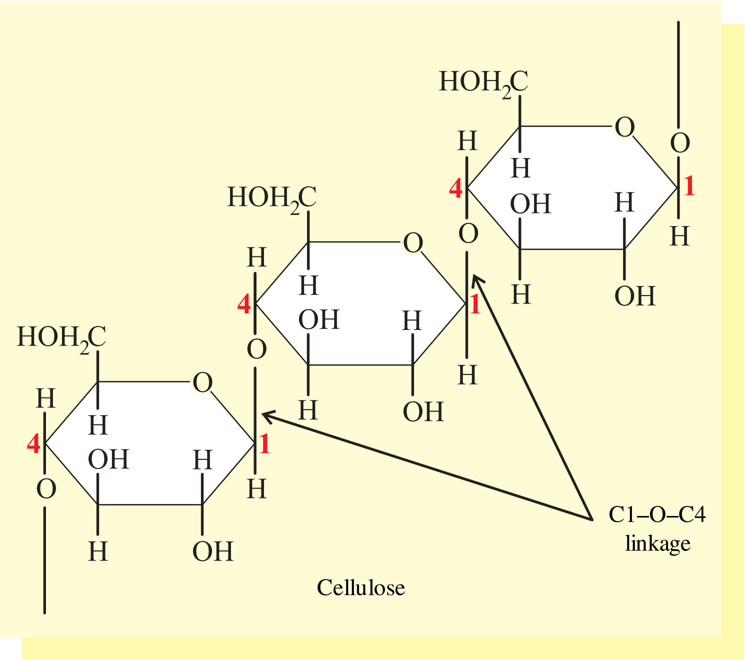
Amylose

In structure of amylopectin α-D-(+)-glucose units are joined by C1–O–C4 linkage, but some α-D-(+)-glucose units are joined by C1–O–C6 linkage and they make branches.



Amylopectin

(2) Cellulose : Cellulose is the main component of cell walls of plants. Cotton is pure form of cellulose. Moreover cellulose is obtained from wood (50% cellulose) and jute (65% cellulose) in moderate proportion. Cellulose is a colourless fibrous compound. It is insoluble in water and in most organic solvents but it is completely soluble in ammonical cupric hyroxide solution. Molecular mass of cellulose is approximately 3 lakh to 5 lakh (1800 to 3000 glucose units). Hydrolysis of cellulose by acid gives D-(+)-glucose. Experimental results have proved that cellulose consists of long chain of β-D-(+)-glucose. In this chain, the glycosidic linkage is formed between C1 of one β-D-(+)-glucose unit and C4 of next β-D-(+)-glucose unit. Thus, **in cellulose, two monosaccharide molecules are joined by C1–O–C4 linkage.**



Cellulose

7.6 Importance of Carbohydrates

- Cellwall of bacteria and plants is made up of cellulose.
- New growing plant uses the starch which is stored in seeds as food for their growth.
- The stored glycogen in animals is converted into glucose and gives energy when required.
- Major component of our food materials is carbohydrates. e.g., table sugar, jaggery, wheat, rice etc.
- Linen, rayon and acetate fibre are form of cellulose. They are used for making clothes.
- Wood is used for construction of building and furniture, wood is also cellulose.
- Carbohydrate compounds are used for preparation of paper, photographic - film, explosive substances, plastics etc.

7.7 Proteins

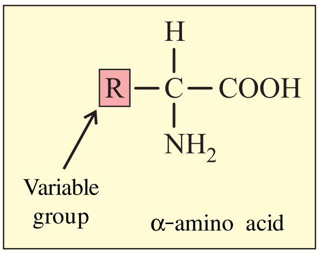
Protein compounds possess very high molecular mass (Approximate 20000 to 2 crore). They are biopolymer complexes of amino acids. They are present in all living cells. Therefore proteins are of prime physiological importance in all living cells. Enzymes, hormones, antibodies are all proteins. A large number of different amino acids are obtained by the hydrolysis of protein. All proteins contain C, H, O, N elements while some may also contain non-metal elements like S,P and metal elements like Fe, Cu, Zn, Mn in trace amount.

$$\text{Proteins} \xrightarrow{\text{Hydrolysis}} \text{Peptides} \xrightarrow{\text{Hydrolysis}} \text{Amino acids}$$

It is necessary to study amino acids before studying the proteins and peptides.

7.7.1 Amino Acids :

In 1901, scientist Emil Fischer had obtained several amino acids by hydrolysis of proteins. Thus, amino acids are the building block of protein structure. The name amino acid indicates that they contain both an amino ($-NH_2$) and carboxyl ($-COOH$) group. Those amino acids which are obtained from hydrolysis of protein are all α-amino acids. This means that in their structure, amino group is on α-carbon atom adjacent to carboxyl group. General structure of α-amino acid is as follows :



$$R-\overset{\displaystyle H}{\underset{\displaystyle NH_2}{C}}-COOH$$

Here –R is not restricted to alkyl group. –R may be open chain, cyclic or aromatic hydrocarbon group; amino, carboxyl, hydroxyl or sulphur containing group (table 7.1). It is necessary to note here that structures of all α-amino acid possess primary amino group, while only proline contains secondary amino group. In this compound nitrogen atom of amino group is involved in five membered ring (table 7.1). All α-amino acids are known by trivial names. From these names general properties or their sources can be known but any information about their structure is not obtained. Glycine got its name because of its sweet taste (in Greek 'Glykos' means 'sweet'). Tyrosine got its name because it was first obtained from cheese (in Greek, 'tyros' means cheese). As we know that amino acid contains one acidic group ($-COOH$) and one basic group ($-NH_2$), therefore acidic, basic and neutral nature of amino acid depends on the nature of attaching group R. Amino acids can be classified in neutral, acidic and basic forms as follows :

(1) **Neutral amino acid :** The amino acid in which the, attaching group-R possesses neutral nature it is known as neutral amino acid (table 7.1). e.g., glycine, alanine.

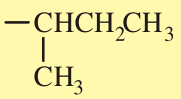
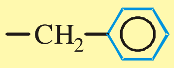
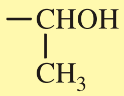
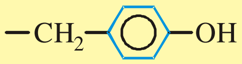
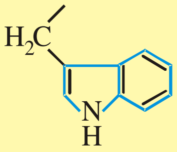
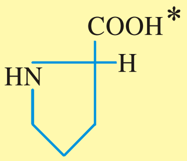
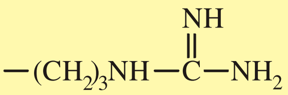
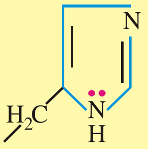
(2) **Acidic amino acid :** The amino acid in which the, attaching group-R possesses acidic nature, it is known as acidic amino acid (table 7.1) e.g., aspartic acid, glutamic acid.

(3) **Basic amino acid :** In which amino acid, attaching group-R possesses basic nature is known as basic amino acid (table7.1). e.g., lysine, arginine.

Amino acids which can be synthesised in body are known as **non-essential amino acids** and those which cannot be synthesised in the body and must be obtained through diet are called **essential amino acids.** Leucine, isoleucine, lysine, methionine, phenyl alanine, threonine, tryptophan, valine, arginine and histidine are essential amino acids. Name and structure of twenty important naturally occurring amino acids are mentioned in table 7.1.

Table 7.1 Important naturally occurring amino acids (For information only)

Sr.	Name of the amino acids	Structure of R	Three letters symbol	One letter symbol
	Neutral amino acid			
1.	Glycine	$-H$	Gly	G
2	Alanine	$-CH_3$	Ala	A
3.	Valine	$-CH(CH_3)_2$	Val	V

4.	Leucine	$-CH_2CH(CH_3)_2$	Leu	L
5.	Isoleucine	 $-\underset{CH_3}{\underset{\vert}{CH}}CH_2CH_3$	Ile	I
6.	Phenylalanine		Phe	F
7.	Asparagine	$-CH_2CONH_2$	Asn	N
8.	Glutamine	$-CH_2CH_2CONH_2$	Gln	Q
9.	Serine	$-CH_2OH$	Ser	S
10.	Threonine	 $-\underset{CH_3}{\underset{\vert}{CH}}OH$	Thr	T
11.	Cysteine	$-CH_2SH$	Cys	C
12.	Methionine	$-CH_2CH_2SCH_3$	Met	M
13.	Tyrosine		Tyr	Y
14.	Tryptophan		Trp	W
15.	Proline		Pro	P
	Acidic amino acids			
16.	Aspartic acid	$-CH_2COOH$	Asp	D
17.	Glutamic acid	$-CH_2CH_2COOH$	Glu	E
	Basic amino acids			
18.	Lysine	$-(CH_2)_4NH_2$	Lys	K
19.	Arginine	 $-(CH_2)_3NH-\overset{\overset{NH}{\Vert}}{C}-NH_2$	Arg	R
20.	Histidine		His	H

* It is not only structure of R but it is entire structure of amino acid