NEET | JEE ESSENTIALS

Class XII

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Unit 7 ORGANIC COMPOUNDS CONTAINING NITROGEN BIOMOLECULES

ORGANIC COMPOUNDS CONTAINING NITROGEN

AMINES

- The derivatives of ammonia formed by the replacement of one or more hydrogen atoms by the corresponding number of alkyl or aryl groups are known as *amines*. Like ammonia, nitrogen is sp^3-hybridised and the geometry is pyramidal in amines.

Classification

Amines

- RNH_2 — 1° Amine
- R_2NH — 2° Amine
- R_3N — 3° Amine

Physical Properties

Physical state and odour

- Lower aliphatic amines are gases which smell like ammonia and lower aromatic amines are liquids with characteristic unpleasant odour.

Solubility

- Amines are soluble in water due to hydrogen bonding while higher amines and aromatic amines are soluble in organic solvents such as benzene, ether, alcohol, etc.
- As the size of the alkyl group increases, solubility decreases.

Physical Properties

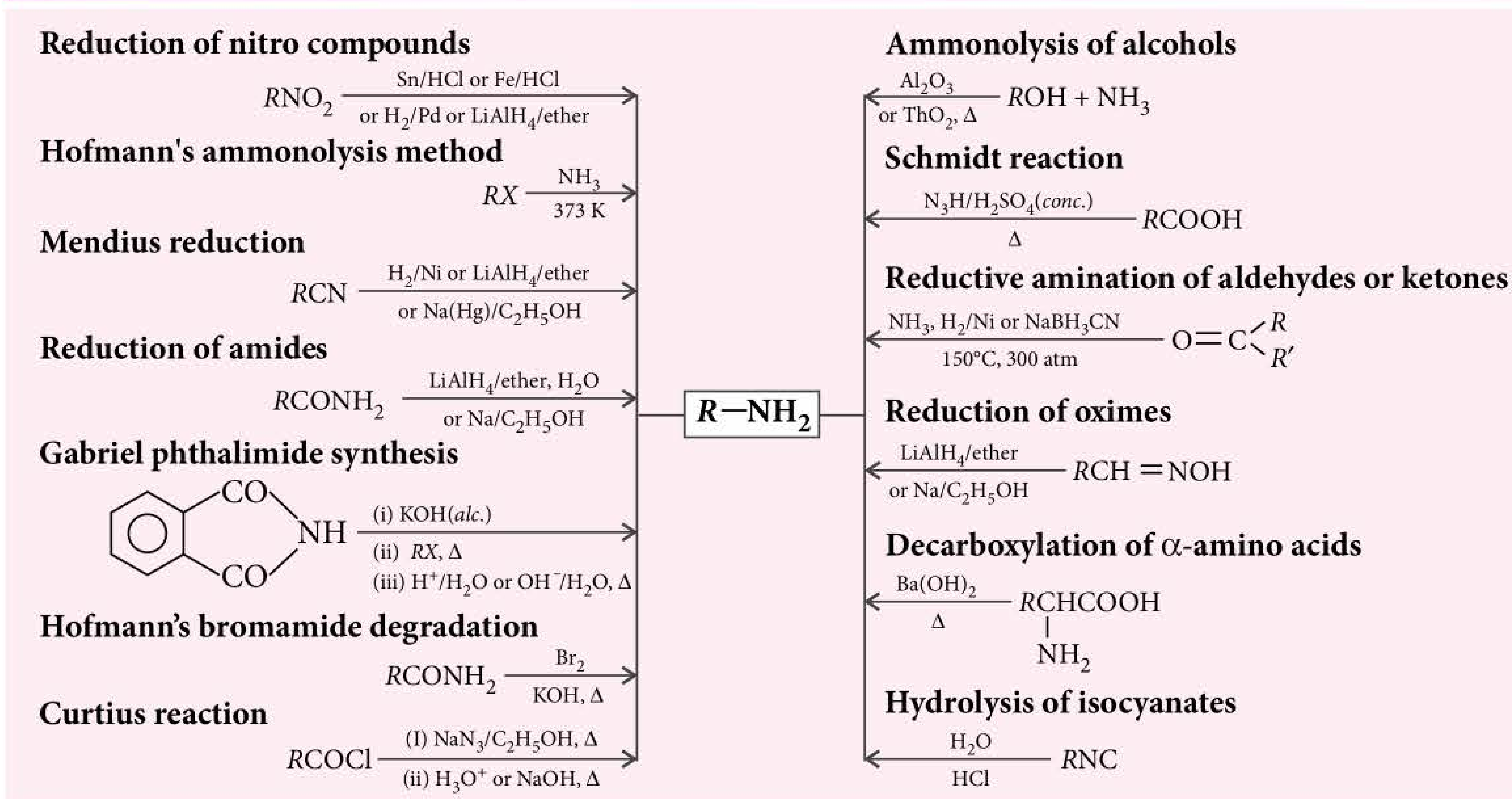
Boiling points

- Tertiary amines have the lowest boiling points as they do not have hydrogen atoms linked to the nitrogen atom.
- The intermolecular association is more in primary amines than in secondary amines due to the presence of two hydrogen atoms. Therefore, the order of boiling points of isomeric amines is 1° > 2° > 3°.

Colour

- Pure amines are colourless but develop colour when exposed to air.

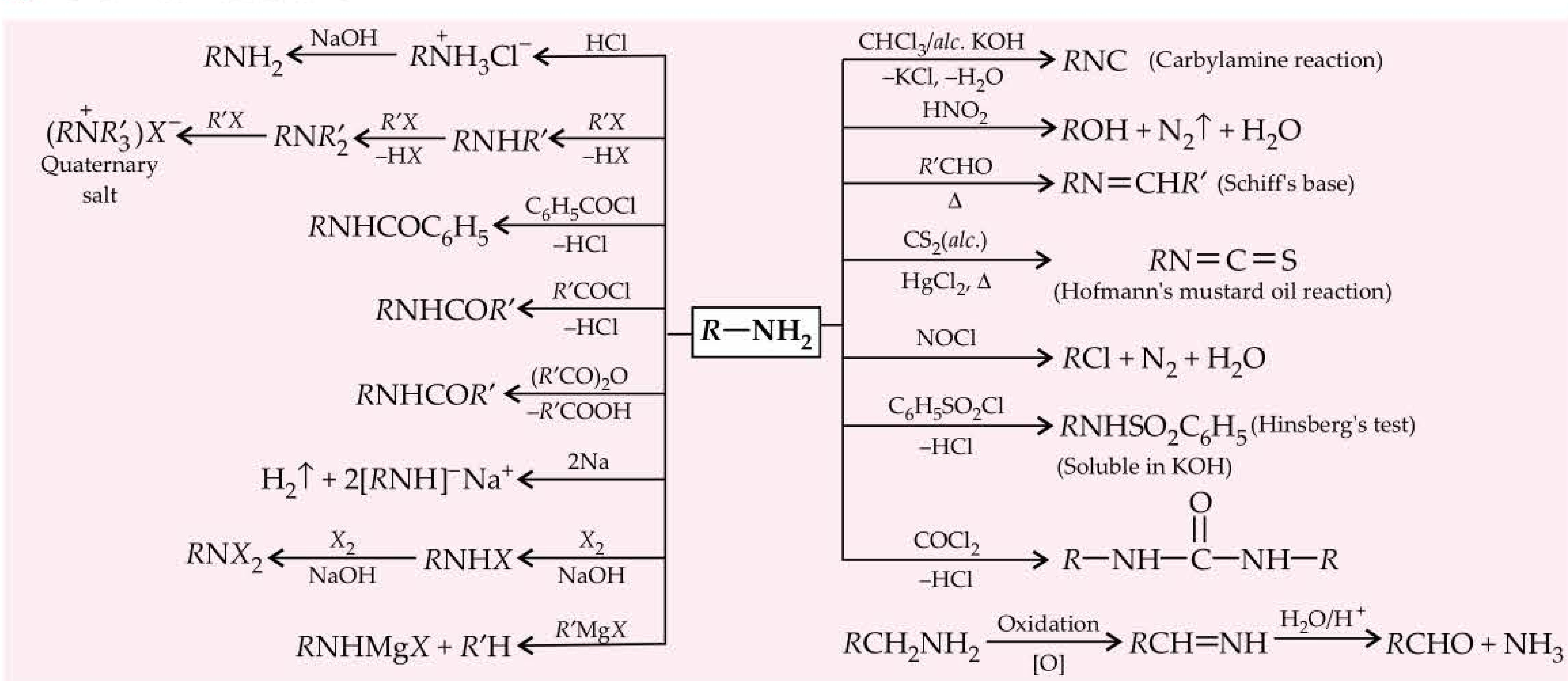
PREPARATION



CHEMICAL PROPERTIES

- **Basic character**
  - In gaseous phase, the order of basicity of amines is : 3° amine > 2° amine > 1° amine > NH_3.
  - In aqueous phase, despite of inductive effect, solvation effect and steric hindrance also play an important role. Thus, the order of basicity in aqueous solution of amines is as follows :
    - $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$
    - $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$
  - Aniline is less basic than alkylamines due to the delocalization of lone pair of electrons of nitrogen atom over benzene ring. Moreover, the anilinium ion obtained by accepting a proton have only two resonating structures and is less stable than aniline.

- **Chemical Reactions**



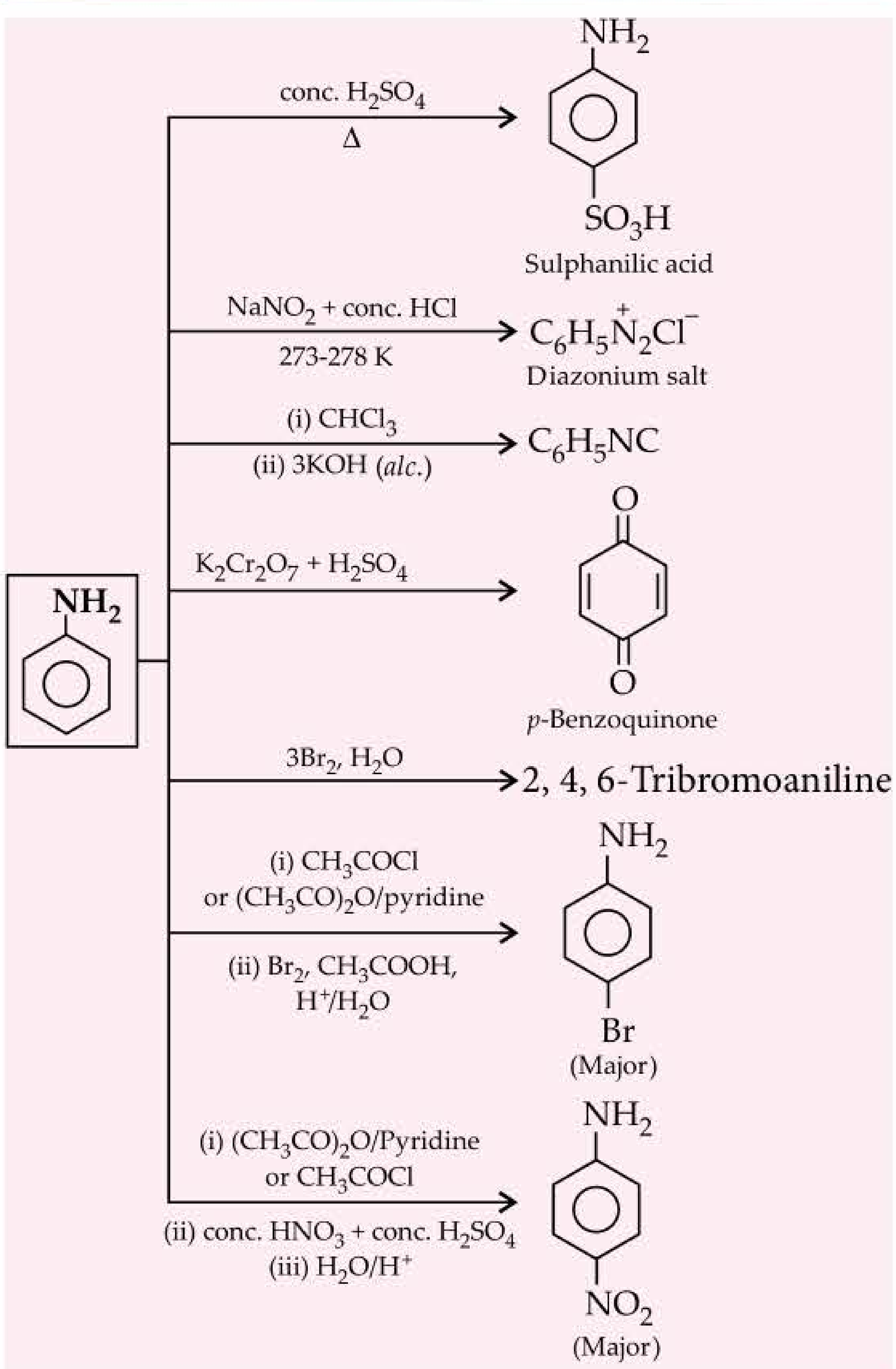
Distinction between 1°, 2° and 3° Amines

Test	Aliphatic			Aromatic
	1°	2°	3°	
Carbylamine test	Bad smelling carbylamine is formed.	No reaction	No reaction	Only aromatic primary amines give this test.
Mustard oil test	Alkyl isothiocyanate is formed.	No reaction	No reaction	Only aromatic primary amines give this test.
Hoffmann's test	Forms solid dialkyl oxamide.	Forms liquid dialkyl oxamic ester.	No reaction	
Hinsberg's test	Monoalkyl sulphonamide is formed which is soluble in KOH.	Dialkyl sulphonamide is formed which is insoluble in KOH.	No reaction	No reaction
Azo dye test	No reaction	No reaction	No reaction	Only primary aromatic amines give this test.

ANILINE

- Aromatic amino compound in which the nitrogen atom of amino group is directly attached to aromatic ring.

Chemical Properties



DIAZONIUM SALTS

- These have the general formula, $ArN_2^+X^-$, where Ar is abbriviated for the aryl group and X^- can be Cl^-, Br^-, HSO_4^-, NO_3^-, etc.

Preparation

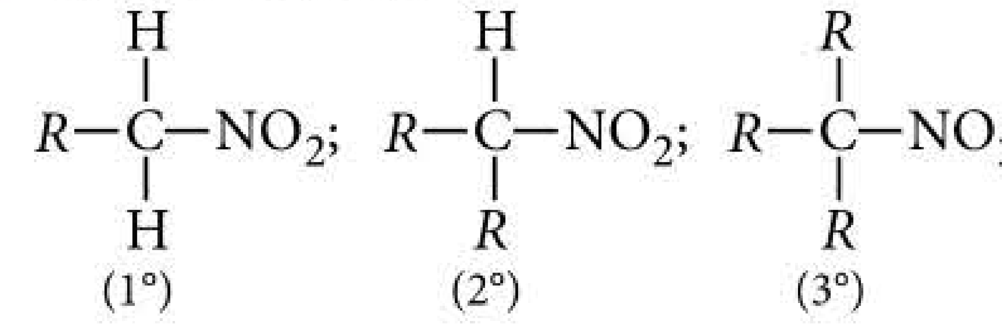
$$ArNH_2 + NaNO_2 + 2HX \xrightarrow{273\text{-}278\ K} ArN_2^+X^- + NaX + 2H_2O$$

Chemical Properties

D I	**Balz-Schiemann reaction** $\xrightarrow[-HCl]{HBF_4} ArN_2^+BF_4^- \xrightarrow{\Delta} ArF + N_2 + BF_3$
A Z	**Gomberg Bachmann reaction** $\xrightarrow[NaOH,\ \Delta]{C_6H_6} Ar{-}C_6H_5 + HCl + N_2\uparrow$ (Diphenyl)
O N	$\xrightarrow[or\ CH_3CH_2OH/\Delta]{H_3PO_2/Cu^+} ArH$
I	**Sandmeyer's reaction** $\xrightarrow{CuBr/HBr} ArBr + N_2$
U M	**Gattermann reaction** $\xrightarrow{Cu/HBr} ArBr + N_2$
S A	**Coupling reaction** $\xrightarrow[pH\ =\ 9\text{-}10,\ 0\text{-}5°C]{C_6H_5OH/OH^-} ArN{=}NC_6H_4OH$
L T S	**Reduction** $\xrightarrow[HCl]{SnCl_2} ArNH{-}NH_2$ Aryl hydrazine

NITRO COMPOUNDS

- **General formula :** RNO_2
- **Classification :**



Preparation		Chemical Properties
$CH_3CH_2CH_3 \xrightarrow[673\ K]{HNO_3} CH_3CH_2CH_2NO_2 + CH_3CH(NO_2)CH_3 + CH_3CH_2NO_2 + CH_3NO_2$	$R-NO_2$	$RNO_2 \xrightarrow[ether]{LiAlH_4} RNH_2$
$RX + AgNO_2 \xrightarrow[(alc.)]{\Delta} RNO_2 + AgX$		$RNO_2 \xrightarrow[6[H]]{Sn/HCl} RNH_2 + 2H_2O$
$CH_2ClCOOH \xrightarrow[-NaCl]{NaNO_2} CH_2NO_2COOH \xrightarrow{\Delta} CH_3NO_2 + CO_2$		$RCH_2NO_2 + H_2O \xrightarrow[\Delta]{H^+} RCOOH + NH_2OH$
$CH_3-C(CH_3)=CHNO_2 \xrightarrow[H^+ \text{or } OH^-]{HOH} CH_3-C(CH_3)=O + CH_3NO_2$		$\underset{(1°)}{RCH_2NO_2} \xrightarrow[NaOH]{HNO_2} R-C(NO_2)=N\overset{-}{O}\overset{+}{Na}$ (Red coloured sodium salt)
		$\underset{(2°)}{R_2CH(NO_2)} + HNO_2 \xrightarrow[\Delta]{-H_2O} R_2C(NO_2)-NO \xrightarrow[NaOH]{\text{Ether or}}$ Blue colour
		$\underset{(3°)}{R_3C-NO_2} \xrightarrow[NaOH]{HNO_2}$ No reaction

CYANIDES AND ISOCYANIDES

- General Formula of cyanides is $R-C\equiv N$ or isocyanides is $R-N\overset{\rightarrow}{=}C$.
- Cyanides are also called nitriles.
  Isocyanides are also called isonitriles or carbylamines.

Preparation of Cyanides

$R-C\equiv N$:

- $RX + KCN \longrightarrow RCN + KX$
- $RCONH_2 \xrightarrow[\Delta]{P_2O_5} RC\equiv N + H_2O$
- $CH_3CH=NOH \xrightarrow[-H_2O]{P_2O_5} CH_3C\equiv N$
- $RMgBr + Cl-CN \longrightarrow RCN + MgBrCl$
- $RCH_2NH_2 \xrightarrow[773\ K]{Cu} RCN + 2H_2$
- $CH_3COOH + NH_3 \longrightarrow CH_3COONH_4 \xrightarrow[773K,\ -H_2O]{Al_2O_3} CH_3CONH_2 \xrightarrow[-H_2O]{Al_2O_3} CH_3C\equiv N$
- $2CH_3CH_3 + 2NH_3 + 3O_2 \xrightarrow[773\text{-}873\ K]{Catalyst} 2CH_3CN + 6H_2O$

Chemical Properties of Cyanides

$R-C\equiv N$:

- $RCN + R'MgX \xrightarrow{Ether} R-C(R')=NMgX \xrightarrow{HOH} R-C(R')=NH \xrightarrow[H^+]{HOH} R-C(R')=O + NH_3$
- $RCN + R'OH + HCl \xrightarrow{H_2O} RCOOR' + NH_4Cl$
- $RCN + 2HCl \xrightarrow[\text{HCl gas}]{Dry} R-C(Cl)_2-NH_2$ (Aminochloride)
- $R-CN + HCl \xrightarrow[\text{HCl gas}]{Dry} R-C(Cl)=NH$ (Iminochloride)
- $CH_3CN + H_2O \xrightarrow{H_2O_2/OH^-} CH_3CONH_2$
- $CH_3C\equiv N + 2H_2O \xrightarrow{H^+} CH_3COOH + NH_4^+$
- $CH_3CN + 2H_2 \xrightarrow[\text{or } LiAlH_4]{\text{Ni/Pt or Na} + C_2H_5OH} CH_3CH_2NH_2$

Stephen's reaction

$R-CN \xrightarrow[2[H]]{SnCl_2/HCl} RCH=NH\cdot HCl \xrightarrow{H_2O} RCHO + NH_4Cl$

$R-CN + 2[H] \xrightarrow[195\ K]{DIBAL\text{-}H} RCH=NH \xrightarrow{H_2O/H^+} RCHO$

Isocyanides

Preparation

$$RI + AgCN \xrightarrow[\Delta]{C_2H_5OH} RN \rightleftarrows C + AgI$$

$$RNH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} RN \rightleftarrows C + 3KCl + 3H_2O$$

$$HCONHR \xrightarrow[\text{Pyridine}]{POCl_3} RN \rightleftarrows C + H_2O$$

$RN \rightleftarrows C$

Chemical Properties

$$CH_3N \rightleftarrows C + 2H_2O \xrightarrow{H^+ \text{ or } OH^-} CH_3NH_2 + HCOOH$$

$$CH_3N \rightleftarrows C + 2H_2 \xrightarrow[Na/C_2H_5OH]{Ni/Pt \text{ or}} CH_3NHCH_3$$

$$RNC \xrightarrow{\Delta} RCN$$

$$RNH_2 + COCl_2 \longrightarrow [CH_3NHCOCl] \xrightarrow{\Delta} CH_3-N=C=O$$

INFO SHOTS

Going against the grain : Nitrogen turns out to be hypersociable!

Nobody expected this. Computer simulations suggest that nitrogen, a very well-known element, with a reputation for being reluctant to react could, at a high enough pressure, break the chemical rules and become extremely gregarious : a single atom would then be able to form even six chemical bonds. This surprising discovery has been made by researchers at the Institute of Physical Chemistry of the Polish Academy of Sciences (IPC PAS) in Warsaw and the New Technology Centre at the University of Warsaw (CeNT UW). Researchers analyzed thousands of crystal structures of nitrogen compounds with fluorine arising at high pressures, hoping to see some structures containing nitrogen pentafluoride NF_5 particles. They were completely unprepared for the fact that, in one of the crystal they ran into ions with the formula NF_6^- in which the nitrogen atom bonds with as many as six fluorine atoms. A reorganization takes place during which the molecular crystal, originally formed of a mixture of gases NF_3 and F_2, transforms into a complex ionic crystal constructed of NF_4^-, NF_2^+ and NF_6^- ions. The pressure required for the synthesis of crystals containing NF_6^- amounts to 400-500 thousand atmospheres which is within the reach of current experiment techniques.

BIOMOLECULES

CARBOHYDRATES

- These are polyhydroxy aldehydes or polyhydroxy ketones or compounds which yield such products on hydrolysis. These are also known as *saccharides*. Their general formula is $C_x(H_2O)_y$ 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

Carbohydrates — Based on taste:

- Non-sugar (tasteless) → Polysaccharides: Give large number of monosaccharide molecules on hydrolysis. General formula, $(C_6H_{10}O_5)_n$, where n = 100 to 3000. *e.g.*, starch, cellulose and glycogen.
- Sugar (sweet in taste)
  - Based on reducing property:
    - **Reducing sugars :** Reduces Fehling's solution and Tollens' reagent. Contains aldehyde or ketone groups. *e.g.*, maltose, glucose, lactose, fructose, etc.
    - **Non-reducing sugars :** Aldehyde and ketone groups are bonded hence, do not reduce Tollens' and Fehling's reagents. *e.g.*, sucrose
  - Based on hydrolysis:
    - Monosaccharides
      - Cannot be hydrolysed further
      - General formula, $(CH_2O)_n$; n = 3 to 9
      - based on functional groups:
        - Aldoses (aldehyde group present) *e.g.*, glucose
        - Ketoses (ketone group present) *e.g.*, fructose
    - Oligosaccharides: Give 2 to 10 monosaccharides on hydrolysis
      - based on number of monosaccharide units obtained:
        - Disaccharides (2) *e.g.*, sucrose, maltose
        - Trisaccharides (3) *e.g.*, raffinose
        - Tetrasaccharides (4) *e.g.*, stachyose

Glucose ($C_6H_{12}O_6$), Aldohexose

Preparation

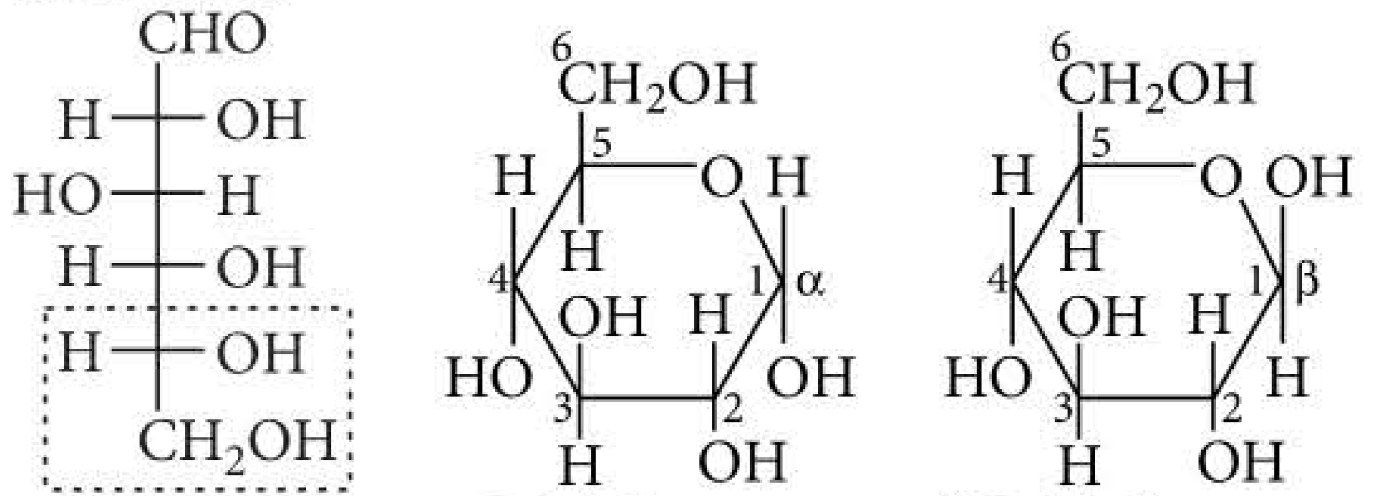
- **Laboratory method :** From sucrose (cane sugar)

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

- **Commercial method :** From starch

$$\underset{\text{Starch or Cellulose}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[\text{393 K, 2-3 atm}]{H^+/\Delta} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

Structure :



D-(+)-Glucose — α-*D*-(+)-Glucopyranose — β-*D*-(+)-Glucopyranose

Fischer projection — Haworth structures

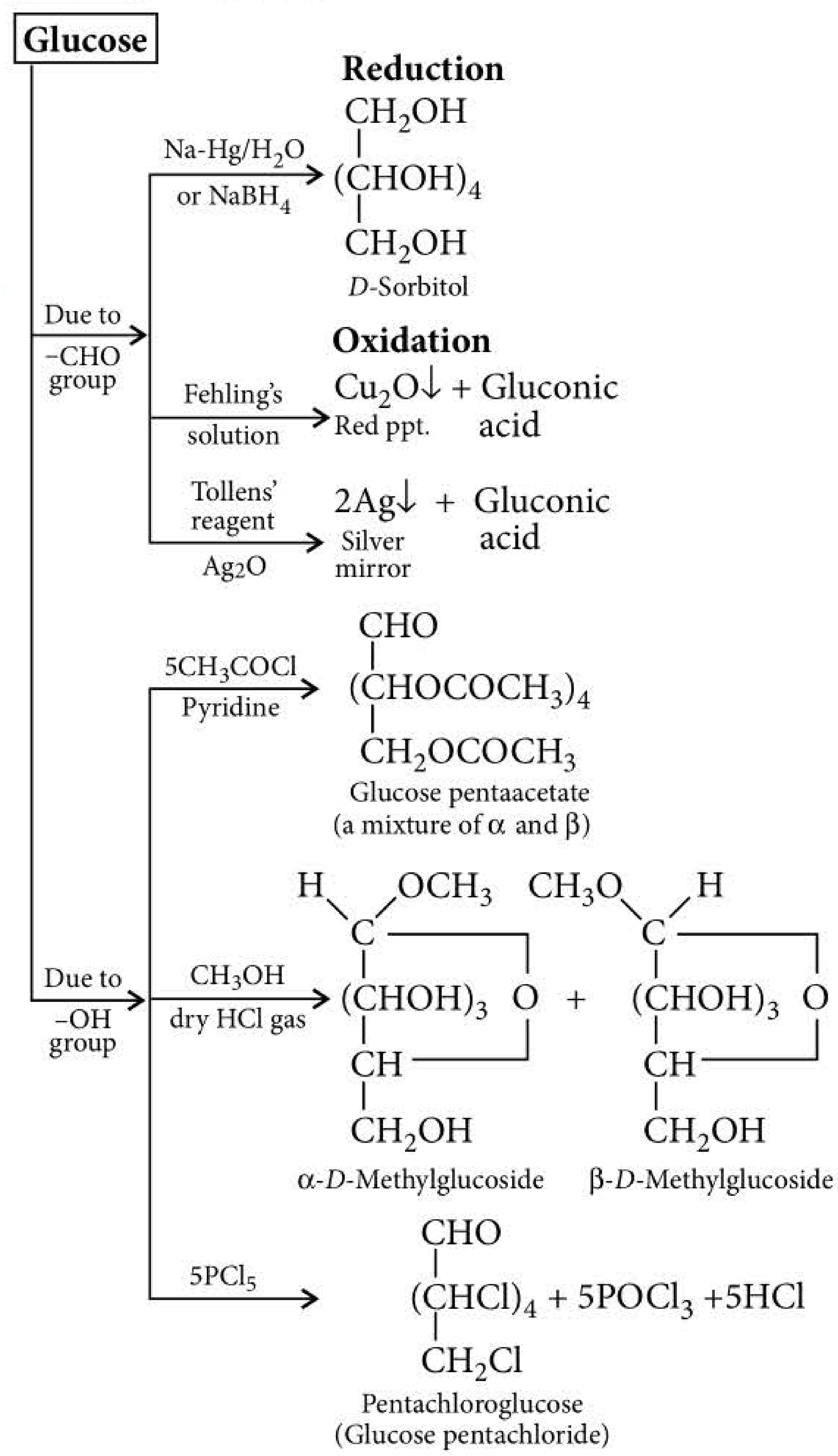
Evidences of open chain structure of glucose

- Glucose + HI $\xrightarrow[\text{Red P}]{\Delta}$ *n*-Hexane
  confirms the presence of six carbon atoms linked in a straight chain.
- Glucose + NH_2OH $\longrightarrow$ Glucose oxime
  confirms the presence of a carbonyl group.
- Glucose + HCN $\longrightarrow$ Glucose cyanohydrin
  confirms the presence of a carbonyl group.
- Glucose + [O]/Br_2-water $\longrightarrow$ Gluconic acid
  indicates aldehydic group.
- Glucose + $5(CH_3CO)_2O$ $\longrightarrow$ Glucose pentaacetate
  confirms the presence of five –OH groups.
- Glucose + HNO_3/oxidation $\longrightarrow$ Glucaric acid
  indicates the presence of a primary alcoholic (–OH) group.

Physical Properties

- It is a colourless, crystalline solid, melts at 146°C and less sweet (three-fourth) than cane sugar.
- It is readily soluble in water, sparingly soluble in alcohol but insoluble in ether.
- It is optically active and the ordinary naturally occurring form is (+)-glucose or dextro form. It shows mutarotation.

Chemical Properties



Mutarotation

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

$$\alpha\text{-}D\text{-Glucose} \rightleftharpoons \text{Equilibrium mixture} \rightleftharpoons \beta\text{-}D\text{-Glucose}$$

$[\alpha]_D = +112°$ — $[\alpha]_D = +52.7°$ — $[\alpha]_D = +19°$

Fructose ($C_6H_{12}O_6$), Ketohexose

Preparation

- **From sucrose (cane sugar)**

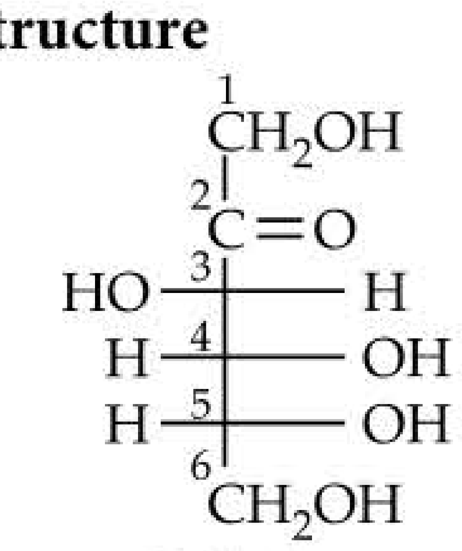
$$\underset{\substack{\text{Cane sugar}\\ \text{(Dextrorotatory)}}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\Delta]{\text{dil. } H_2SO_4} \underset{\substack{D\text{-Glucose}\\ \text{(Dextrorotatory)}}}{C_6H_{12}O_6} + \underset{\substack{D\text{-Fructose}\\ \text{(Laevorotatory)}}}{C_6H_{12}O_6}$$

The solution containing equimolar mixture of *D*-(+)-glucose and *D*-(–)-fructose is called *invert sugar* and the process is known as *inversion*.

- **From inulin**

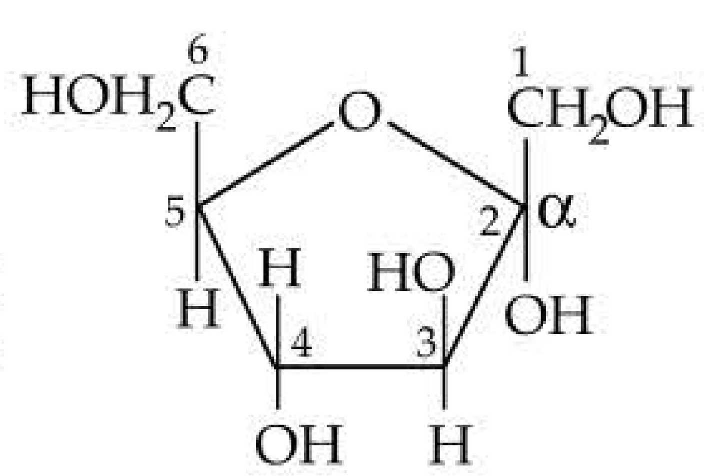
$$\underset{\text{Inulin}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{dil. } H_2SO_4} \underset{\text{Fructose}}{nC_6H_{12}O_6}$$

Structure



D-(–)-Fructose

Fischer structure

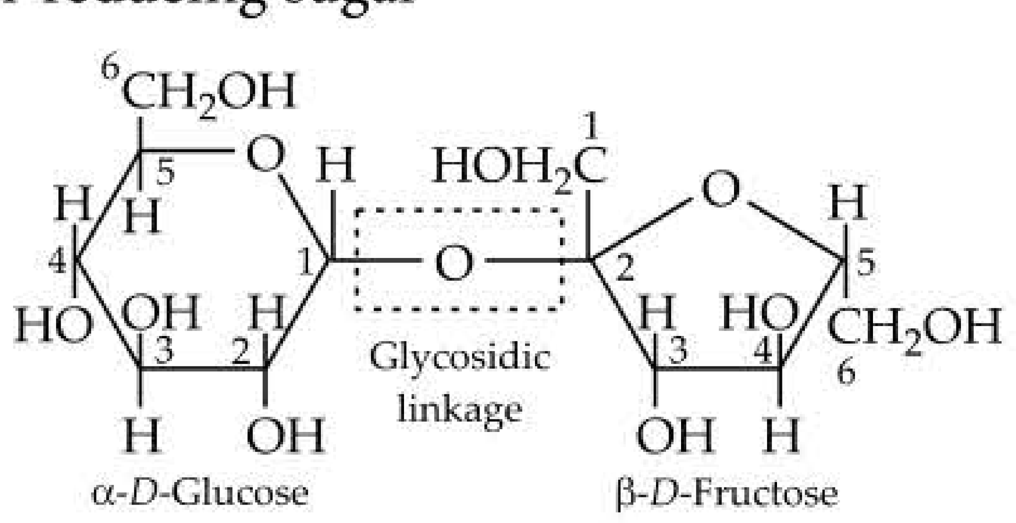


α-*D*-(–)-Fructofuranose

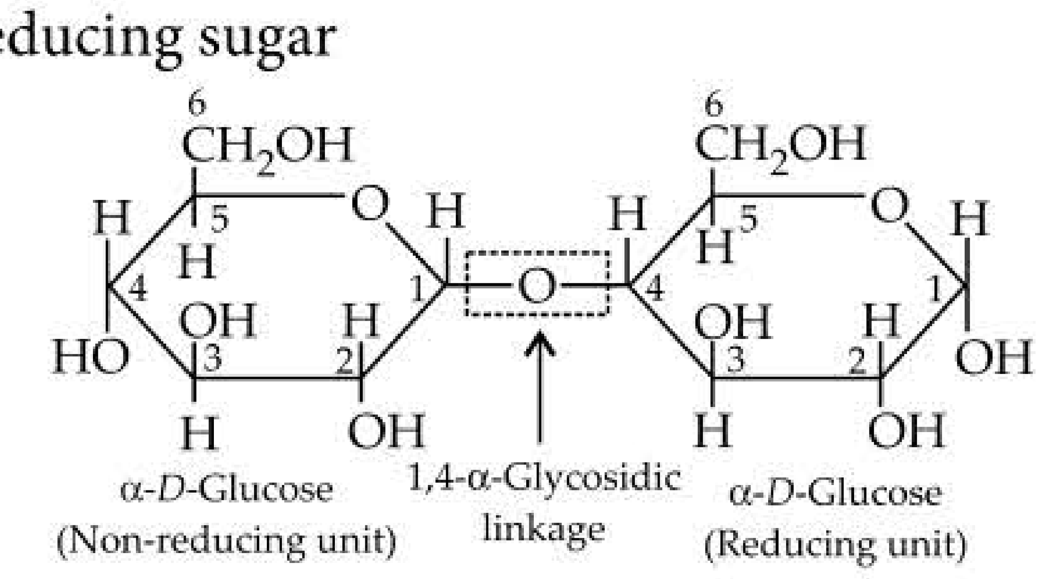
Haworth structure

Disaccharides

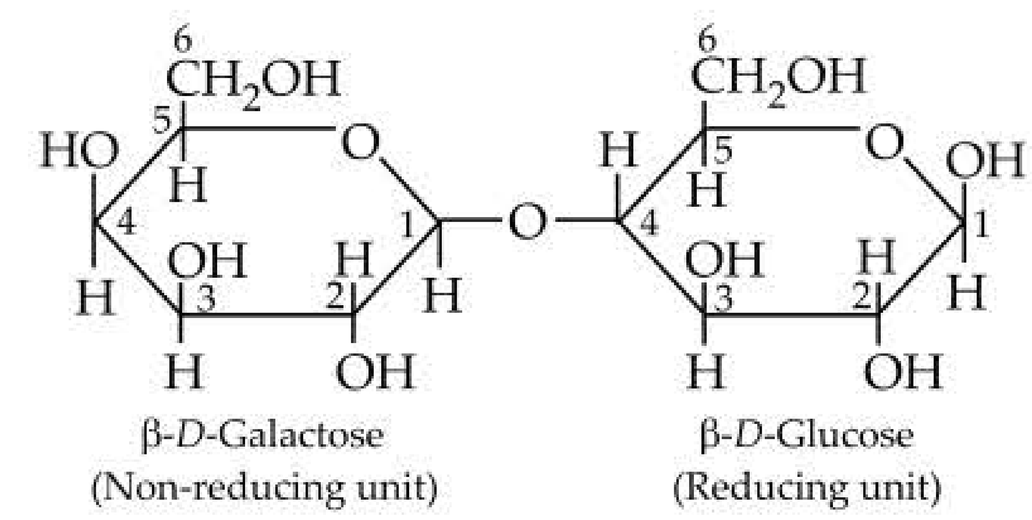
- **Sucrose ($C_{12}H_{22}O_{11}$)**
  - Cane sugar and Dextrorotatory
  - Non-reducing sugar



- **Maltose ($C_{12}H_{22}O_{11}$)**
  - Malt sugar and Dextrorotatory
  - Reducing sugar

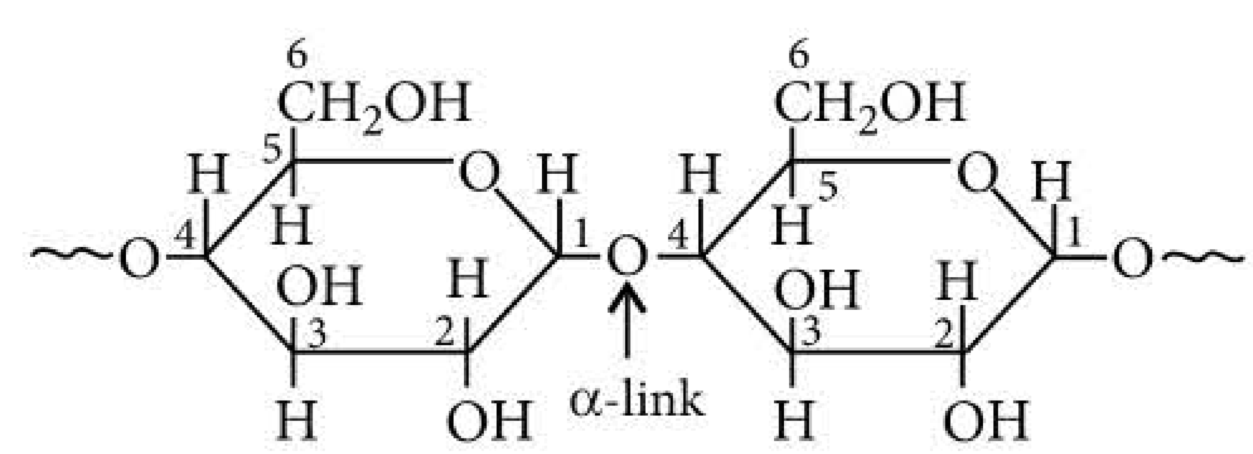


- **Lactose ($C_{12}H_{22}O_{11}$)**
  - Milk sugar and epimeric in nature
  - Reducing sugar

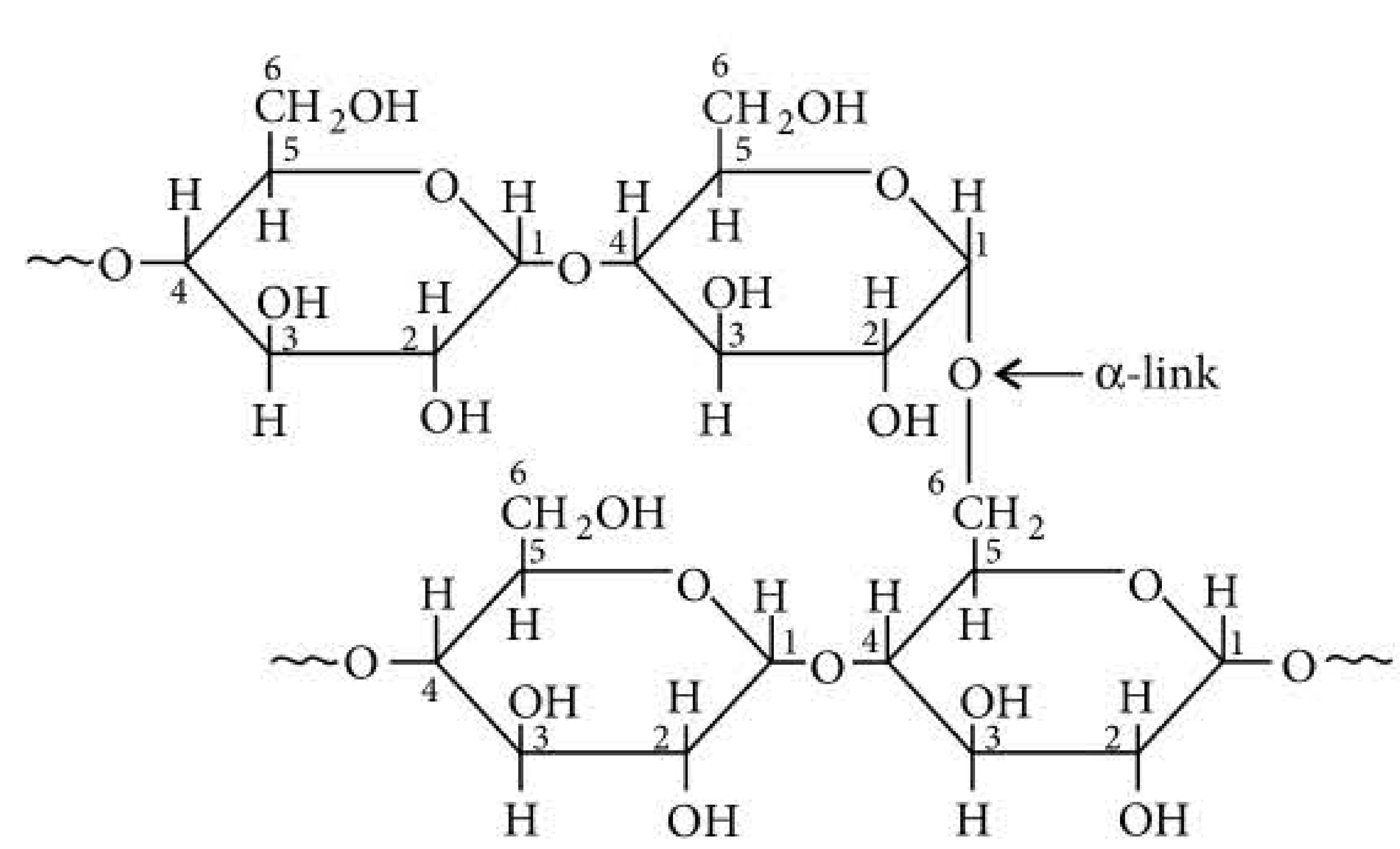


Polysaccharides

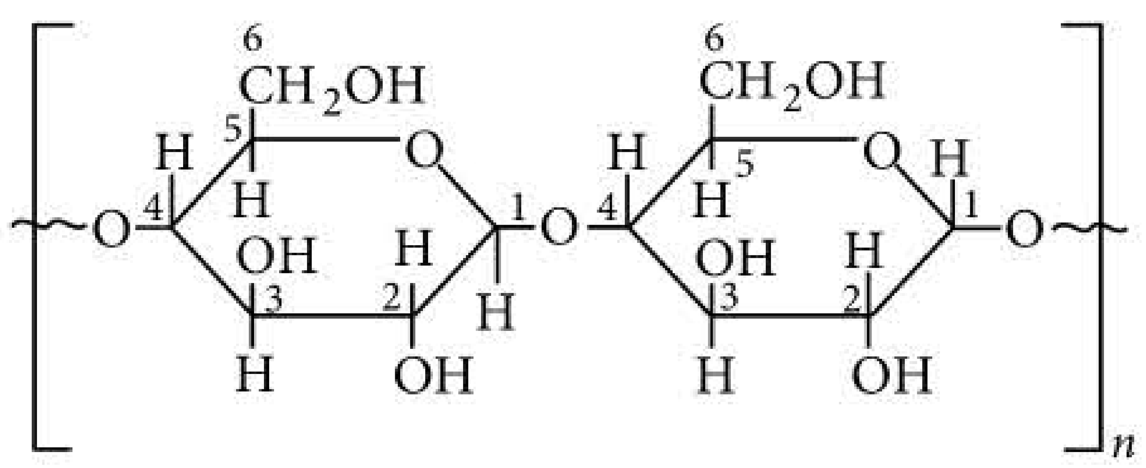
- **Starch :** It is a polymer of α-*D*-glucose units and consists of two components : amylose and amylopectin.
  - **Amylose**
    - It is a long unbranched chain with 200-1000 α-*D*-(+)-glucose units held by 1,4-α-glycosidic linkage.
    - Water soluble
    - It constitutes about 15-20% of starch.



  - **Amylopectin**
    - It is a branched chain polymer of α-*D*-glucose units in which chain is formed by 1,4-α-glycosidic linkage whereas branching occurs by 1,6-α-glycosidic linkage.
    - Insoluble in water
    - It constitutes 80-85% of starch.



- **Cellulose $(C_6H_{10}O_5)_n$:** It is a straight chain polysaccharide composed only of β-*D*-glucose units joined together by 1,4-β-glycosidic linkages between C-1 of one glucose and C-4 of the next glucose unit.



- **Glycogen $(C_6H_{10}O_5)_n$:** It is stored in liver and muscles and has a similar structure to that of amylopectin and consists of long chains of glucose units.

PROTEINS

- Proteins are fundamental basis of structure and functions of life. They are high molecular mass complex biopolymers of α-amino acids. They occur naturally in milk, cheese, pulses, peanuts, fish, meat, etc.

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

Amino Acids

- Amino acids are the bifunctional molecules with both acidic carboxyl group (– COOH) and basic amino group ($-NH_2$).
- Amino acids can be further divided into three categories :
  - **Acidic :** No. of –COOH groups > No. of $-NH_2$ groups
  - **Basic :** No. of –COOH groups < No. of $-NH_2$ groups
  - **Neutral :** No. of –COOH groups = No. of $-NH_2$ groups

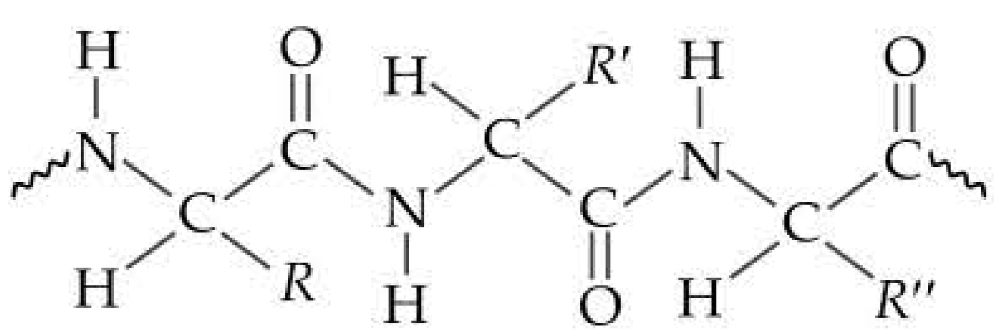
Classification of Proteins

On the basis of molecular structure :

- **Globular proteins :** Globular proteins results when the polypeptide chains coil around itself to give three dimensional spherical shape. These are soluble in water, *e.g.*, insulin and albumins.
- **Fibrous proteins :** In fibrous proteins, polypeptide chains are parallel and are held together by hydrogen and disulphide bonds. These are insoluble in water, *e.g.*, keratin and myosin.
- **Isoelectric point :** The pH at which dipolar ion (zwitter ion) exists as neutral ion, *i.e.*, +ve and –ve charges are equal and it does not migrate to either electrode, is called isoelectric point. The amino acids have least solubility in water at isoelectric point which helps in their separation.

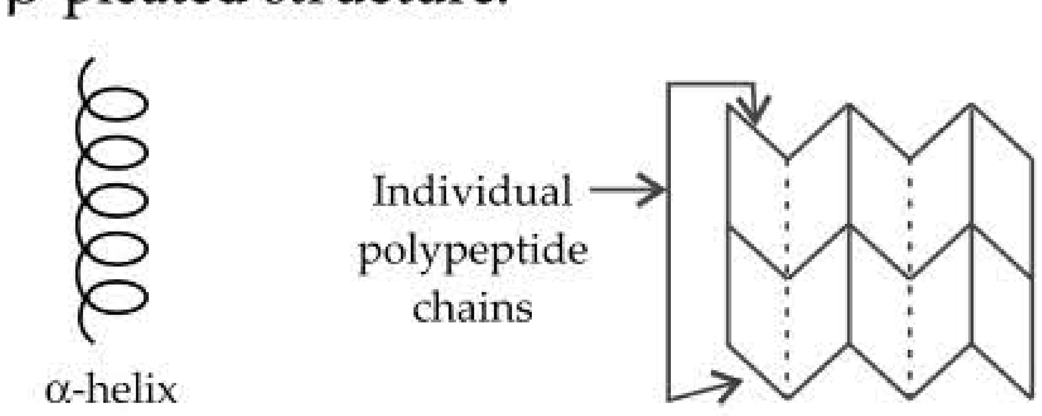
Structure of Proteins

- **Primary structure :** It refers to the number and linear sequence of amino acids held together by peptide bonds.



Primary structure

- **Secondary structure :** It is due to the folding or coiling of the peptide chain.
  It is mainly of two types :
  - **α-helix :** These coils are stabilised by intramolecular hydrogen bonds between carbonyl oxygen of first amino acid to amide hydrogen of fourth amino acid.
  - **β-pleated sheet :** β-pleated sheet structure is formed when hydrogen bonds are formed between the carbonyl oxygens and amide hydrogens of two or more adjacent polypeptide chains. The bonding in β-pleated sheet structure is intermolecular H-bonding. The structure is not planar but is slightly pleated. Silk fibroin has β-pleated structure.



α-helix *e.g.*, myosin (nucleus), keratin (hair), etc. | β-pleated sheet *e.g.*, silk protein (fibroin)

- **Tertiary structure :** It represents overall folding of the polypeptide chains, *i.e.*, further folding of the secondary structure and the bonds responsible for such interaction are hydrophobic interactions, hydrogen bonds, ionic interactions, van der Waals' forces and disulphide bonds.

- **Quaternary structure :** The spatial arrangement of the subunits (two or more polypeptide chains) with respect to each other.

VITAMINS

- These are the complex organic molecules which cannot be produced by the body and must be supplied in small amounts in diet to carry out essential metabolic reactions and biological functions which are required for normal growth and maintenance of the body.

CLASSIFICATION

Vitamins
- **Water soluble vitamins**
  Must be supplied regularly in diet as they are regularly excreted in urine (expect vitamin B_{12}).
  e.g., Vitamin - B_1, B_2, B_5, B_6, B_{12} and C
- **Fat soluble vitamins**
  Stored in liver and adipose tissues.
  e.g., Vitamin - A, D, E and K

NUCLEIC ACIDS

- 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

Nucleic acids (Sugar + base + phosphoric acid)		
DNA	**Components**	**RNA**
2-Deoxy-D-(–)-ribose	Sugar	*D*-(–)-ribose
Cytosine and thymine	Pyrimidine base	Uracil and cytosine
Adenine and guanine	Purine base	Adenine and guanine
H_3PO_4	Phosphoric acid	H_3PO_4
Double stranded α-helix	Structure	Single stranded α-helix
Possible	Replication	Not possible

ENZYMES

- The enzymes are biocatalysts produced by living cells which catalyse biochemical reactions in living organisms. Chemically, they are naturally occurring simple or conjugated proteins.
- **Importance**
  - They play a vital role in living organisms as they catalyse many biological processes.
  - Enzyme deficiency causes diseases *e.g.*, the deficiency of phenylalanine hydroxylase enzyme causes phenylketone urea (PKU) and the deficiency of tyrosinase causes albinism.
  - They are used for the production of beer, wine, syrup and cheese, etc.

HORMONES

- A hormone may be defined as a specific organic product of an endocrine gland secreted into the blood which carries it to some part of the body (target organ) where it regulates a definite physical effect. These are the molecules that act as intercellular messengers and are poured directly in the blood stream by endocrine glands.

CLASSIFICATION

Hormones
- **Amines**
  e.g., epinephrine, thyroxine
- **Peptides**
  e.g., oxytocin, vasopressin
- **Proteins**
  e.g., insulin, glucagon
- **Steroids**
  e.g., sex hormones
  - **Female sex hormones**
    e.g., oestrogens, progesterone
  - **Male sex hormones**
    e.g., androgens