

NEET | JEE

ESSENTIALS

Class
XII

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Unit 7

Organic Compounds Containing Nitrogen | Biomolecules

ORGANIC COMPOUNDS CONTAINING NITROGEN

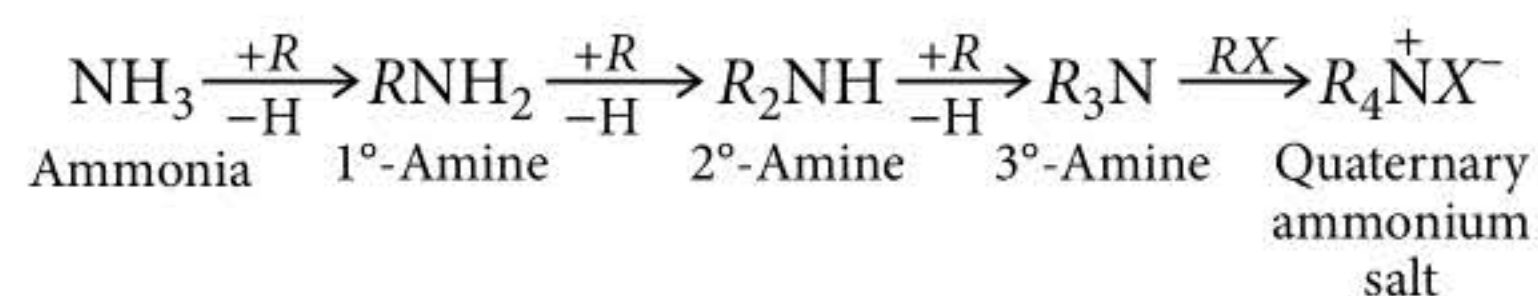
INTRODUCTION

- Nitrogen is an important constituent of many organic compounds. The important classes of organic compounds containing nitrogen as a part of functional group are :


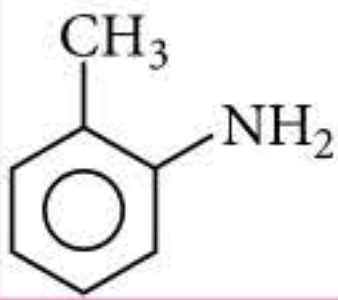
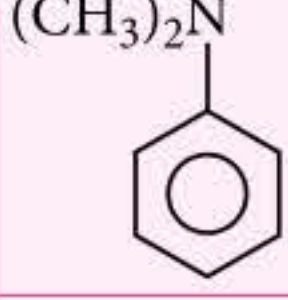
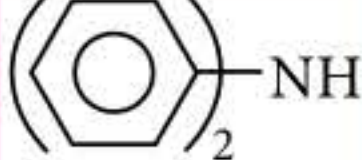
Functional group	Class of compounds
$-\text{NH}_2$	Amines
$-\text{C}\equiv\text{N}$	Cyanides
$-\text{N}\equiv\text{C}$	Isocyanides
$-\text{N}\begin{matrix} \text{O} \\ // \\ \text{O} \end{matrix}$	Nitro compounds
$-\text{O}-\text{N}=\text{O}$	Nitrites
$-\text{N}_2^+\text{X}^-$	Diazonium salts

AMINES

- Amines are regarded as derivatives of ammonia in which one, two or all three hydrogen atoms are replaced by alkyl and/or aryl groups.

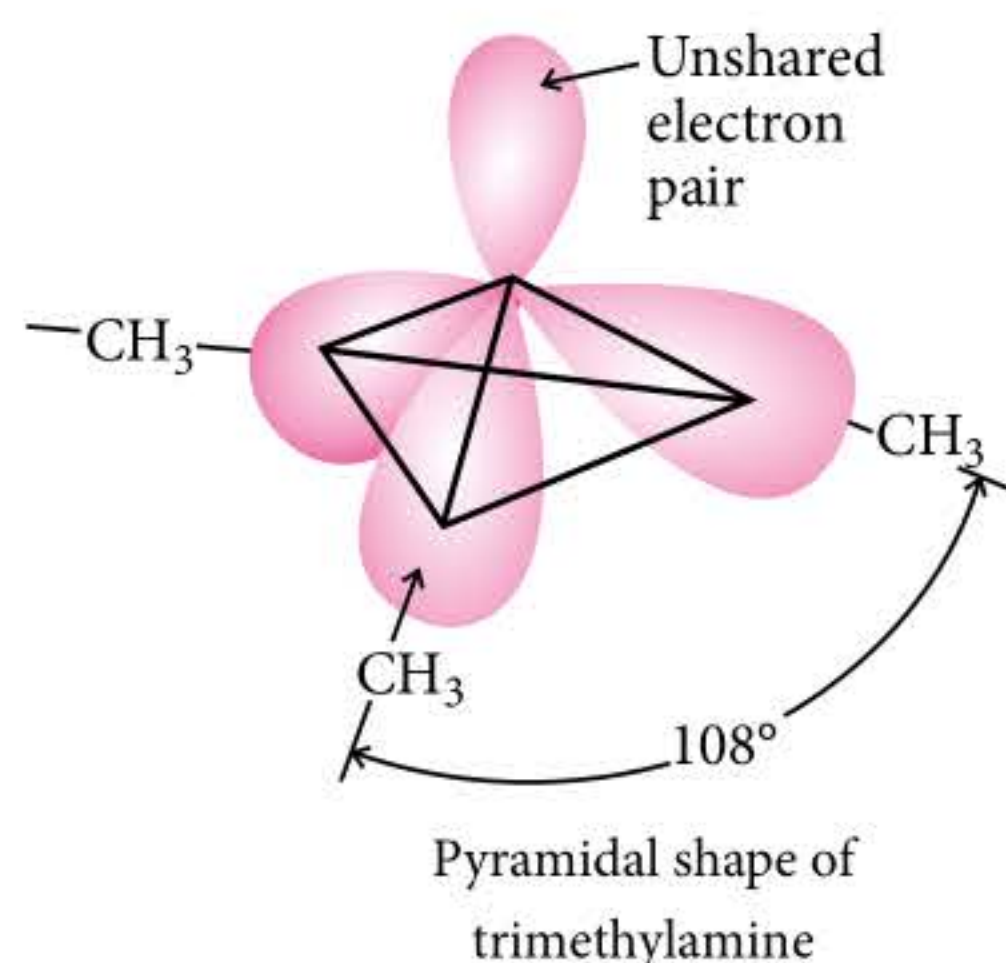


Nomenclature

Aliphatic amine	Common name	IUPAC name
CH_3NH_2	Methylamine	Methanamine
$(\text{CH}_3)_2\text{CHNH}_2$	Isopropylamine	Propan-2-amine
$\text{CH}_3\text{NHC}_2\text{H}_5$	Ethylmethylamine	N-Methylethanamine
$(\text{CH}_3)_3\text{N}$	Trimethylamine	N, N-Dimethylmethanamine
Aromatic amine	Common name	IUPAC name
	Aniline	Benzenamine
	o-Toluidine	2-Methylbenzenamine
	N,N-Dimethylaniline	N, N-Dimethylbenzenamine
	Diphenylamine	N-Phenylbenzenamine

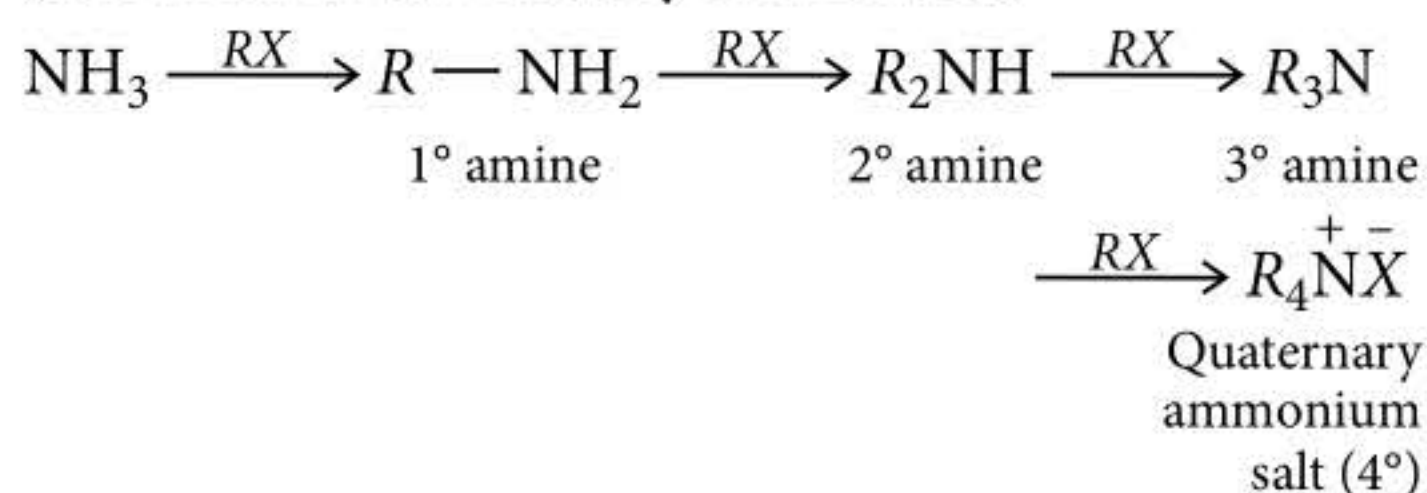
Structure

- N-atom in amines is sp^3 -hybridised with tetrahedral structure where one position of the tetrahedral is occupied by a lone pair. Thus, the actual geometry is pyramidal with bond angle little less than 109.5° .



Preparation

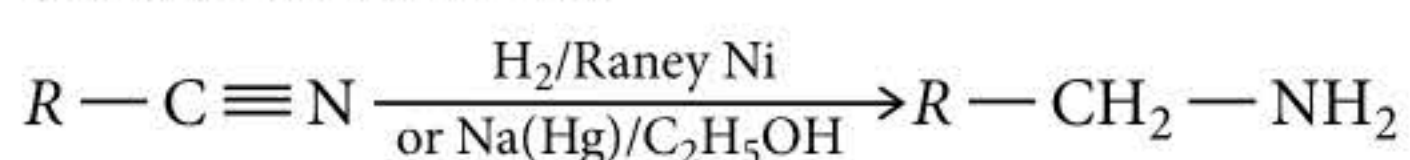
Ammonolysis of alkyl halides (Hoffmann's ammonolysis method)



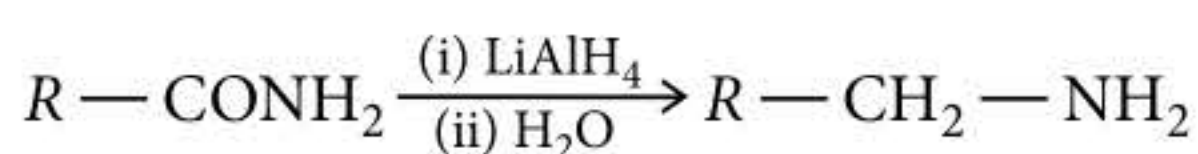
(Reactivity order : $\text{R-I} > \text{R-Br} > \text{R-Cl}$)

Reduction of nitriles

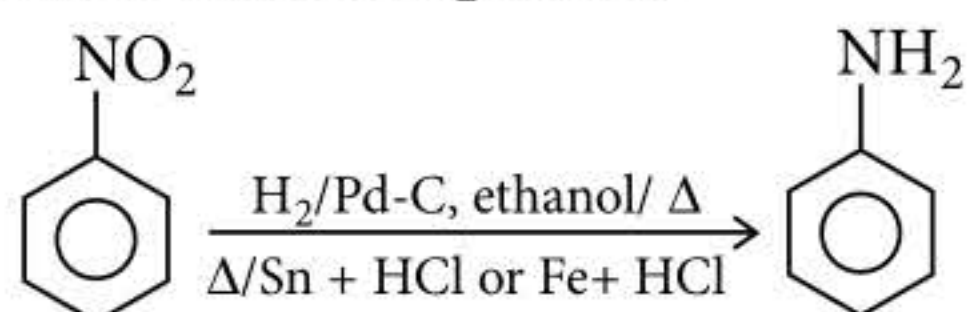
(Mendius reduction)



Reduction of amides



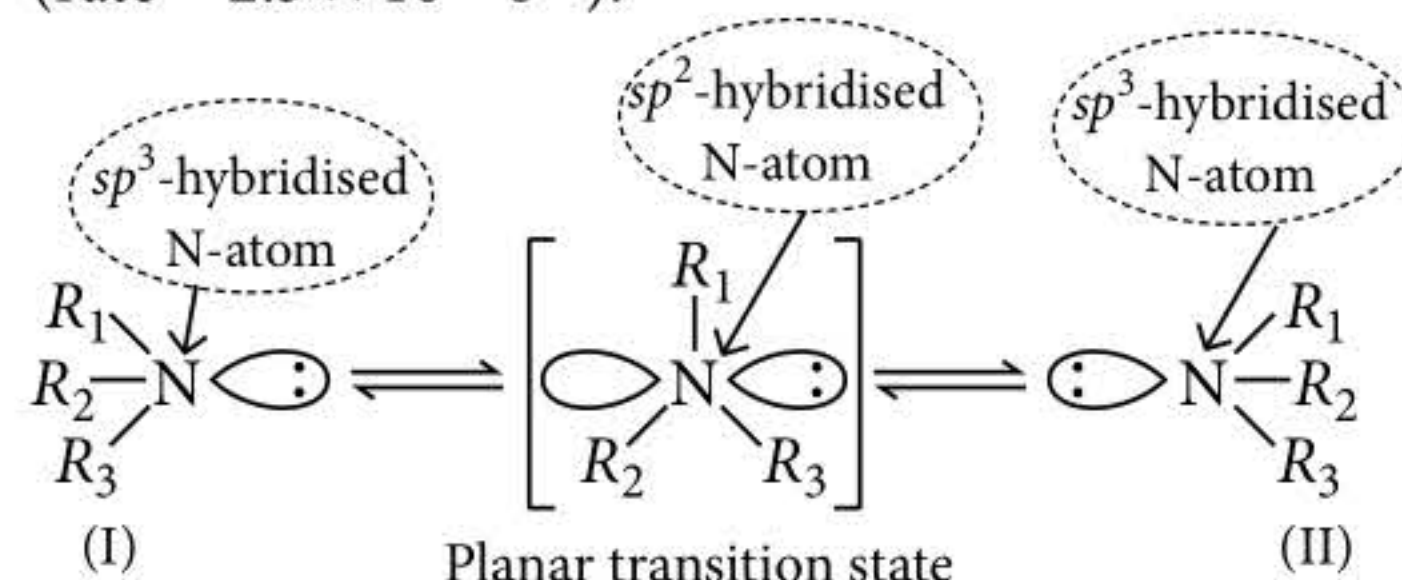
Reduction of nitro compounds



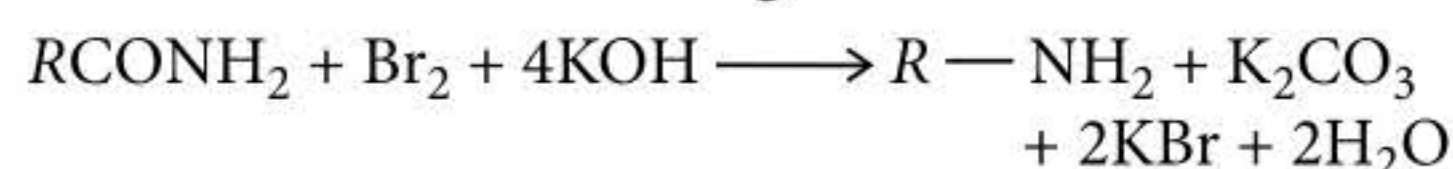
(Fe/HCl is preferred because FeCl_2 formed gets hydrolysed to release HCl gas.)

Optical Activity

- Amines containing different substituents on nitrogen are chiral. 2° and 3° amines exhibit optical activity or enantiomerism. However, unlike chiral carbon compounds, most chiral amines cannot be resolved as two enantiomeric forms rapidly interconvert into one another by **nitrogen inversion** or **amine inversion**. This is also known as **flipping**, (resembles an umbrella turning inside out) which occurs very rapidly (rate = $2.3 \times 10^{10} \text{ s}^{-1}$).

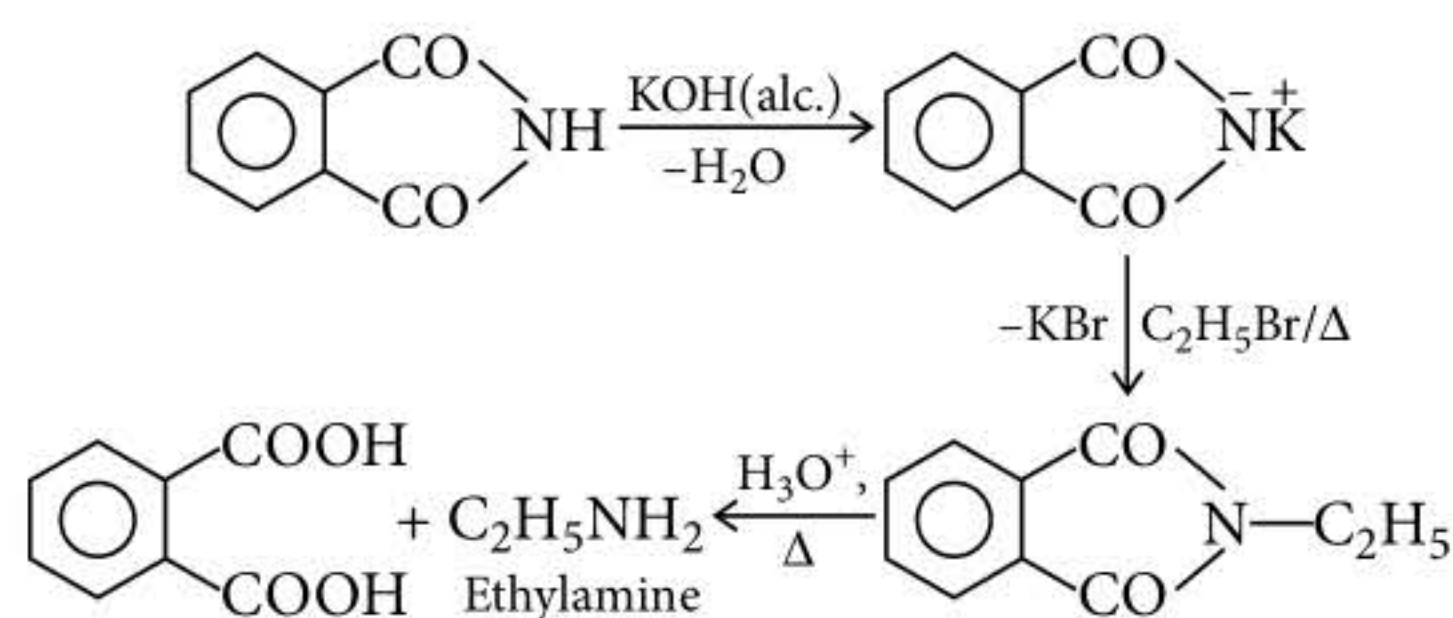


Hoffmann bromamide degradation reaction



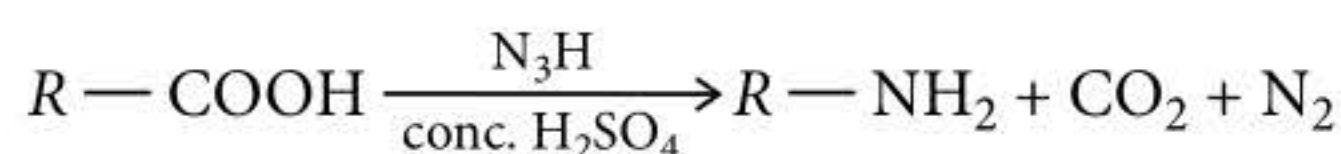
(Migration of alkyl group from carbonyl to nitrogen)

Gabriel phthalimide synthesis

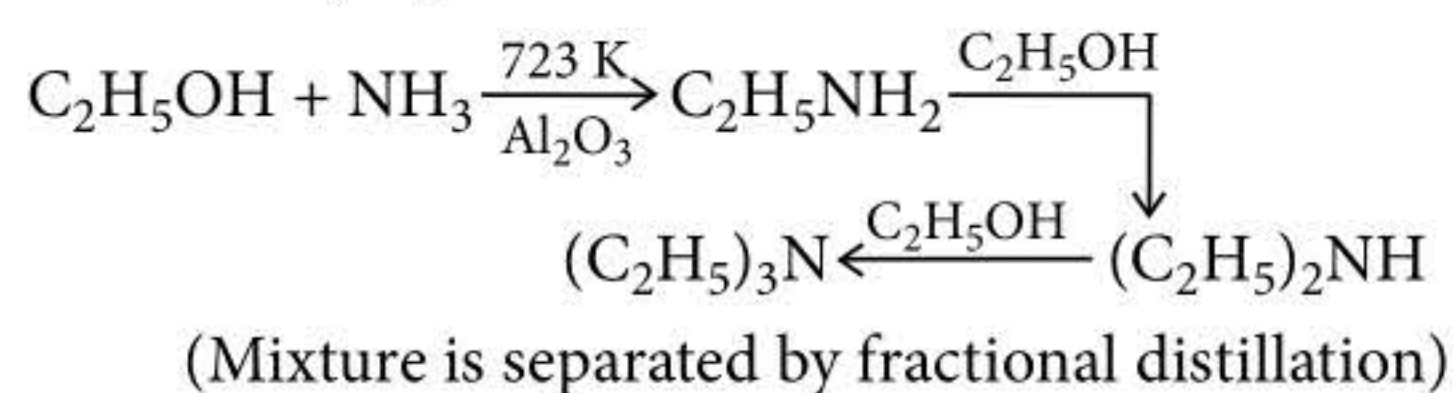


(Only for preparation of aliphatic primary amines)

Schmidt reaction



Industrial preparation



Physical Properties

- Pure amines are almost colourless but develop colour on keeping in air due to oxidation.
- Amines have higher b.pt. than hydrocarbons due to hydrogen bonding but have lower b.pt. than alcohols and carboxylic acids as electronegativity of nitrogen is lower than that of oxygen.
- Lower aliphatic amines are soluble in water due to hydrogen bonding, solubility decreases with increase in molar mass of amines.

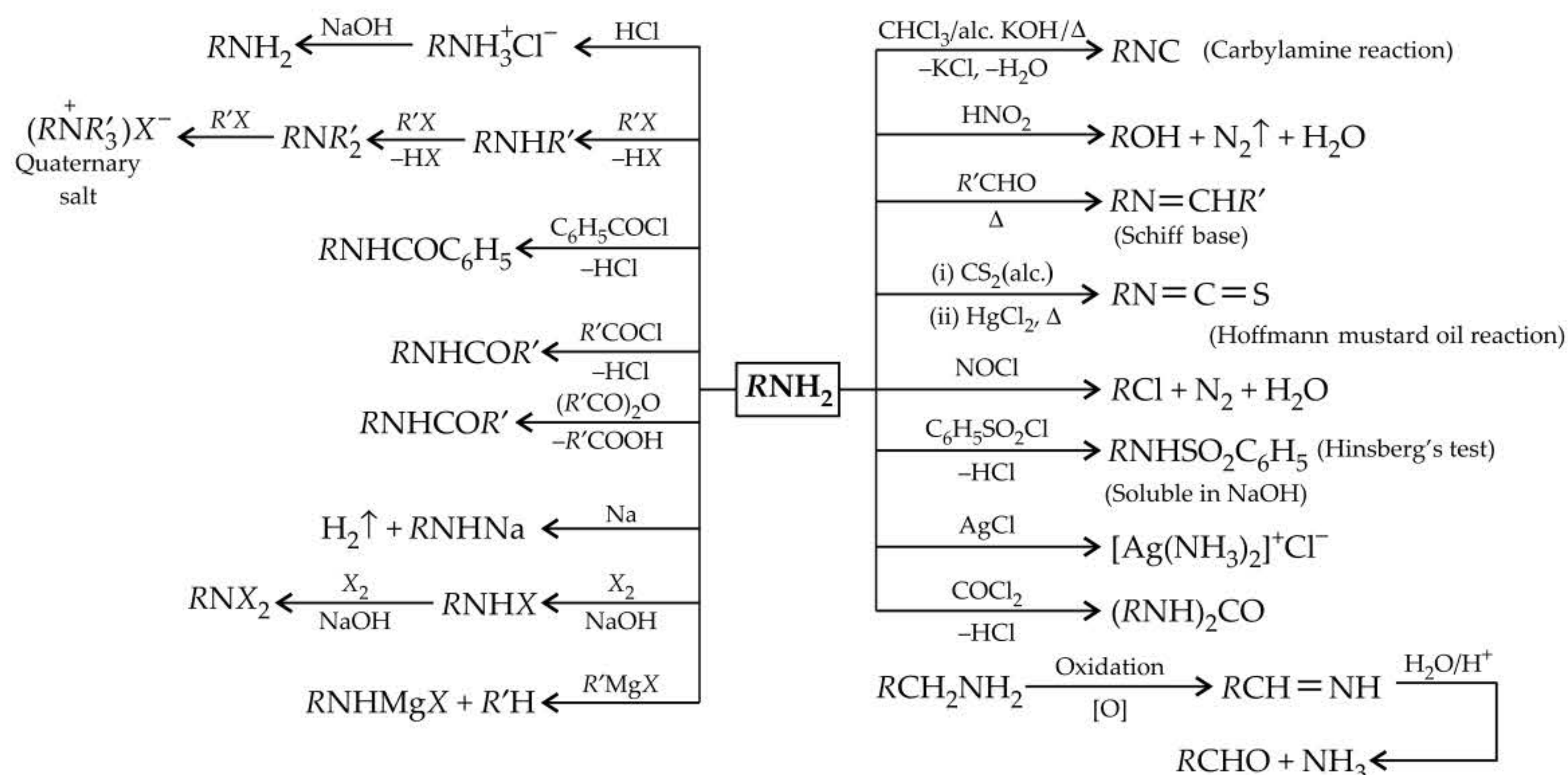
Basic Character

Aliphatic amines :

- All aliphatic amines are stronger bases than ammonia due to +I effect of alkyl groups.
- In aqueous solutions, the basicity of methylamines follows the order : $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N}$ (i.e., $2^\circ > 1^\circ > 3^\circ$) but for ethylamines and all other higher amines basicity follows the order : $\text{R}_2\text{NH} > \text{R}_3\text{N} > \text{RNH}_2$ (i.e., $2^\circ > 3^\circ > 1^\circ$).
- In non-aqueous solvents (e.g., chlorobenzene) and in gaseous phase, the order of basicity is : $3^\circ \text{ amine} > 2^\circ \text{ amine} > 1^\circ \text{ amine}$.
- Greater the value of K_b or smaller the value of $\text{p}K_b$, stronger is the base.

Chemical Properties

Aliphatic amines :



Aromatic amines :

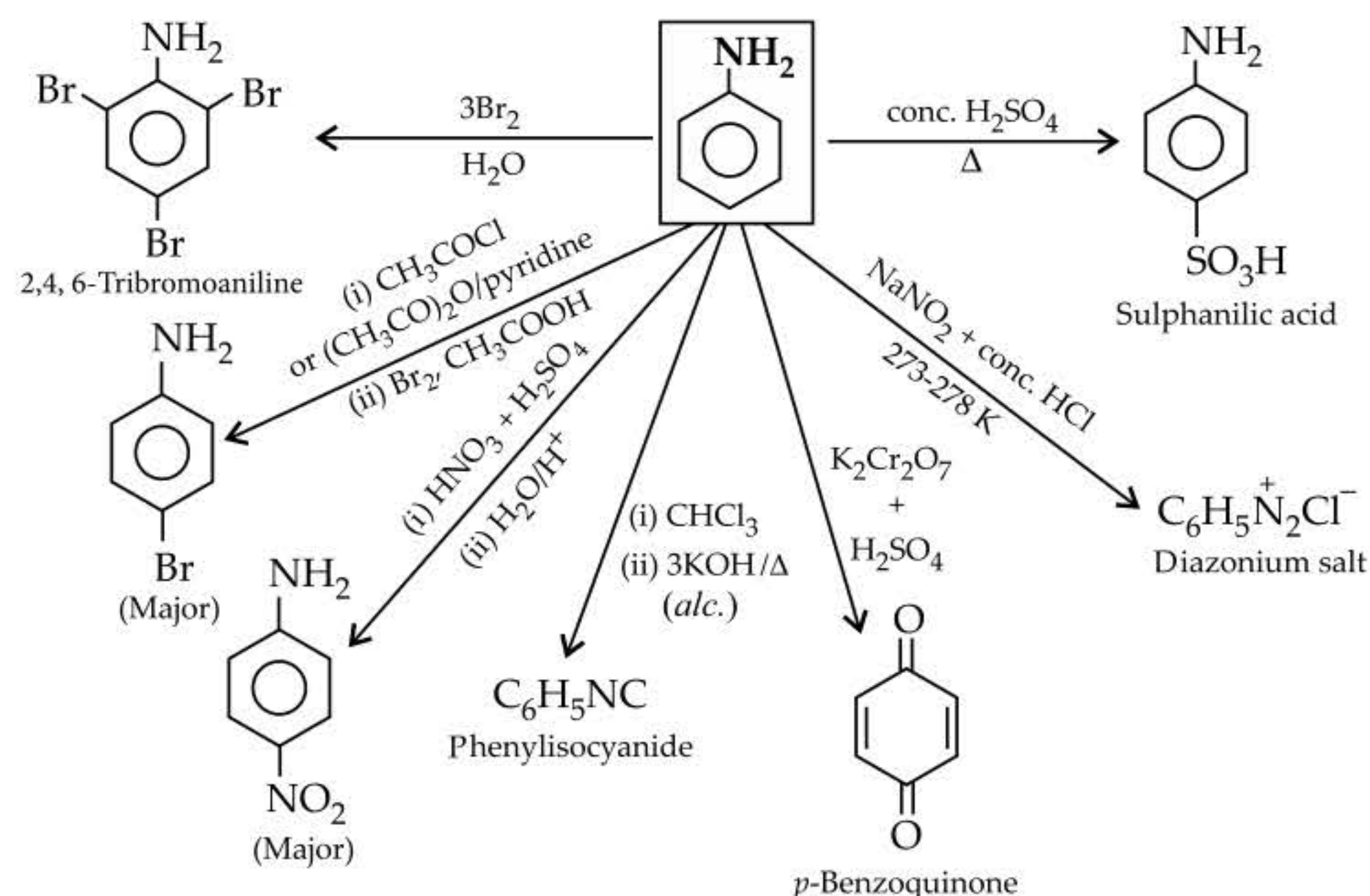
- All aromatic amines are weaker bases than ammonia due to the -I effect of aryl groups.
- Electron donating groups such as $-\text{CH}_3$, $-\text{OCH}_3$, $-\text{NH}_2$, etc., increase the basicity while electron withdrawing groups such as $-\text{NO}_2$, $-\text{CN}$, $-\text{SO}_3\text{H}$, $-\text{COOH}$, halogens, etc. decrease the basicity of amines. The effect of these substituents is more pronounced at *p*-positions than at *m*-positions.
- *o*-Substituted anilines are weaker bases than aniline regardless of the nature of the substituent whether electron donating or electron withdrawing. This is called *ortho*-effect.

INFOSHOTS

Sustainable amine production !

A new catalyst has been recently developed for amide hydrogenation that operates under mild conditions. This catalyst has numerous favorable features, including the ability to be isolated and reused, high selectivity and most importantly it catalyzes amide conversion to amines at just 70 °C and a hydrogen pressure of 30 bar.

Aniline :

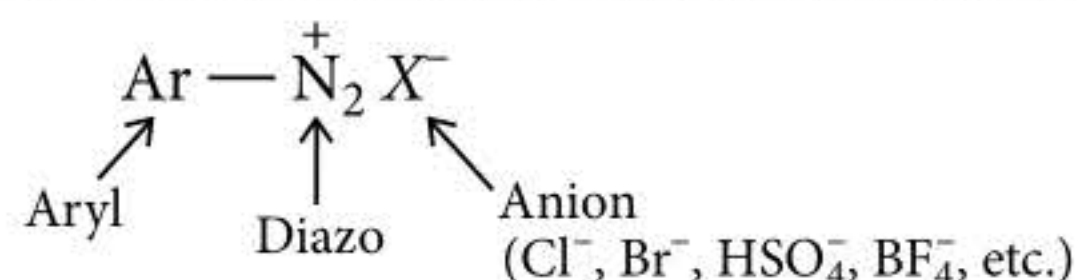


Identification of 1°, 2°, 3° Amines

Test	Primary amines	Secondary amines	Tertiary amines
Action of alkyl halides	Combine with three molecules of alkyl halides to form the quaternary salts.	Combine with two molecules of alkyl halides to form the quaternary salts.	Combine with one molecule of alkyl halide to form the quaternary salts.
Reaction with acid chlorides and acid anhydrides	Form monoalkyl substituted amide.	Form dialkyl substituted amide.	No reaction
Reaction with nitrous acid	Form mixture of alcohols and alkenes with evolution of nitrogen gas.	Form yellow oily nitrosoamine characterised by Liebermann's nitroso test.	Form nitrite salt which on decomposition gives mixture of nitrosoamine, alcohols and aldehydes or ketones.
Hinsberg's test with benzenesulphonyl chloride (C ₆ H ₅ SO ₂ Cl)	Form monoalkyl benzenesulphonamide which on treatment with alkali gives a water soluble salt.	Form dialkylbenzenesulphonamide which does not dissolve in alkali.	No reaction

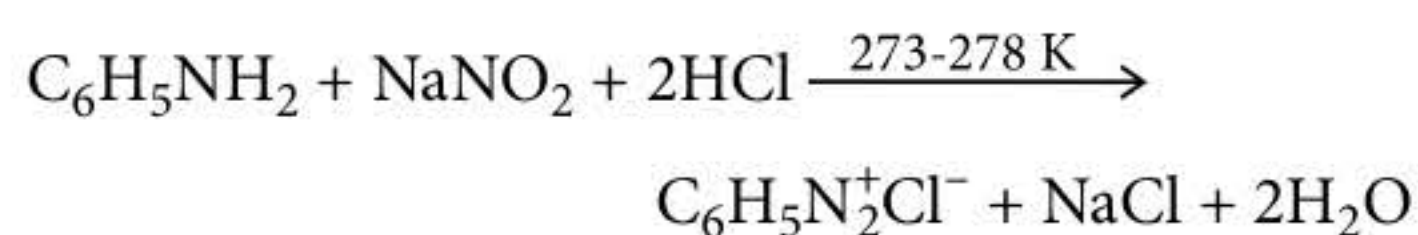
DIAZONIUM SALTS

- General formula of arenediazonium salts is :



- Primary aliphatic amines form highly unstable alkanediazonium salts.
- Arenediazonium salts are more stable than alkanediazonium salts. The stability of arenediazonium ion is explained on the basis of resonance.

Method of Preparation (Diazotisation)



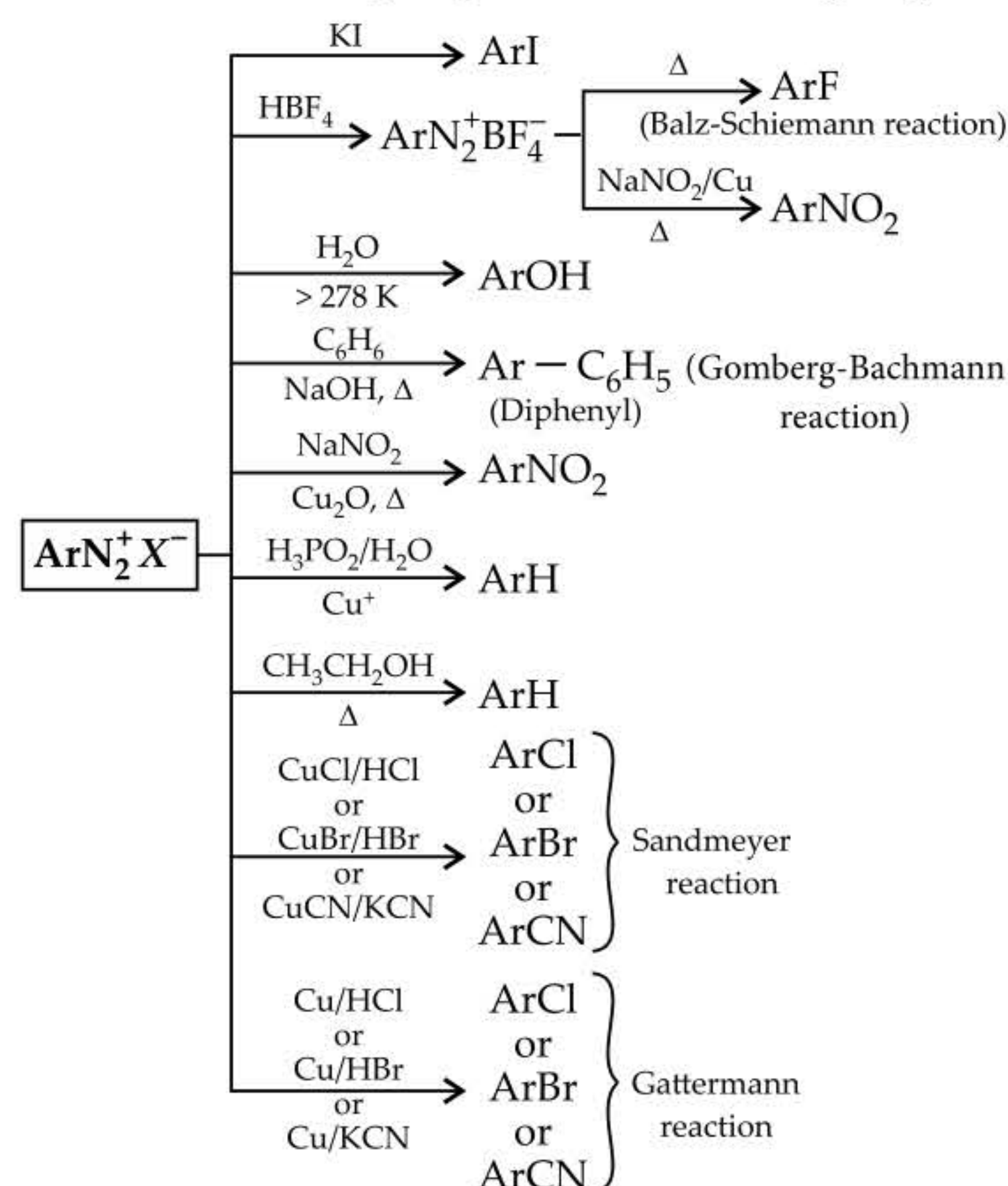
- Prepared in situ and used immediately after preparation.

Physical Properties

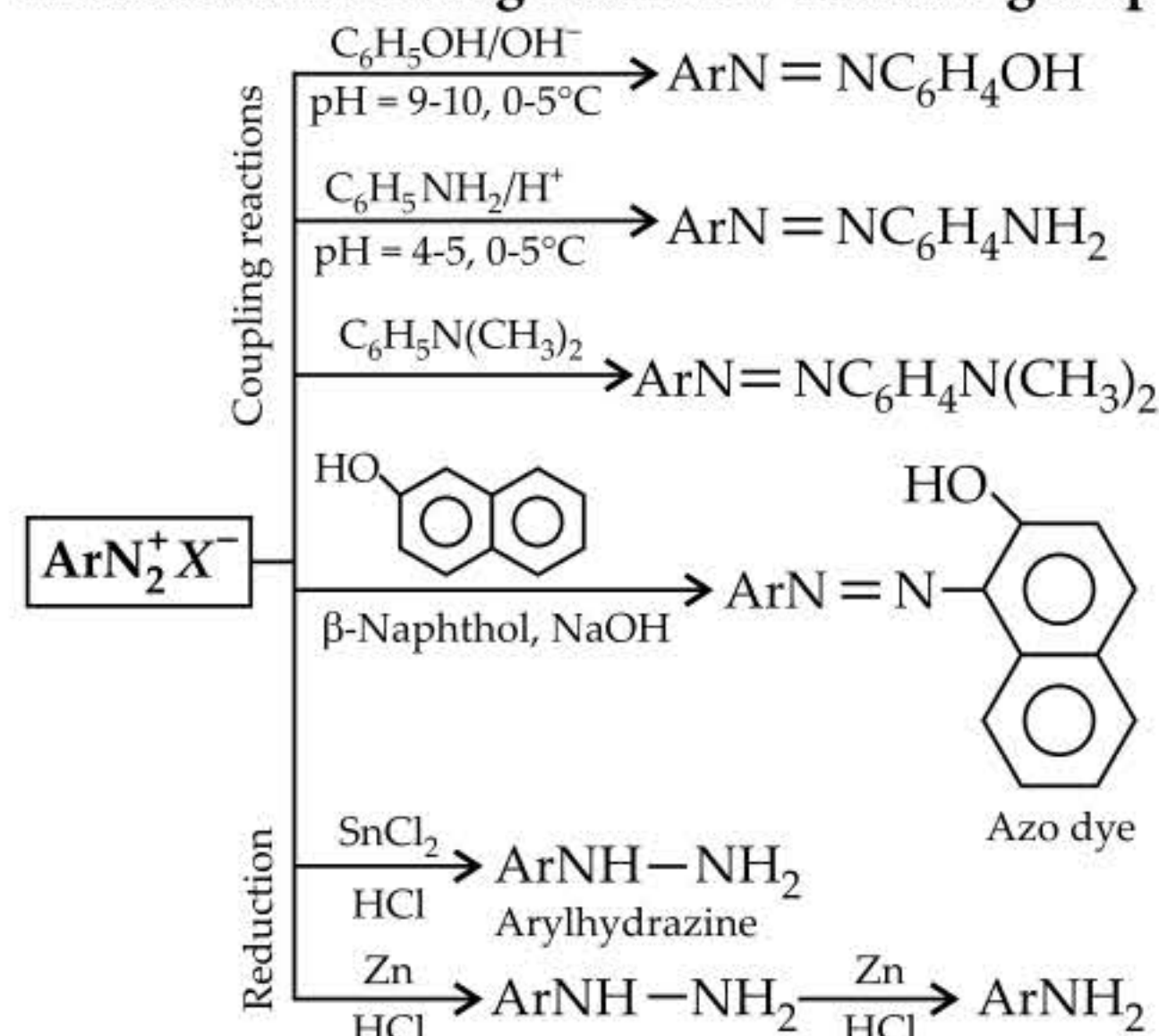
- Colourless crystalline solid, soluble in water.
- Stable only between 273-278 K.

Chemical Properties

Reactions involving displacement of diazo group :



Reactions involving retention of diazo group :



Uses

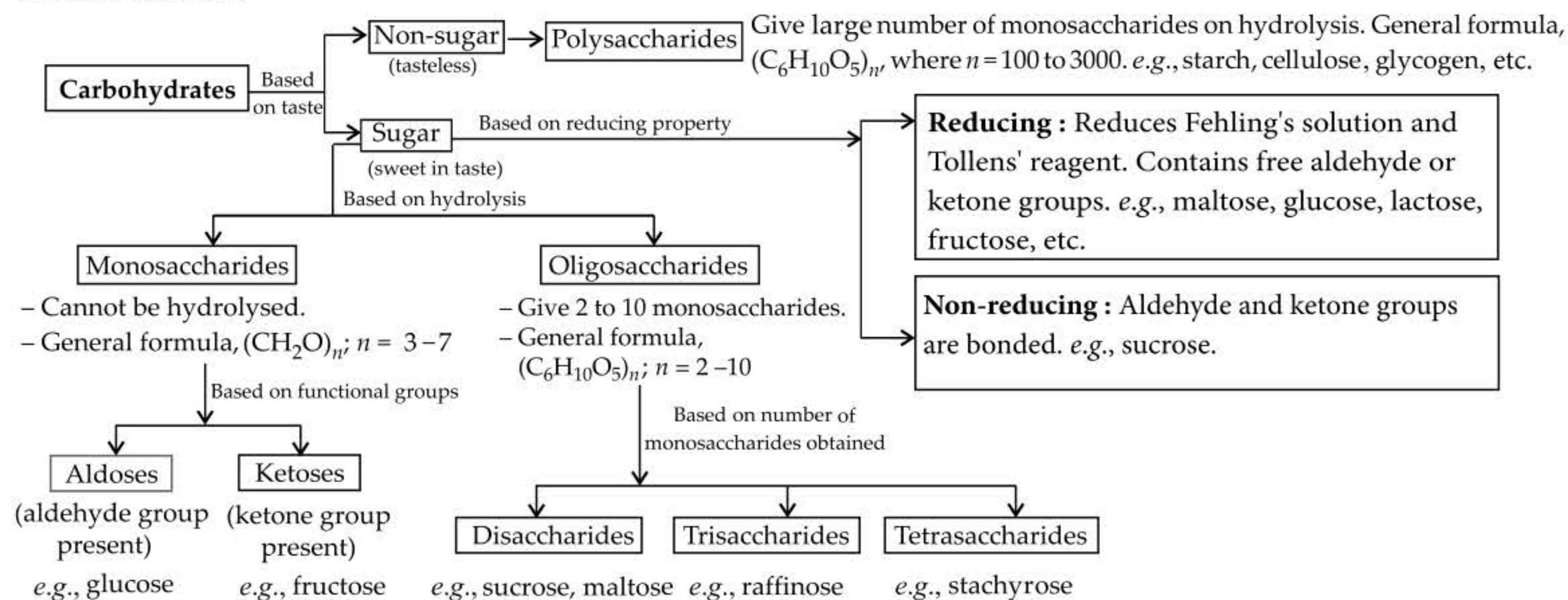
- There are large number of groups which can be attached to aromatic rings by the replacement of diazo group.
- Aryl fluorides and iodides cannot be prepared by direct halogenation but can be easily prepared by diazonium salts.
- Coupling reactions of diazonium salts are highly important in dye industry.

BIOMOLECULES

CARBOHYDRATES

- The polyhydroxy aldehydes or polyhydroxy ketones or substances which yield such products on hydrolysis, are known as saccharides. Their general formula is $\text{C}_x(\text{H}_2\text{O})_y$, where, x and y can be 3, 4, 5, ... etc. They occur naturally in animal and plant kingdom and are composed of carbon, hydrogen and oxygen only.

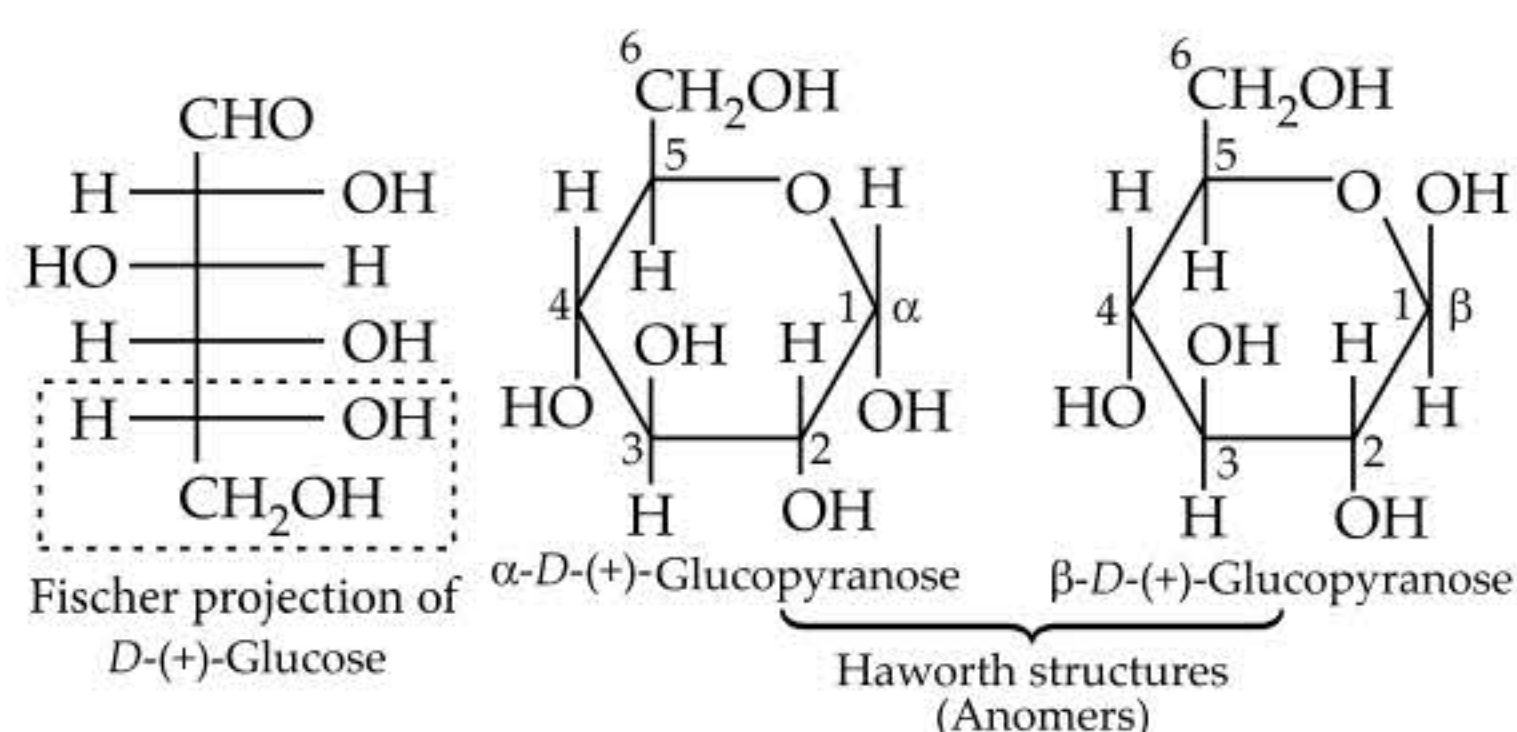
Classification



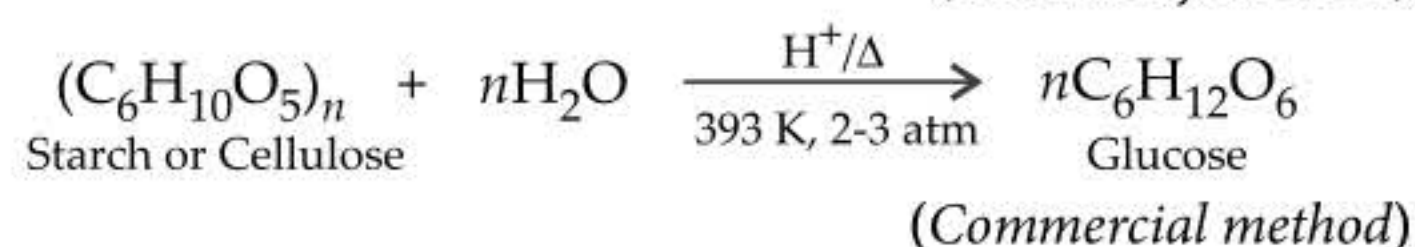
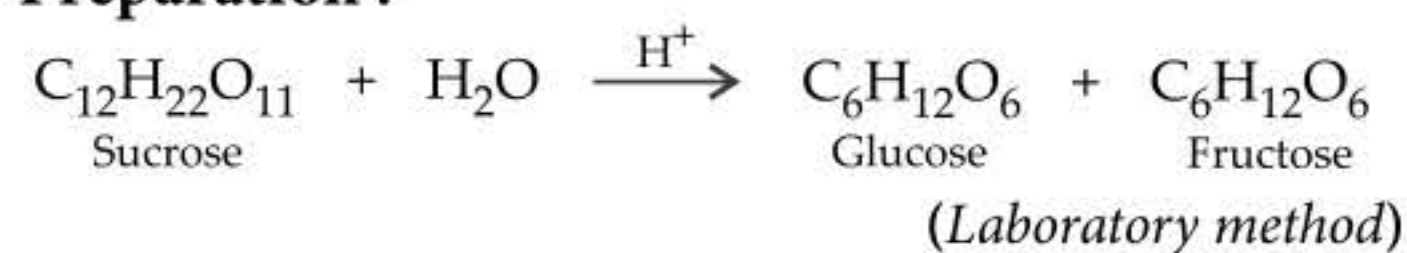
MONOSACCHARIDES

Glucose (C₆H₁₂O₆)

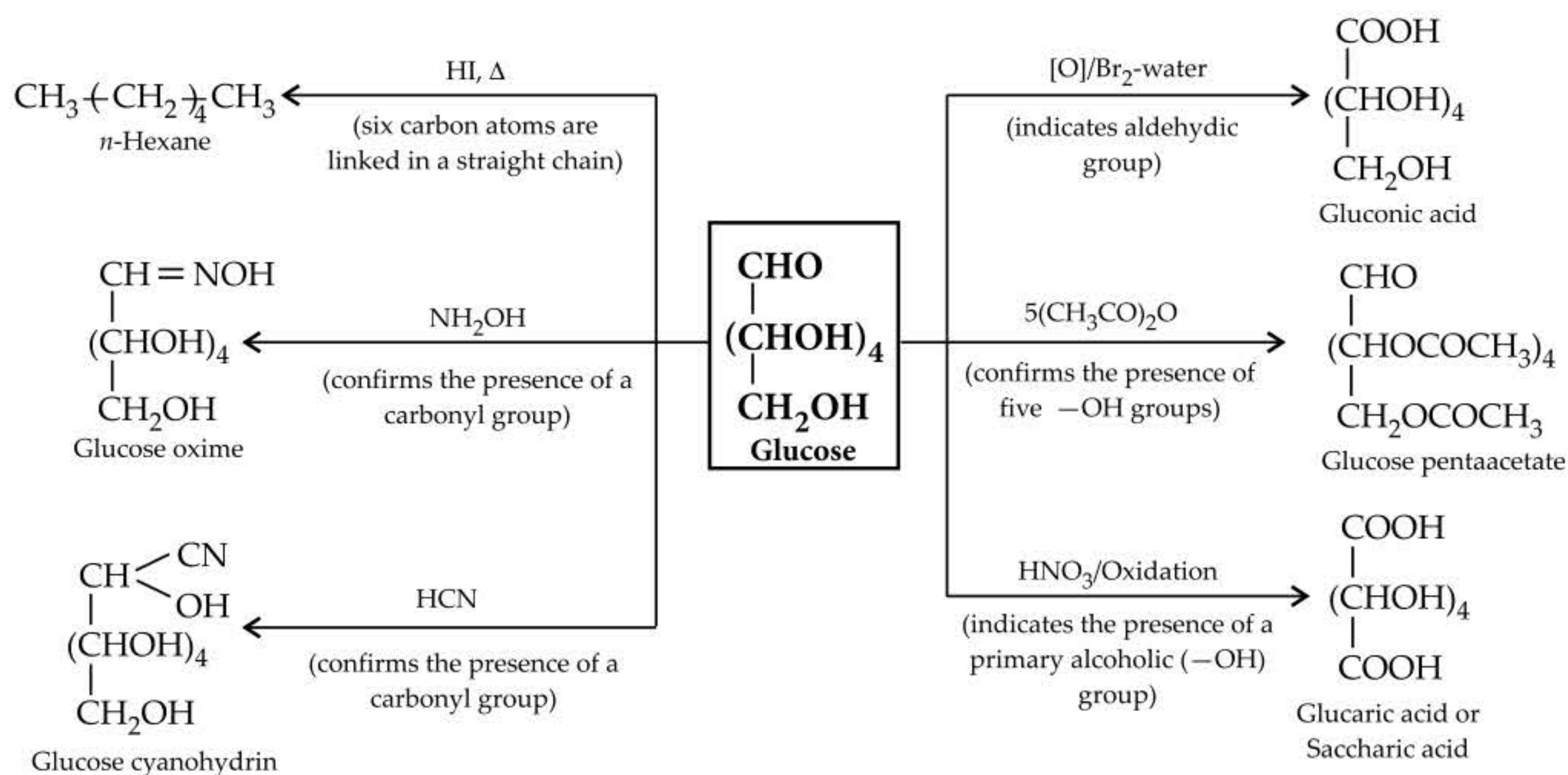
- An aldohexose as it contains six carbon atoms and aldehydic group.
- Structure** : During hemiacetal formation, C₅-OH of glucose combines with the C₁-aldehydic group. As a result, C₁ becomes chiral or asymmetric and thus, has two possible arrangements of H and OH groups around it. So, D-glucose exists in two stereoisomers *i.e.*, α-D-glucose and β-D-glucose. Such a pair of stereoisomers which differs in conformation only around C₁ are called anomers.



- Preparation** :

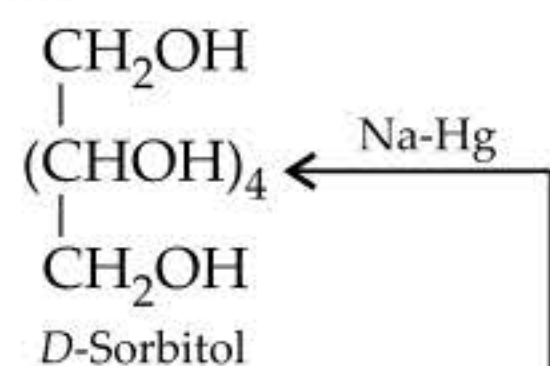


- Open chain structure on the basis of following evidences :**

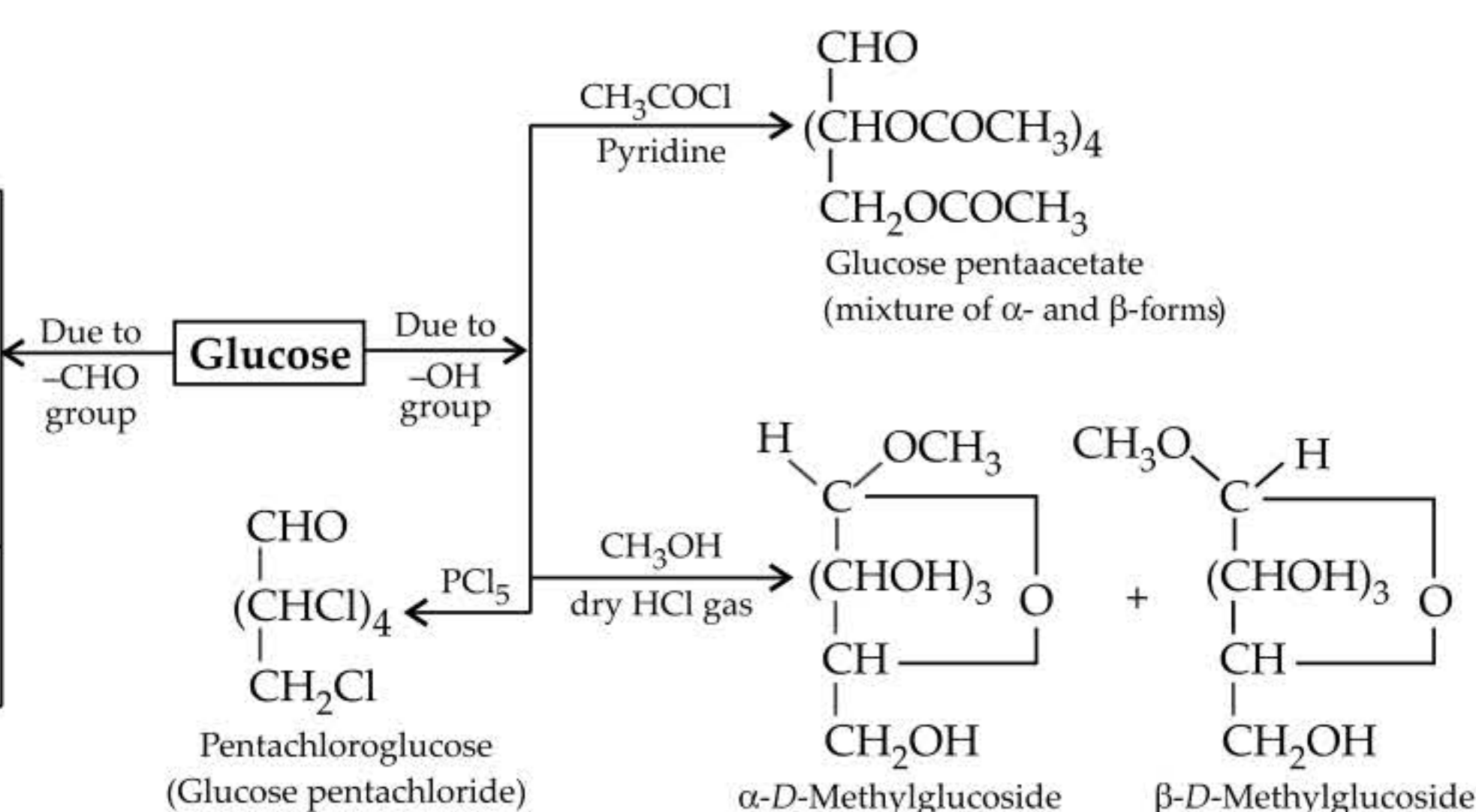
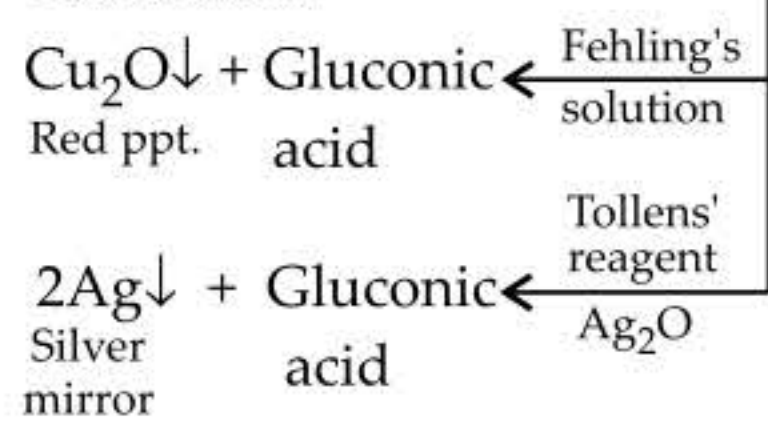


- Chemical reactions :**

Reduction:

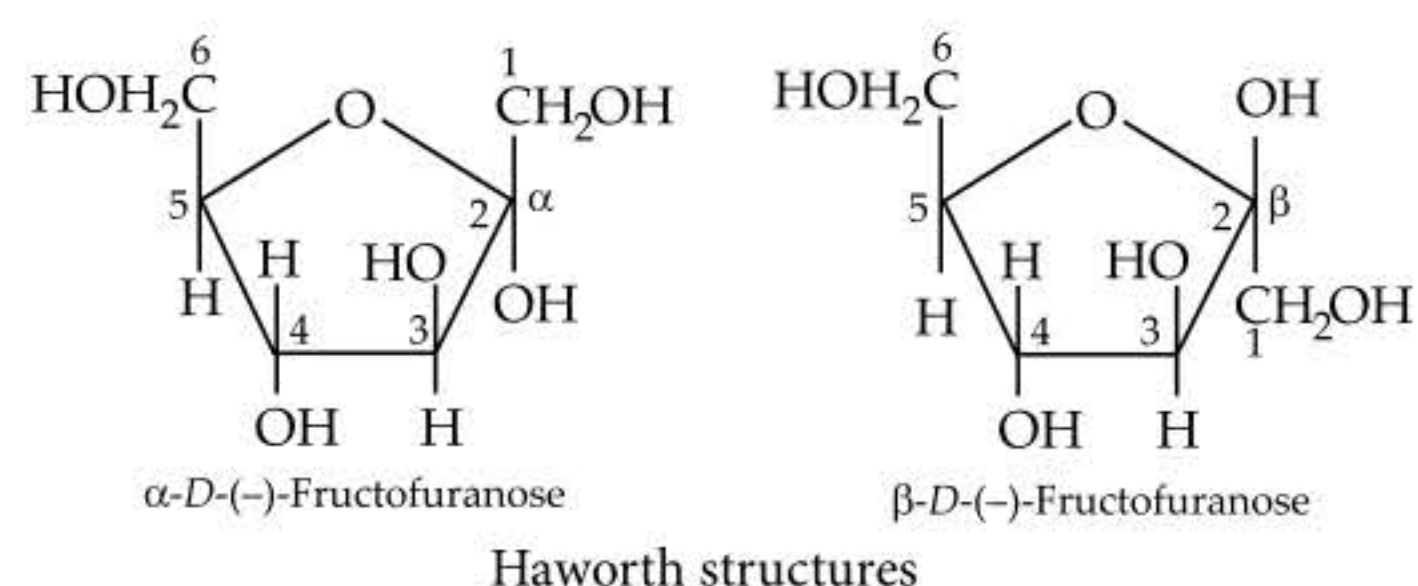
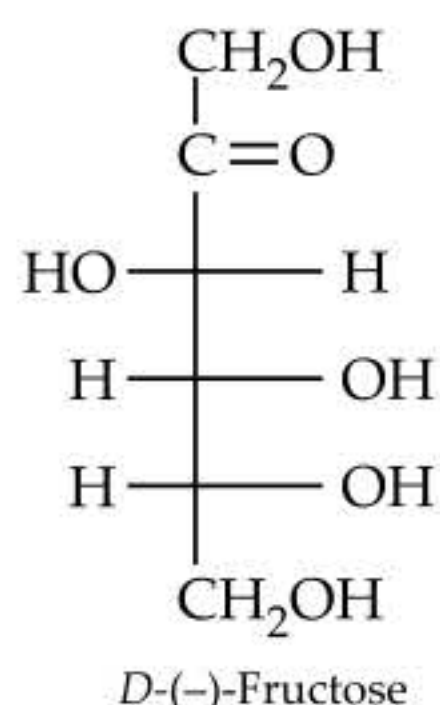


Oxidation:



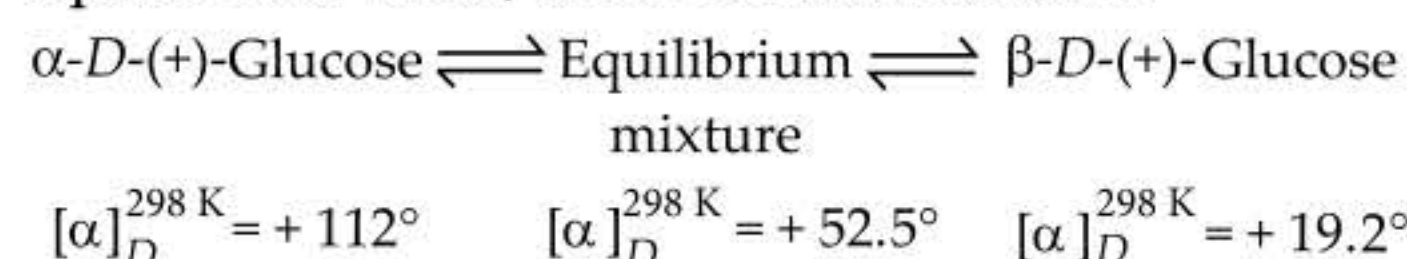
Fructose (C₆H₁₂O₆)

- A ketohexose as it contains six carbon atoms and ketonic group.
- **Structure :**



Mutarotation

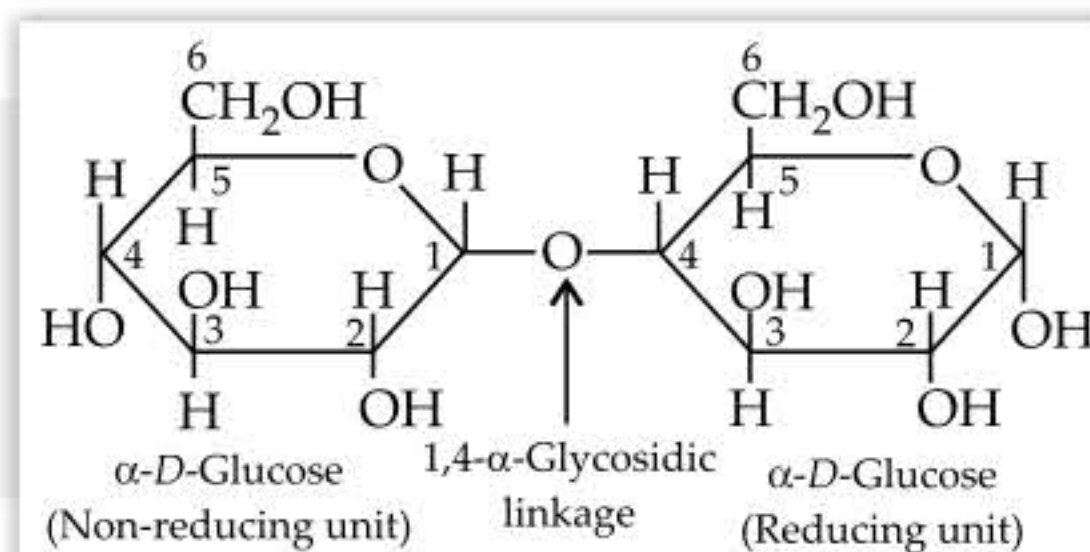
- The spontaneous change in specific rotation of an optically active compound with time, to an equilibrium value, is called mutarotation.



DISACCHARIDES

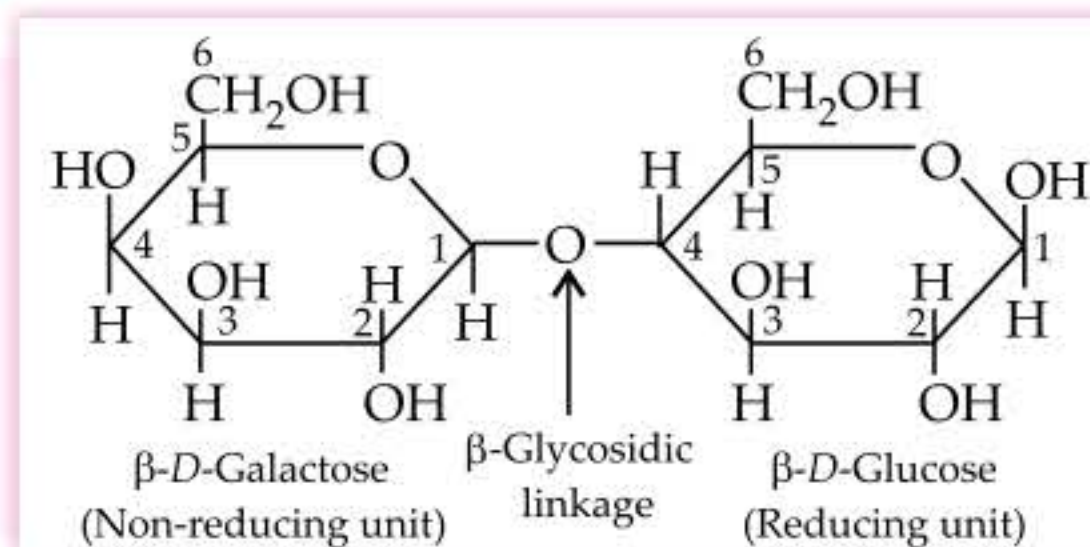
Maltose

- Maltose is composed of two α -D-glucose units in which C1 of one glucose is linked to C4 of another glucose unit.
- Reducing sugar.



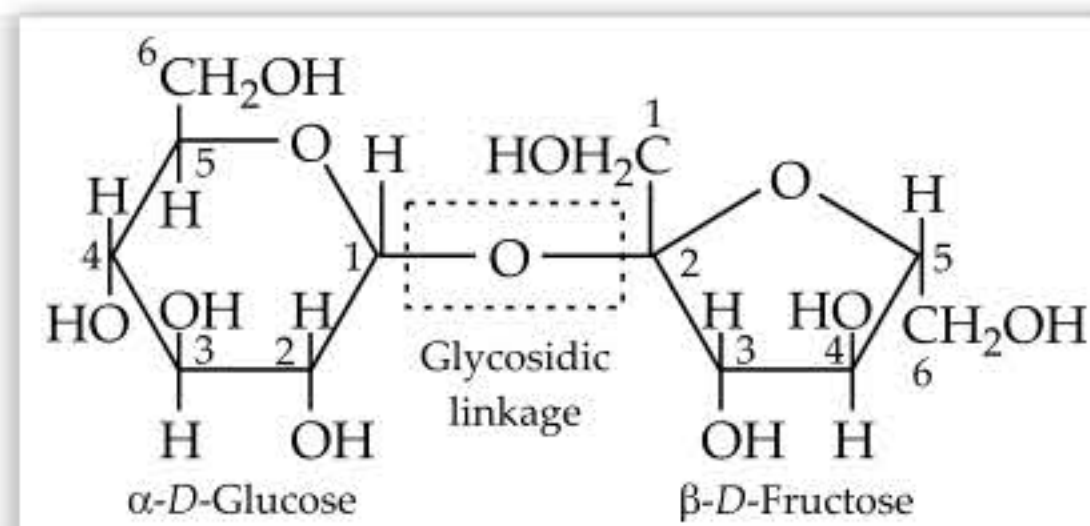
Lactose

- Known as milk sugar.
- It is composed of β -D-galactose and β -D-glucose in which linkage is between C1 of galactose and C4 of glucose.
- Reducing sugar.



Sucrose

- On hydrolysis gives equimolar mixture of α -D-(+)-glucose and β -D-(-)-fructose.
- Glycosidic linkage between C1 of α -glucose and C2 of β -fructose.
- Non-reducing sugar.



INFOSHOTS

Folding biomolecule model !

Proteins are fundamental macromolecules for life, with a diversity of functions. To perform these functions, what matters is the layout of these proteins secondary branches. Scientists have developed a theoretical method to calculate the most stable deposition that biomolecules try to adopt when they are together, or in close contact in cases where the bond is weak.

POLYSACCHARIDES

Starch

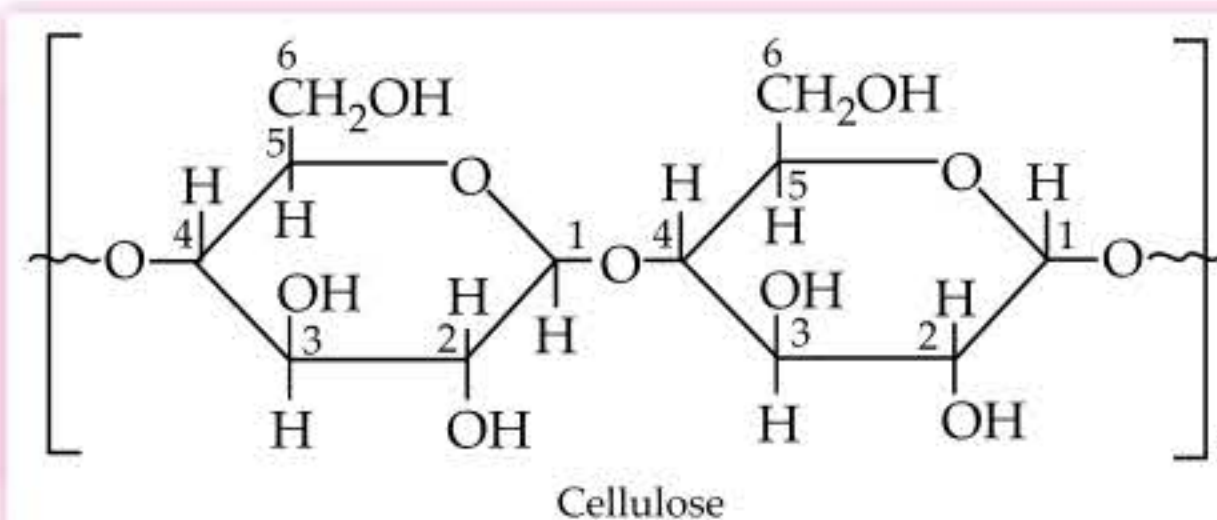
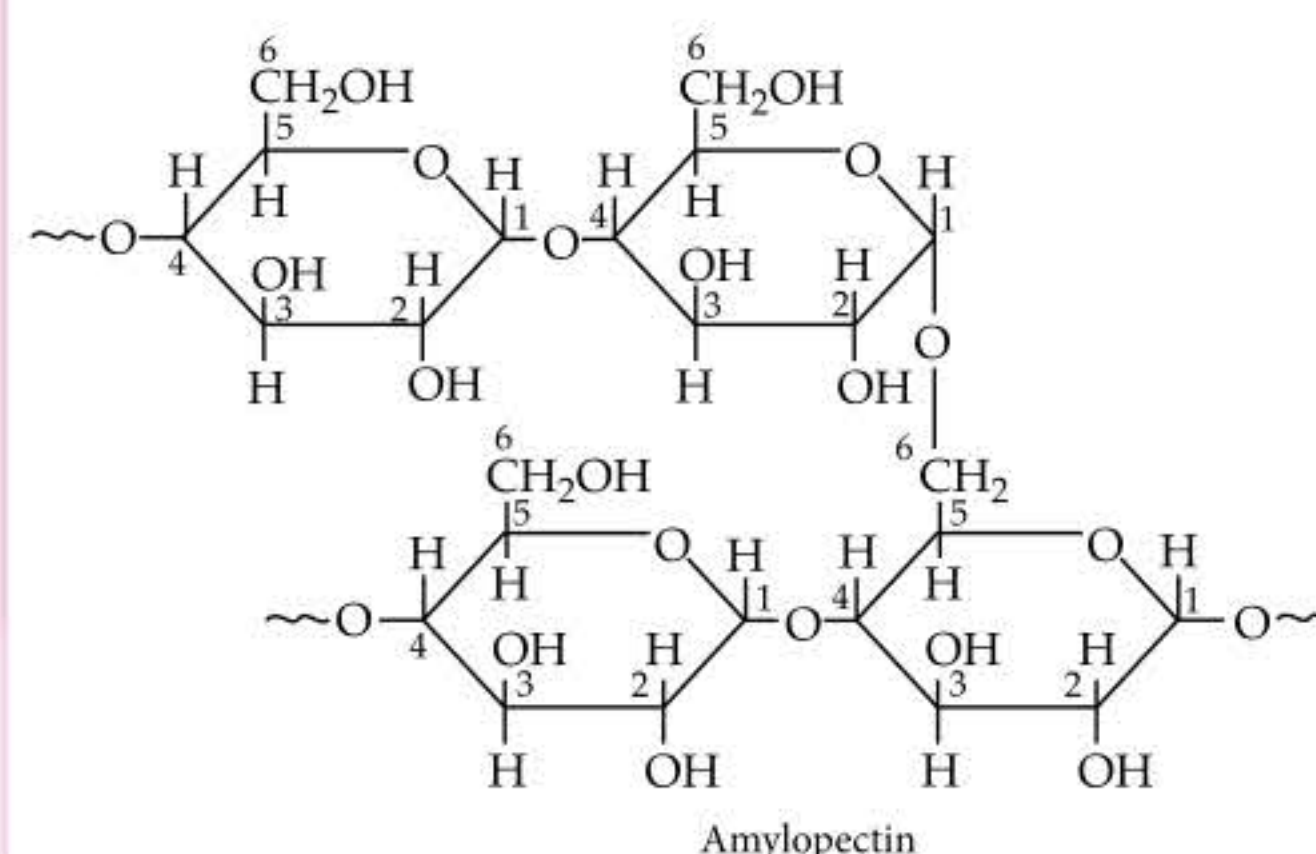
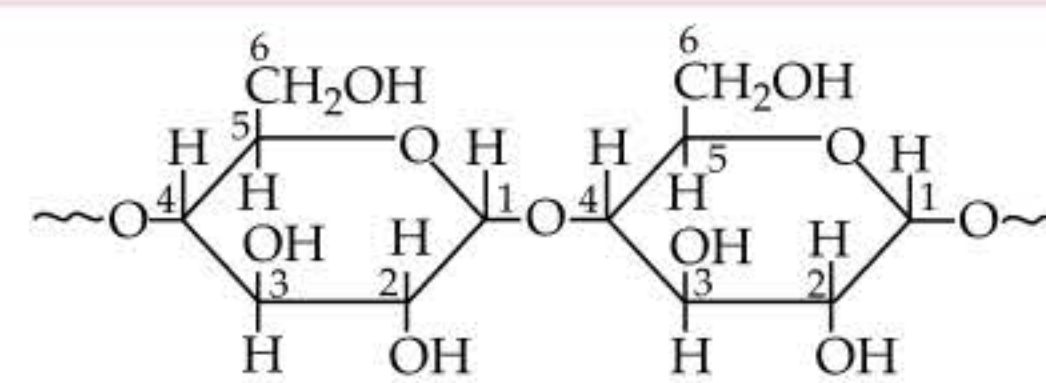
- Polymer of α -D-glucose units and consists of two components amylose and amylopectin.
- Amylose is water soluble, long unbranched chain of α -D-(+)-glucose units held by 1,4- α -glycosidic linkage.
- Amylopectin is water insoluble, branched chain polymer of α -D-glucose units held by 1,4- α -glycosidic linkage whereas branching occurs by 1,6- α -glycosidic linkage.

Glycogen

- Known as animal starch because its structure is similar to amylopectin and is more highly branched.

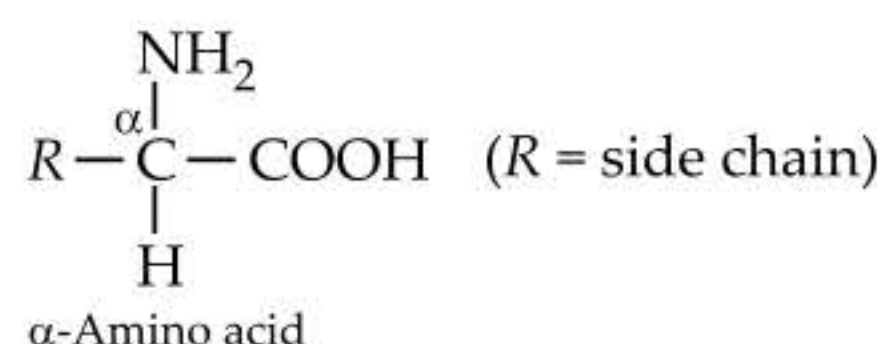
Cellulose

- Most abundant organic substance in plant kingdom.
- Straight chain polysaccharide of β -D-glucose units joined together by 1,4- β -glycosidic linkage.



PROTEINS

- Proteins are condensation polymers of α -amino acids which are essential for the growth and maintenance of life.



Classification of Amino Acids

- On the basis of relative number of amino ($-\text{NH}_2$) and carboxyl ($-\text{COOH}$) groups in the molecule :
 - **Neutral** : No. of $-\text{COOH}$ groups = No. of $-\text{NH}_2$ groups *e.g.*, glycine, alanine, valine, etc.
 - **Acidic** : No. of $-\text{COOH}$ groups > No. of $-\text{NH}_2$ groups *e.g.*, aspartic acid, asparagine, glutamic acid, etc.
 - **Basic** : No. of $-\text{NH}_2$ groups > No. of $-\text{COOH}$ groups *e.g.*, lysine, arginine, histidine, etc.

- On the basis of their synthesis in the body :
 - **Essential amino acids** : Cannot be synthesised in the body and must be obtained through diet *e.g.*, valine, leucine, lysine, isoleucine, arginine, phenylalanine, methionine, tryptophan, threonine and histidine.
 - **Non-essential amino acids** : Can be synthesised in the body. *e.g.*, glycine, alanine, glutamic acid, aspartic acid, etc.

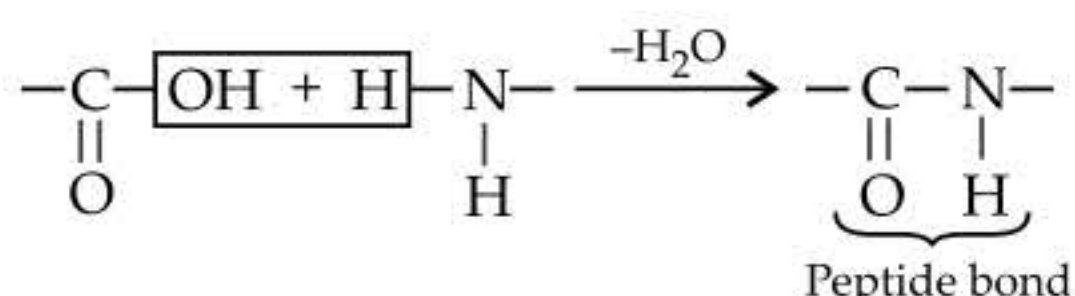
Properties of Amino Acids

- In aqueous solution, the carboxylic group can lose a proton and amino group can accept a proton giving rise to a dipolar ion known as zwitter ion.

$$\text{R}-\underset{\text{:NH}_2}{\text{CH}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} \rightleftharpoons \text{R}-\underset{+\text{NH}_3}{\text{CH}}-\overset{\text{O}^-}{\parallel}{\text{C}}-\text{O}^-$$

Zwitter ion
- **Isoelectric point** : The pH at which no net migration of amino acid under the influence of applied electric field, is called isoelectric point.
- They exist in both *D*- and *L*-forms. Most naturally occurring α -amino acids have *L*-configuration.

- **Peptide bond** : During amide formation, the bond formed between two amino acids by the elimination of a water molecule, is called peptide linkage or peptide bond.



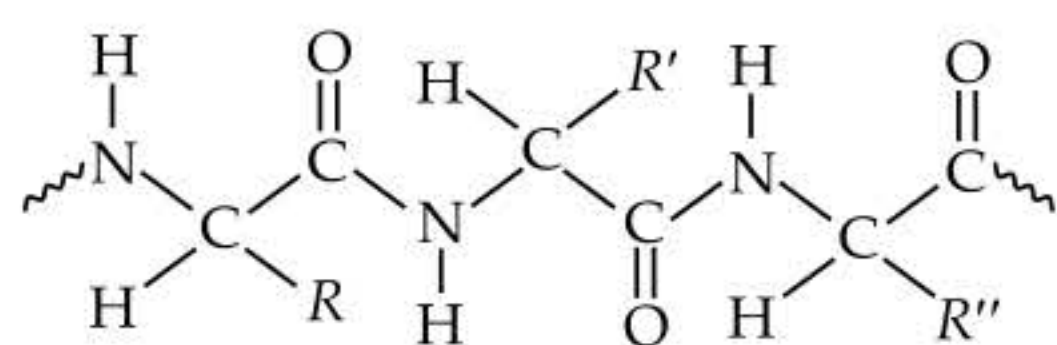
- Peptides are further divided into *di*, *tri*, *tetra* depending upon the number of amino acids combined.
- **Polypeptides** : Product which are formed by more than ten amino acids are known as polypeptides.
- A polypeptide with more than hundred amino acid residues, having molecular mass higher than 10,000 u, is called a protein.

Classification of Proteins

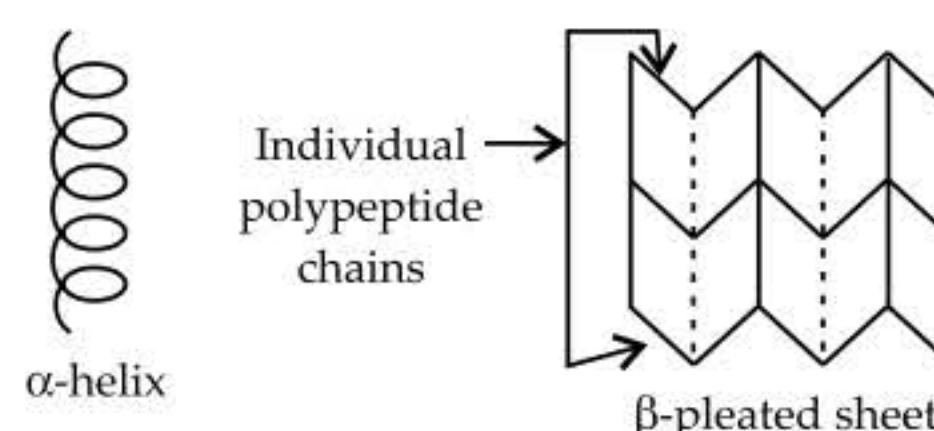
- **Fibrous proteins** : In fibrous proteins, polypeptide chains run parallel and held together by hydrogen and disulphide bonds. These are insoluble in water, e.g., keratin (in hair, wool) and myosin (in muscles).
- **Globular proteins** : In globular proteins, polypeptide chains coil around to give three dimensional spherical shape. These are soluble in water, e.g., insulin and albumins.

Structure of Proteins

- **Primary structure** : It refers to the specific sequence of α -amino acids held together in a protein.



- **Secondary structure** : Due to folding or coiling of the peptide chain, these are of two types :
 - **α -helix** : Coils are stabilized by hydrogen bonds between carbonyl oxygen of first amino acid to amide nitrogen of fourth amino acid.
 - **β -pleated sheet structure** : Intermolecular H-bonds are formed between the carbonyl oxygens and amide hydrogens of two or more adjacent polypeptide chains, giving a β -pleated sheet structure e.g., silk fibroin.



- **Tertiary structure** : Refers to overall folding of the polypeptide chains or its complete 3-D structure.
- **Quaternary structure** : Refer to spatial arrangement of two or more polypeptide chains with respect to each other.

Denaturation of Proteins

- When a protein in its native form, is subjected to physical changes (like temperature) or chemical changes (like pH), the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of protein.
- The denaturation causes change in secondary and tertiary structures but primary structure remains intact e.g., coagulation of egg white on boiling, curdling of milk, formation of cheese, etc.

ENZYMES

- Enzymes are biocatalysts produced by living cells which catalyse the following biochemical reactions in living organisms :

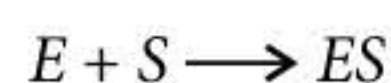
Enzyme	Reaction catalysed
Maltase	Maltose \rightarrow Glucose + Glucose
Lactase	Lactose \rightarrow Glucose + Galactose
Amylase	Starch $\rightarrow n \times$ Glucose
Invertase	Sucrose \rightarrow Glucose + Fructose
Pepsin	Proteins $\rightarrow \alpha$ -Amino acids
Trypsin	Proteins $\rightarrow \alpha$ -Amino acids
Urease	Urea \rightarrow CO ₂ + NH ₃
Nuclease	DNA, RNA \rightarrow Nucleotides

Properties

- Required in very small amount.
- They reduce magnitude of activation energy.
- They are highly specific.
- They work at specific pH.
- They work well at moderate temperature.

Mechanism

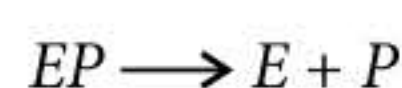
- Binding of the enzyme (*E*) to substrate (*S*) to form a complex called the enzyme-substrate complex.



- Formation of complex of enzyme and product.



- Release of product from the enzyme-product complex.



VITAMINS

- Required for normal growth and maintenance of the body. They cannot be produced in the body and hence must be supplied in diet.

Classification

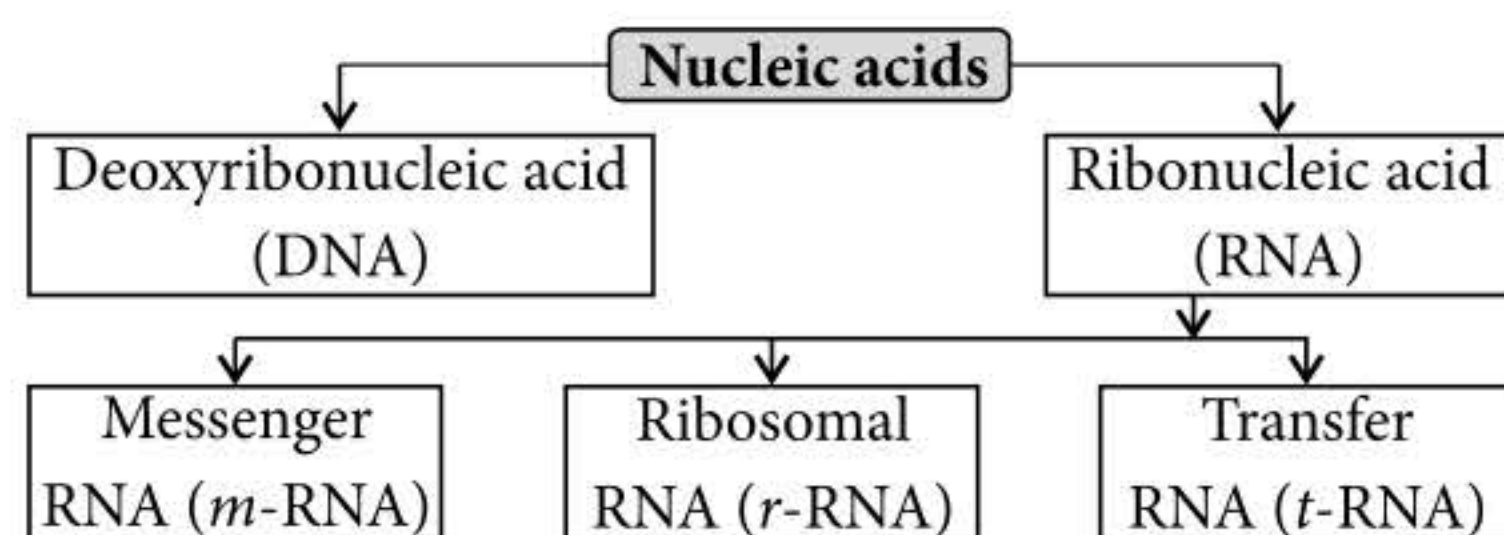
- **Water soluble vitamins :** These are water soluble and must be supplied regularly in diet. *e.g.*, vitamin - B₁, B₂, B₆, B₁₂ and C.
- **Fat soluble vitamins :** These are soluble in fat and oils and stored in liver and adipose tissues. *e.g.*, vitamin - A, D, E and K.

Vitamin name	Chemical name	Solubility	Sources	Deficiency disease
Vitamin A	Retinol	Fat	Milk, butter, eggs, fish, cod liver oil, green vegetables, etc.	Night-blindness, xerophthalmia.
Vitamin B ₁	Thiamine	Water	Pulses, nuts, cereals, yeast, egg yolk, green vegetables, etc.	Beri-beri, loss of appetite.
Vitamin B ₂	Riboflavin	Water	Milk, green vegetables, egg white, meat, liver, kidney, etc.	Anaemia, inflammation of tongue, dermatitis, cheilosis.
Vitamin B ₆	Pyridoxine	Water	Rice bran, whole cereal, yeast, fish, meat, eggs, etc.	Affects central nervous system, weakness, convulsions, etc.
Vitamin H	Biotin	Water	Milk, yeast, liver, kidney, etc.	Dermatitis.
Vitamin B ₁₂	Cyanocobalamin	Water	Eggs, milk, liver of ox, sheep, fish, etc.	Pernicious anaemia.
Vitamin C	Ascorbic acid	Water	Citrus fruits, chillies, sprouted pulses, etc.	Pyorrhoea, scurvy (bleeding of gums).
Vitamin D (a mixture of vitamins D ₁ and D ₃)	Ergocalciferol and cholecalciferol	Fat	Butter, milk, eggs, fish liver oil, liver and meat etc.	Rickets (bending of bones) and osteomalacia.
Vitamin E	Tocopherol	Fat	Wheat germ oil, milk, nuts, peanut oil, cotton seed oil, eggs, fish, etc.	Loss of fertility in males, muscles degeneration.
Vitamin K	Phylloquinone	Fat	Leafy vegetables like cabbage, spinach, etc.	Haemorrhages and lengthens time of blood clotting.

NUCLEIC ACIDS

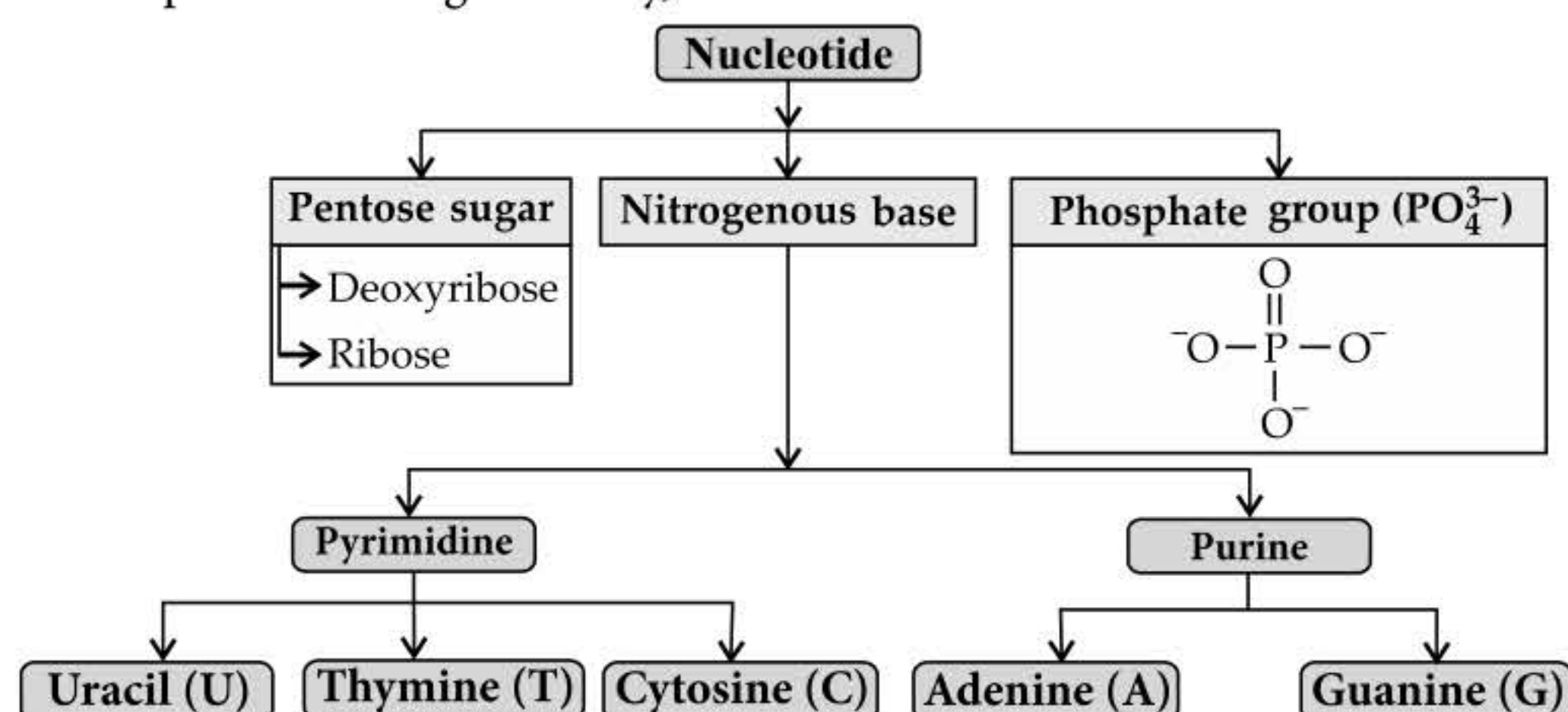
- Nucleic acids are the polymers of nucleotides present in nucleus of all living cells and play an important role in transmission of the hereditary characteristics and biosynthesis of proteins.

Classification

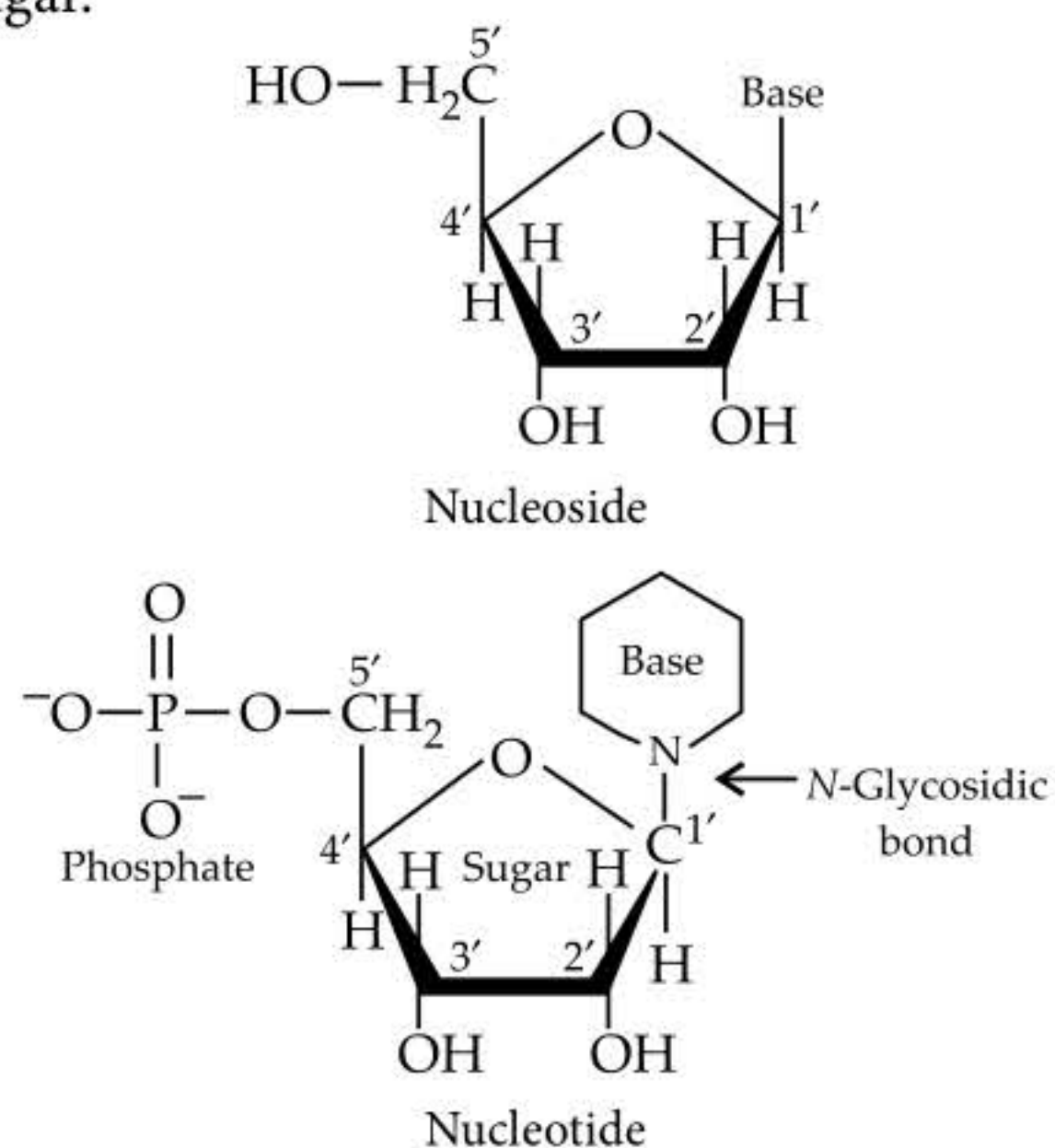


Structure

- A unit formed by attachment of a base to 1' position of sugar is known as nucleoside. When nucleoside is linked to phosphoric acid at 5' position of sugar moiety, a nucleotide is formed.



- Nucleotides are joined together by phosphodiester linkages between 5' and 3' carbon atoms of pentose sugar.



- Primary structure** : Refers to the sequence of nucleotides in the chain of nucleic acid.
- Secondary structure** : Two strands of polynucleotides coil around each other in the form of double helix. James Watson and Francis Crick gave a double strand helix structure for DNA.
- Chargaff's rule** : Amount of purine bases is always equal to pyrimidine bases. Purine base of one strand of DNA molecule pairs with pyrimidine base of the other strand. Adenine (A) pairs with thymine (T) through two H-bonds (A = T) and guanine (G) pairs with cytosine (C) through three H-bonds (G ≡ C). In case of RNA, adenine (A) pairs with uracil (U), (A = U).

Differences between DNA and RNA

Components	DNA	RNA
Sugar	2-deoxy-D-(-) ribose	D-(-)ribose
Pyrimidine base	Cytosine and thymine	Uracil and cytosine
Structure	Double stranded α-helix	Single stranded α-helix
Replication	Possible	Not possible

Biological Functions

- Replication** : Single DNA molecule produces two identical copies of itself.
- Protein synthesis** : It is carried out by RNA molecules in two steps :
 - Transcription** : Synthesis of RNA from DNA in the cytoplasm of the cell.
 - Translation** : Protein synthesis by RNA molecules.

DNA Fingerprinting

- Every individual has unique fingerprints.
- The unique fingerprints are due to unique sequences of bases on DNA for every person.
- The technique for identifying individual person based upon the uniqueness of their DNA pattern is called DNA fingerprinting.