

BRUSH UP for NEET/JEE

Brush up your concepts to get high rank in NEET/JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

2020

Unit
7

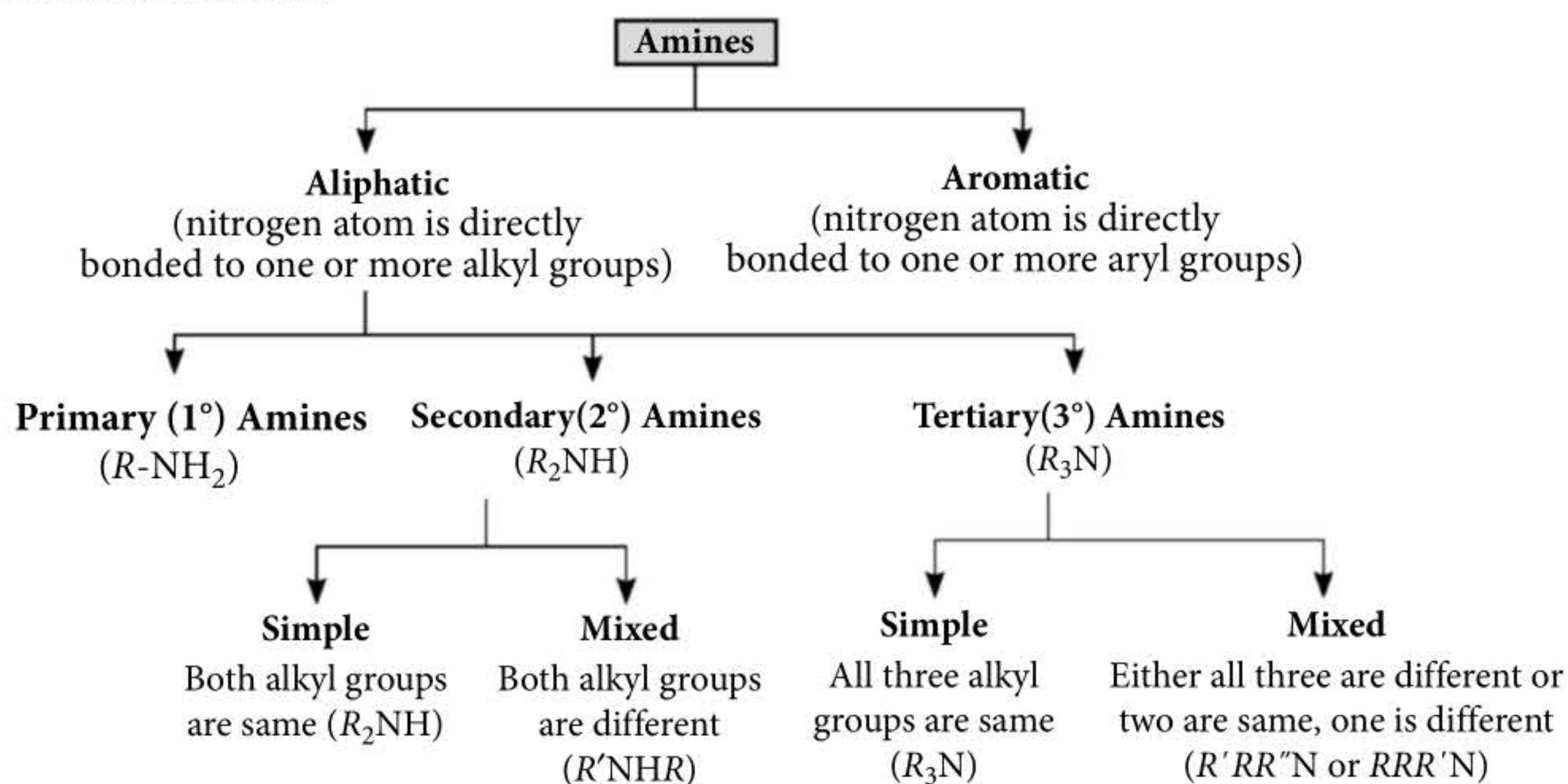
Organic Compounds Containing Nitrogen | Biomolecules

Organic Compounds Containing Nitrogen

AMINES

- Amines are derivatives of ammonia, in which one or more hydrogen atoms are replaced by alkyl or aryl groups.

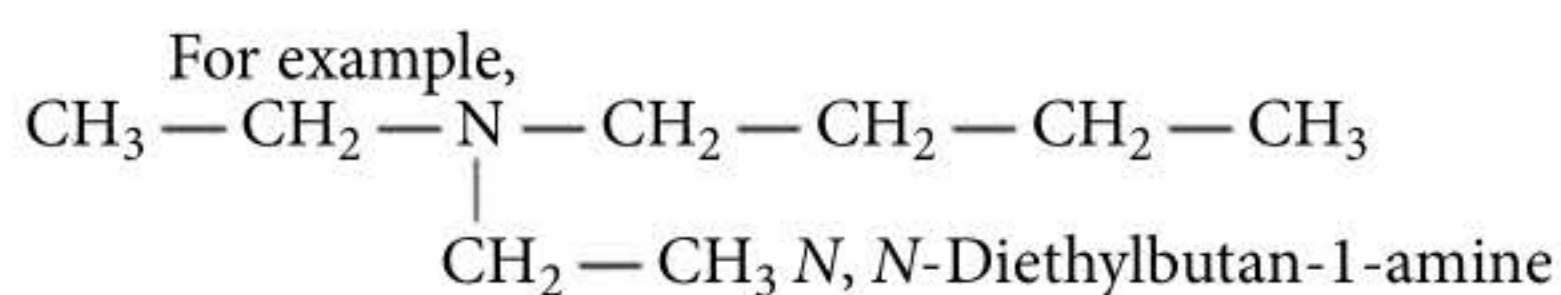
Classification of amines



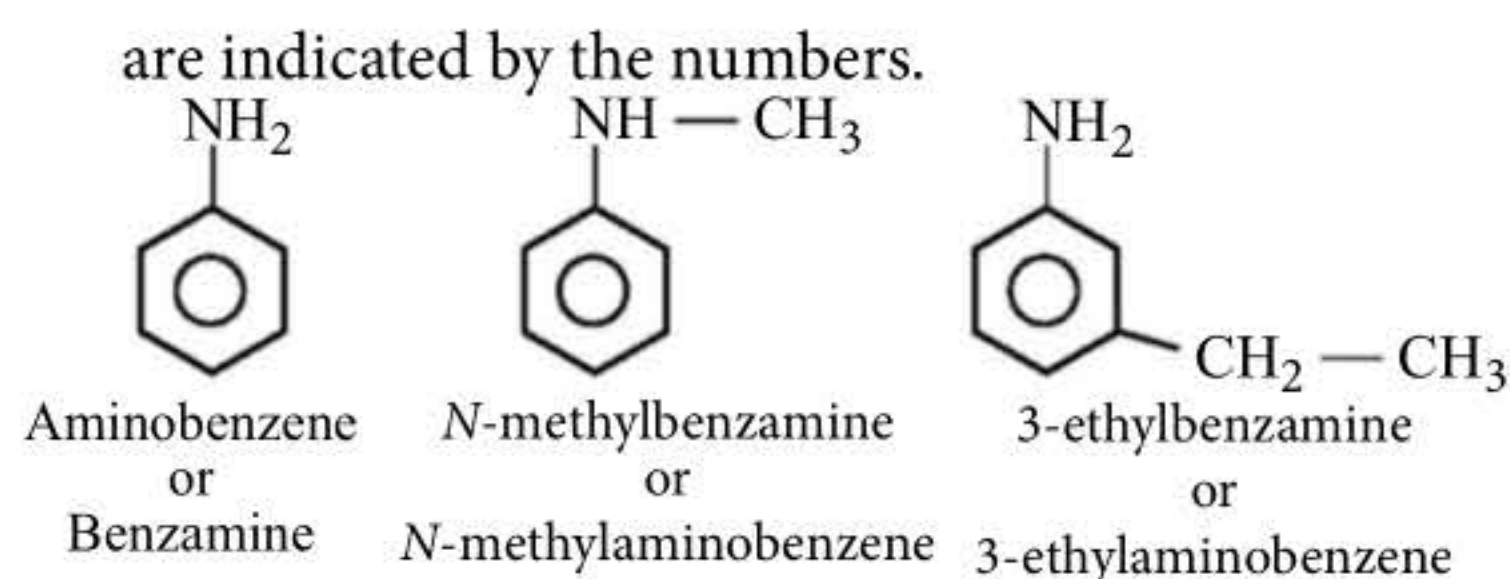
Nomenclature

- Aliphatic amines are called alkanamines in which 'e' of alkane is replaced by amine. For example,
 $\text{CH}_3 - \text{CH}_2\text{NH}_2$ $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$
 Ethanamine Propan-1-amine or 1-propanamine
- The secondary and tertiary amines are named

as nitrogen substituted primary amine *i.e.*, *N*-alkylaminoalkanes (for 2° amine) and *N,N*-dialkylaminoalkanes (for 3° amine). The largest alkyl part is considered as a part of aminoalkane. *N*- and *N,N*- means that alkyl groups are linked to *N*-atom, not to carbon atom.

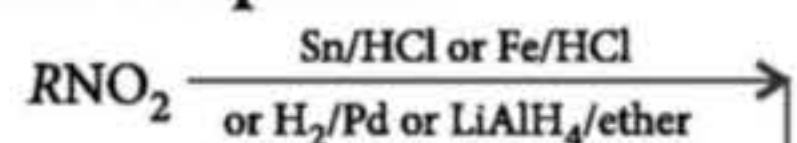


- The simplest aromatic amine is aniline. Other aromatic amines are named as derivatives of benzamine and the positions of the other groups

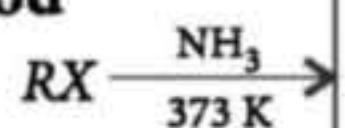


Preparation

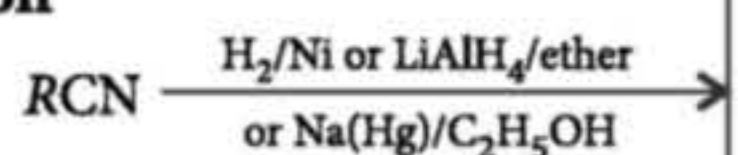
Reduction of nitro compounds



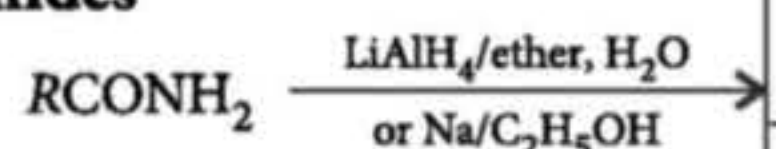
Hofmann's ammonolysis method



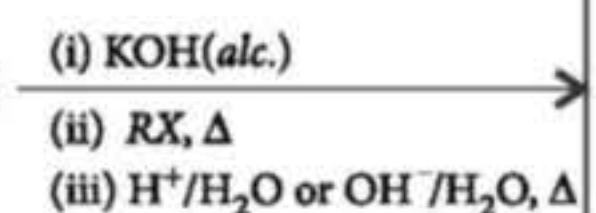
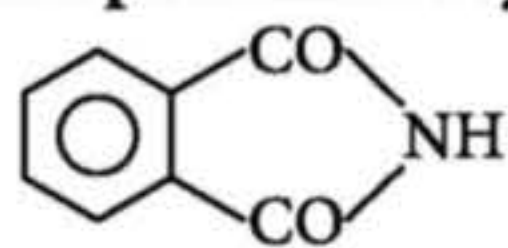
Mendius reduction



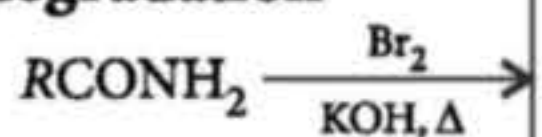
Reduction of amides



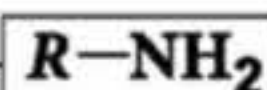
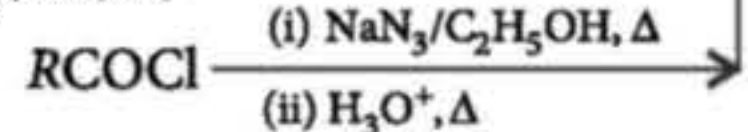
Gabriel phthalimide synthesis



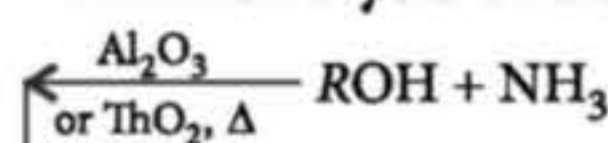
Hofmann's bromamide degradation



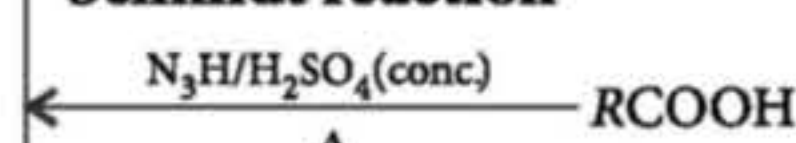
Curtius rearrangement



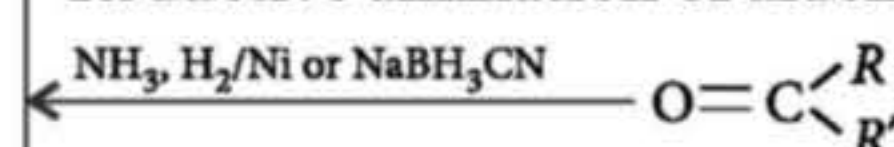
Ammonolysis of alcohols



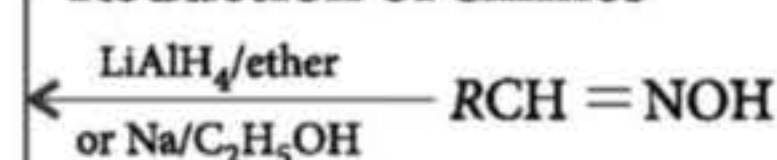
Schmidt reaction



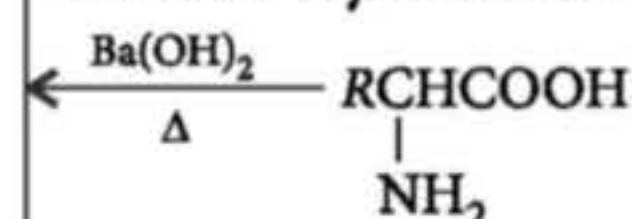
Reductive amination of aldehydes or ketones



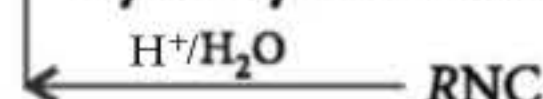
Reduction of oximes



Decarboxylation of α -amino acids



Hydrolysis of isocyanides



Chemical Properties of amine

- Basic character :** The amines are basic in nature due to the presence of a lone pair of electron on N-atom of the $-\text{NH}_2$ group, which it can donate to electron deficient compounds. Aliphatic amines are stronger bases than NH_3 because of the $+I$ effect of the alkyl groups. Greater the number of alkyl groups attached to N-atom, higher is the electron density on it and more will be the basicity. Thus, the order of basic nature of amines is expected to be $3^\circ > 2^\circ > 1^\circ$, however the observed order is $2^\circ > 1^\circ > 3^\circ$. This is explained on the basis of crowding of N-atom of the amine by alkyl groups which hinders the approach and bonding by a proton, consequently, the electron pair which is present on N is unavailable for donation and hence 3° amines are the weakest bases. The order of basicity varies with the nature of alkyl group.

Alkyl group

Basic strength

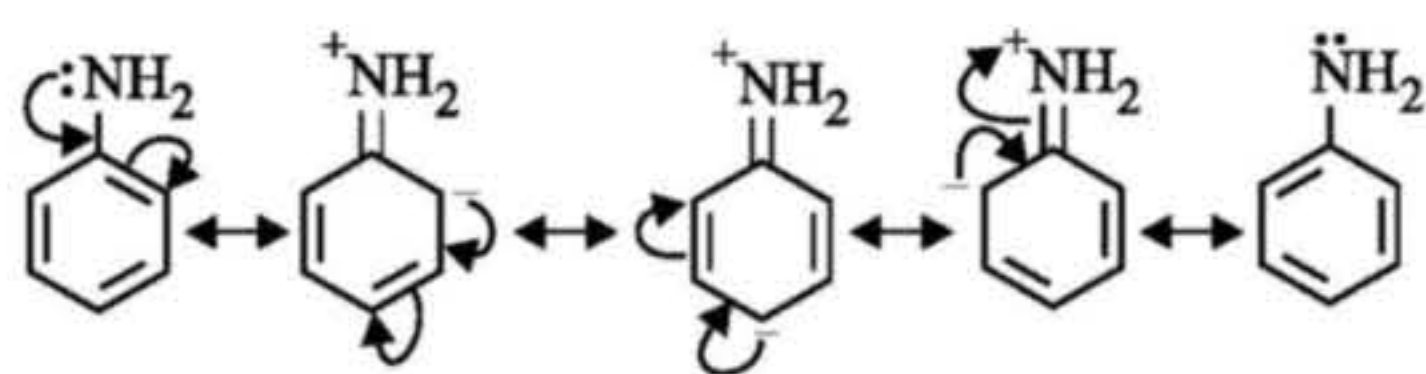
$\text{CH}_3 -$

$\text{R}_2\text{NH} > \text{RNH}_2 > \text{R}_3\text{N} > \text{NH}_3$

$\text{C}_2\text{H}_5 -$

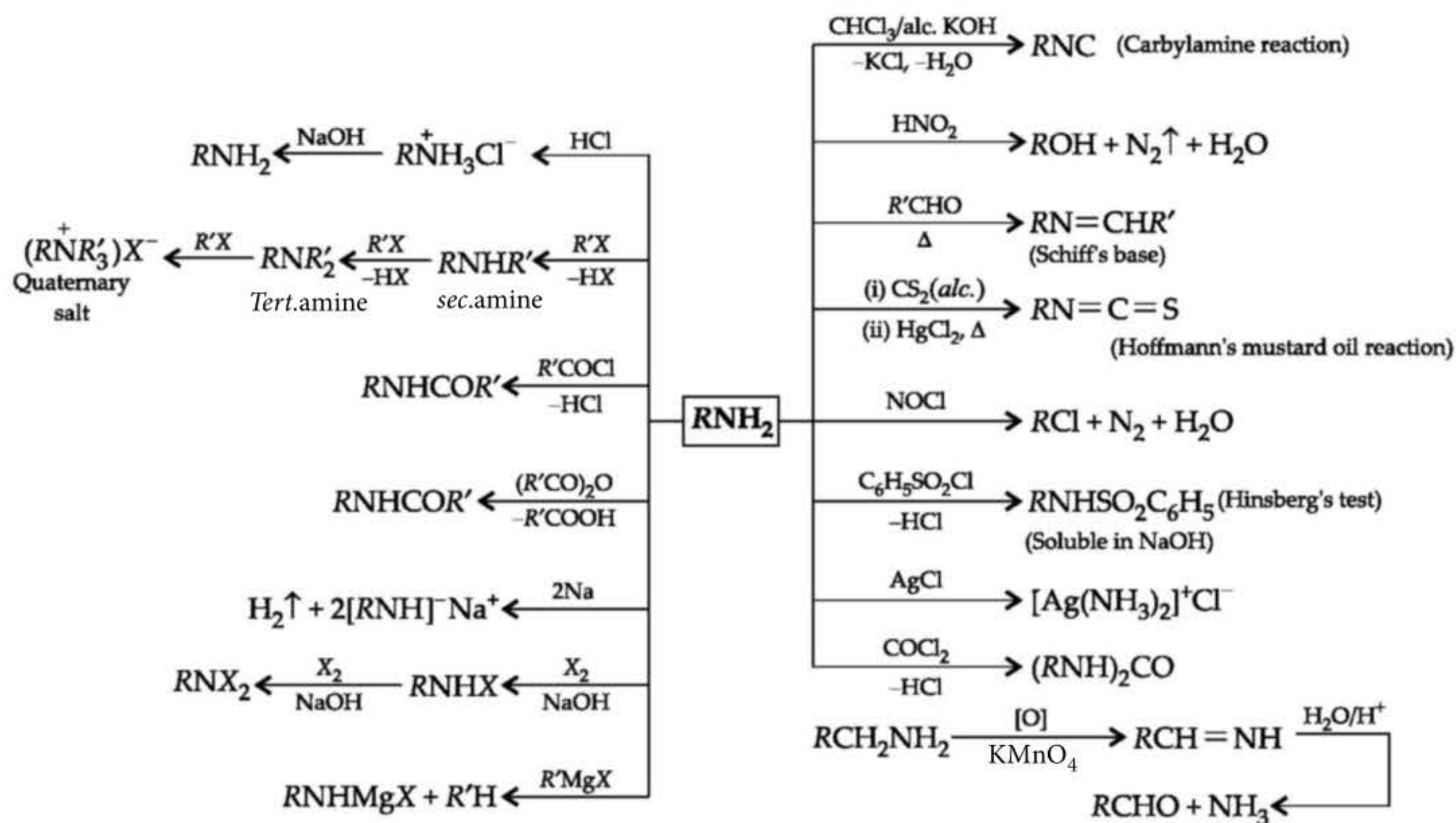
$\text{R}_2\text{NH} > \text{R}_3\text{N} > \text{RNH}_2 > \text{NH}_3$

Aniline is a weaker base as compared to ammonia. This is because the lone pair of electrons on N-atom of aniline is less available for protonation due to its involvement in conjugation with the π -electrons of the benzene ring.



Further the presence of electron withdrawing groups like $-\text{NO}_2$, $-\text{CN}$, $-\text{X}$, etc., decreases the basicity while, the presence of electron donating groups like $-\text{OCH}_3$, $-\text{CH}_3$, $-\text{NH}_2$, etc., activates the benzene ring and also increases the basicity.

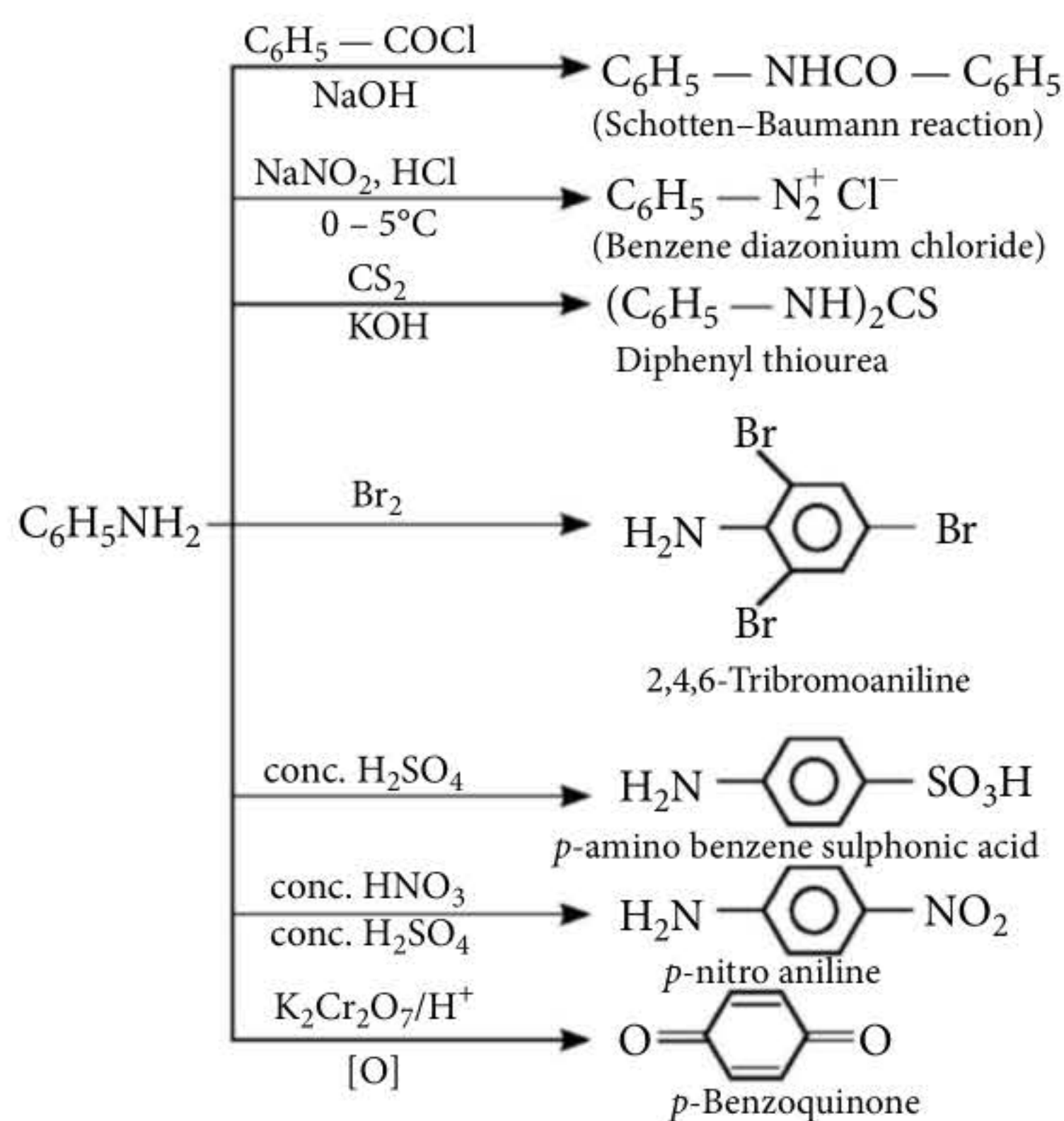
Chemical Reactions



Distinction between 1°, 2° and 3° Amines

- Hinsberg's test** : It involves the treatment of the mixture with benzene sulphonyl chloride ($\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$) called Hinsberg's reagent. The solution is then made alkaline with aqueous alkali.
 - Primary amine forms *N*-alkylbenzene sulphonamide which is soluble in alkali.
 - Secondary amine forms *N,N*-dialkylbenzene sulphonamide which is insoluble in alkali.
 - Tertiary amines do not react with benzene sulphonyl chloride.
- Hofmann's test** : It involves the treatment of the mixture with diethyl oxalate (Hofmann's reagent).
 - Primary amine forms a solid dialkyl oxamide.
 - Secondary amine forms a liquid dialkyl oxamic ester.
 - Tertiary amine does not react.
- Carbylamine test** : It involves the heating of the mixture with chloroform in presence of alcoholic potassium hydroxide to form isocyanides (or carbylamines) which possess foul smell.
 - Only aliphatic and aromatic primary amines give this test.

Chemical Properties of Aniline

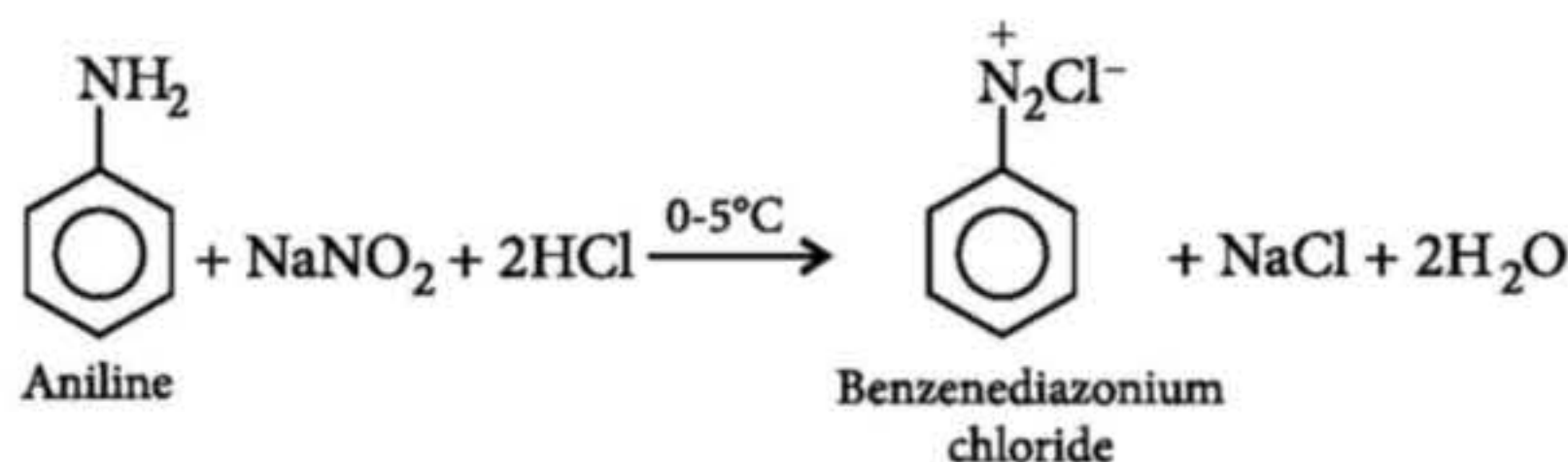


DIAZONIUM SALTS

- Arenediazonium salts** : They have the general formula $\text{ArN}_2^+ \text{X}^-$, Ar stands for the aryl ($-\text{C}_6\text{H}_5$) group and X^- is Cl^- , Br^- , NO_3^- , HSO_4^- , BF_4^- .

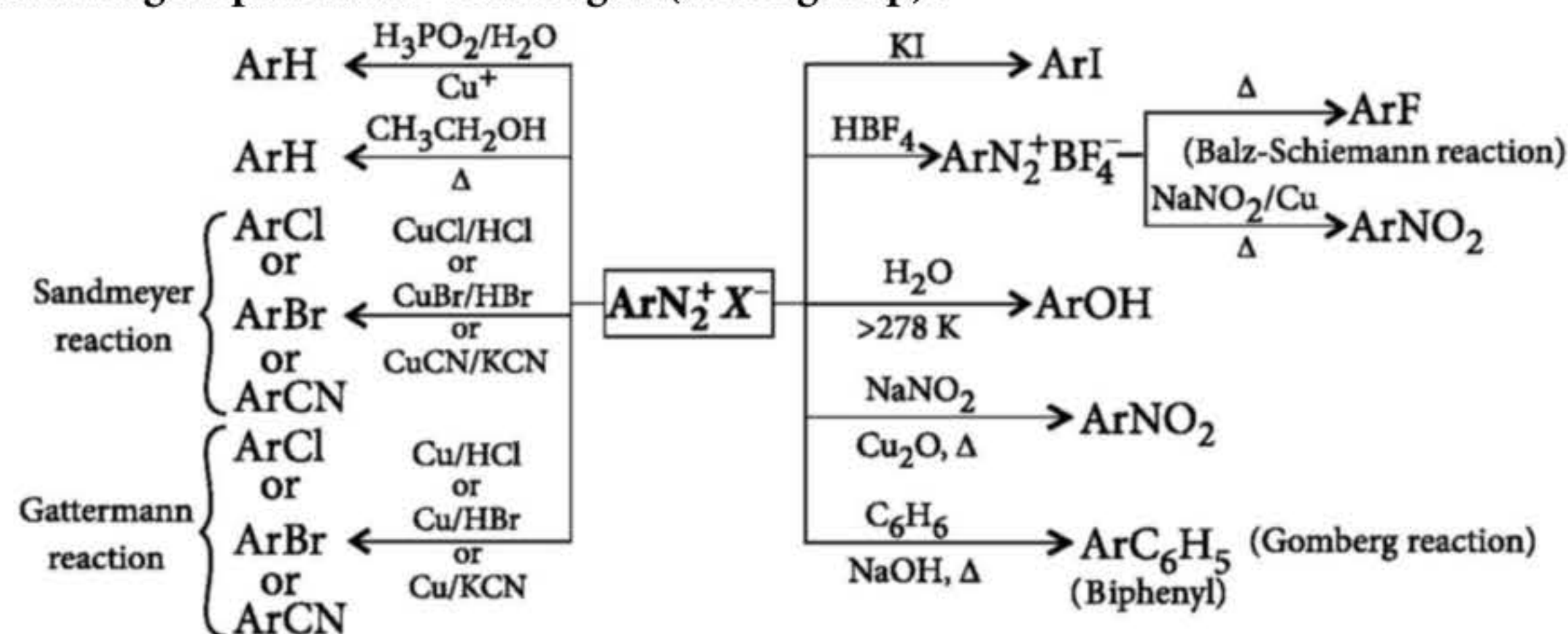
Preparation

- Aromatic diazonium salts are prepared by adding cold aqueous solution of sodium nitrite to the ice cold solution (0-5°C) of a primary aromatic amine in excess of acid.

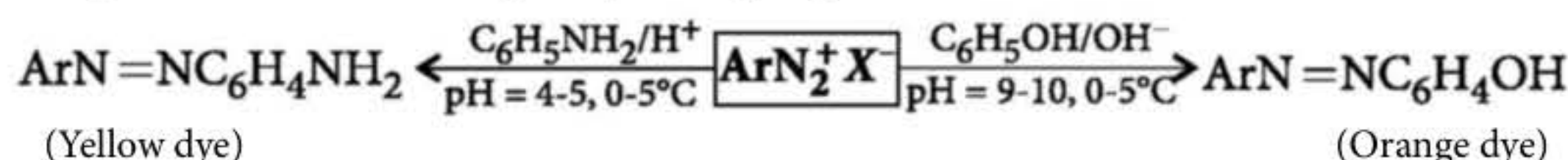


Chemical Properties

- Reactions involving displacement of nitrogen (diazo group) :



- Reactions involving retention of diazo group (coupling reactions) :



PEEP INTO PREVIOUS YEARS

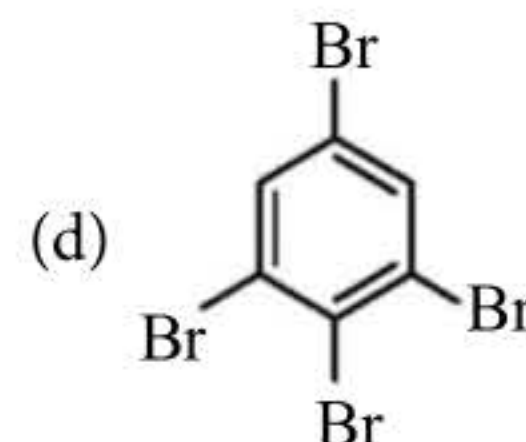
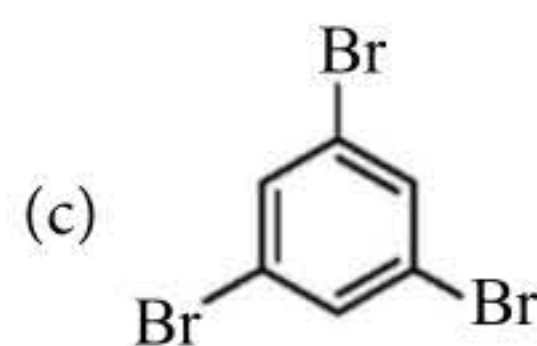
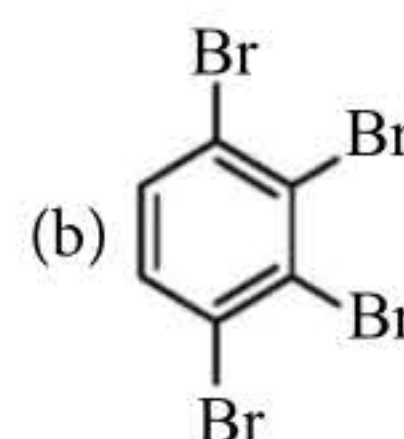
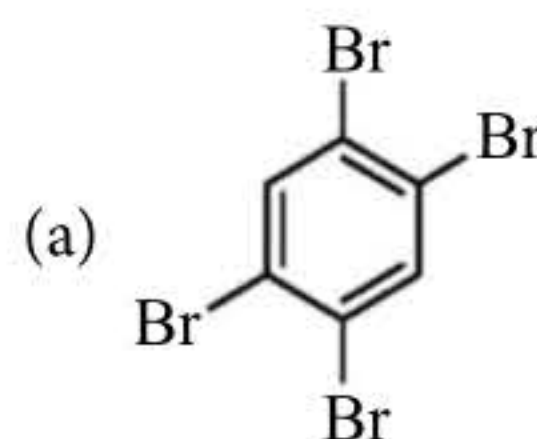
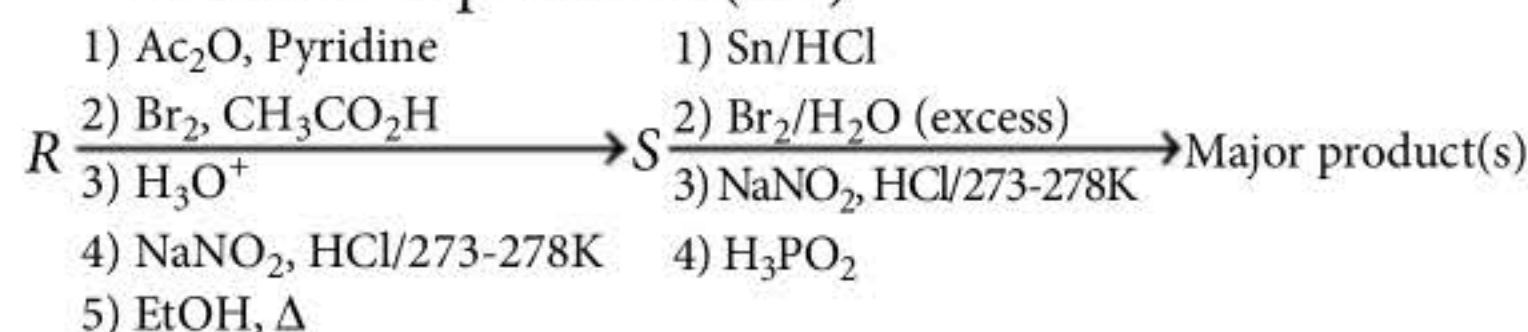
- The correct order of the basic strength of methyl substituted amines in aqueous solution is
 - $\text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH} > (\text{CH}_3)_3\text{N}$
 - $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N}$
 - $(\text{CH}_3)_3\text{N} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH}$
 - $(\text{CH}_3)_3\text{N} > (\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2$

(NEET 2019)

- Ethylamine ($\text{C}_2\text{H}_5\text{NH}_2$) can be obtained from *N*-ethylphthalimide on treatment with
 - H_2O
 - NH_2NH_2
 - NaBH_4
 - CaH_2

(JEE Main 2019)

- Aniline reacts with mixed acid (conc. HNO_3 and conc. H_2SO_4) at 288 K to give *P* (51%), *Q* (47%) and *R* (2%). The major product(s) of the following reaction sequence is (are)



(JEE Advanced 2018)

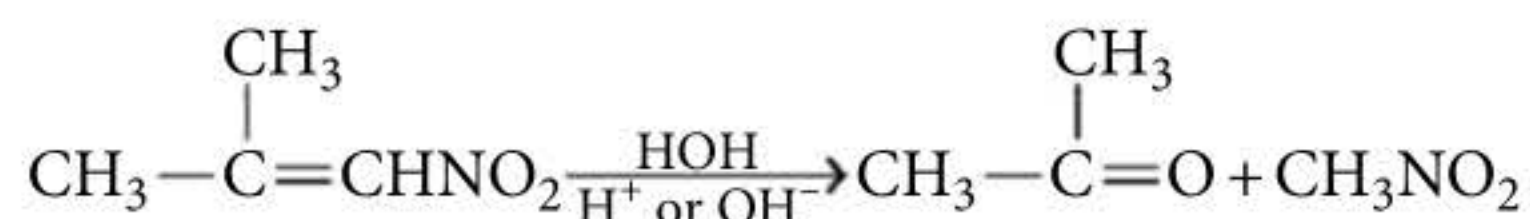
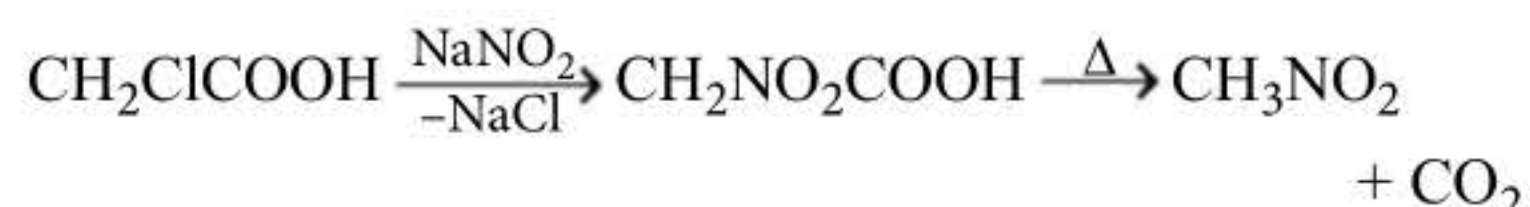
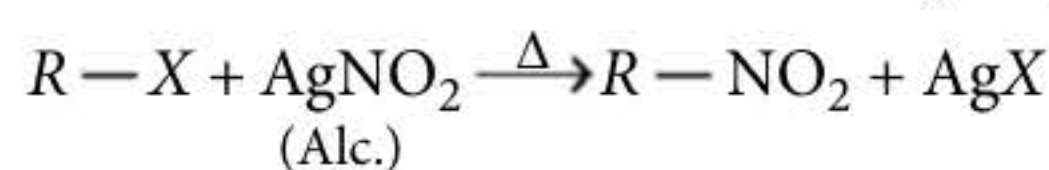
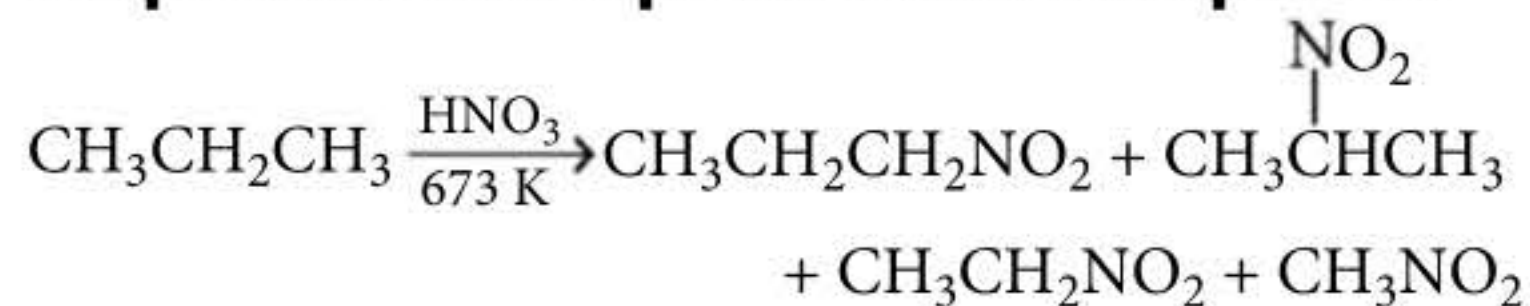
Monthly Test Drive CLASS XI ANSWER KEY

- | | | | | |
|-----------|-------------|-------------|---------|-------------|
| 1. (c) | 2. (d) | 3. (c) | 4. (d) | 5. (a) |
| 6. (a) | 7. (d) | 8. (c) | 9. (a) | 10. (a) |
| 11. (c) | 12. (b) | 13. (c) | 14. (b) | 15. (a) |
| 16. (d) | 17. (a) | 18. (c) | 19. (a) | 20. (a,b,d) |
| 21. (a,b) | 22. (a,b,c) | 23. (a,c,d) | 24. (3) | 25. (6) |
| 26. (2.5) | 27. (a) | 28. (d) | 29. (c) | 30. (d) |

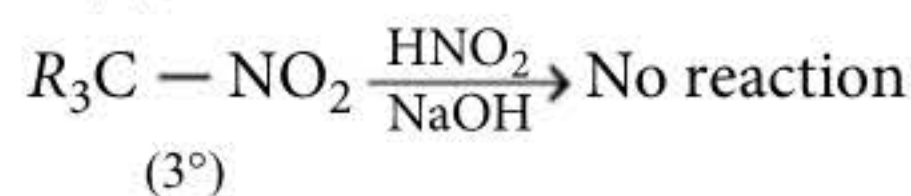
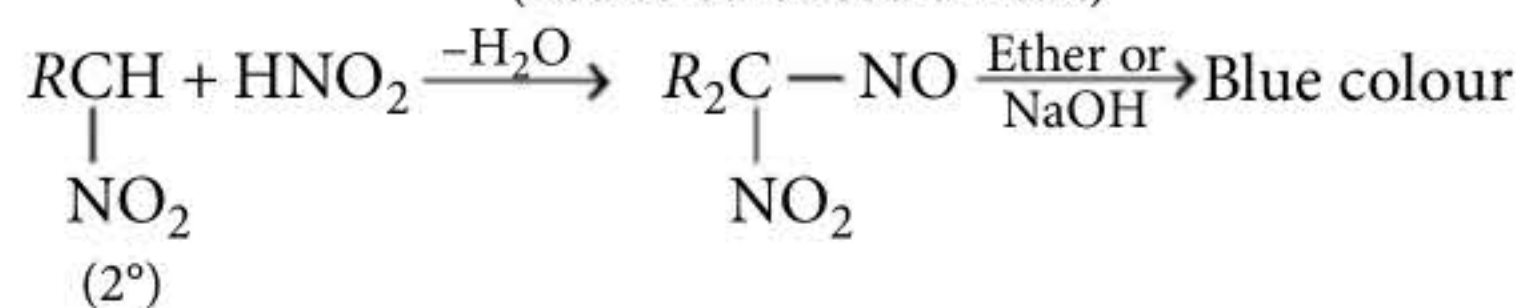
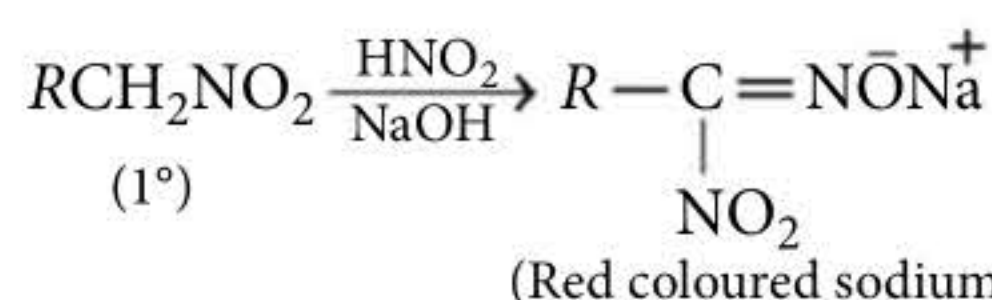
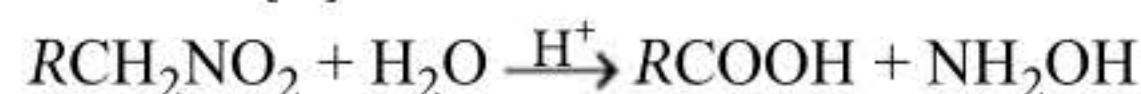
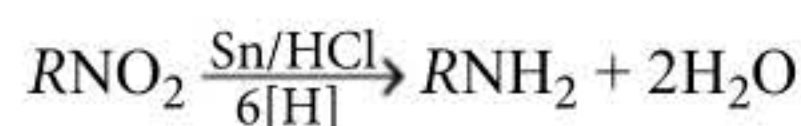
NITRO COMPOUNDS

- Nitro compounds have the general formula RNO_2 or $ArNO_2$, where R is alkyl and Ar is aryl groups e.g., CH_3NO_2 , $C_6H_5NO_2$

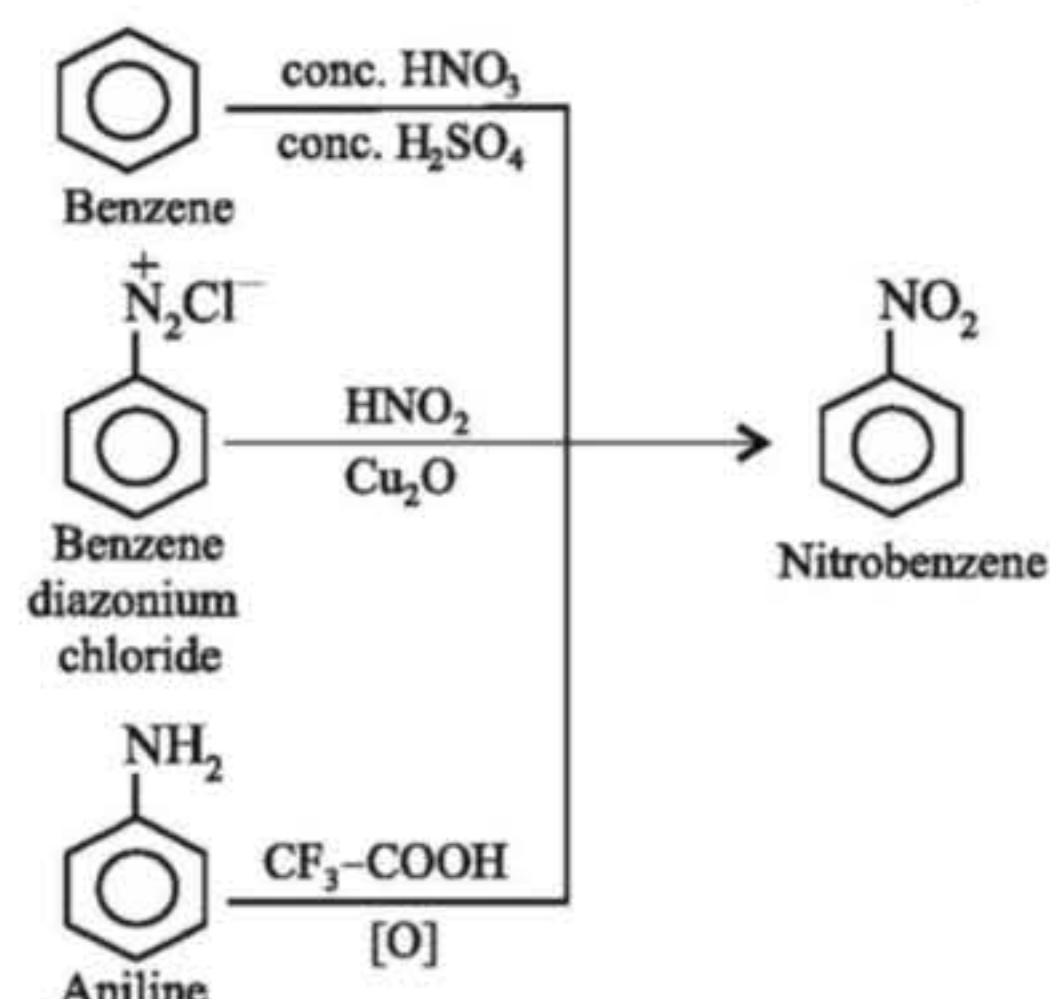
Preparation of Aliphatic Nitro compound



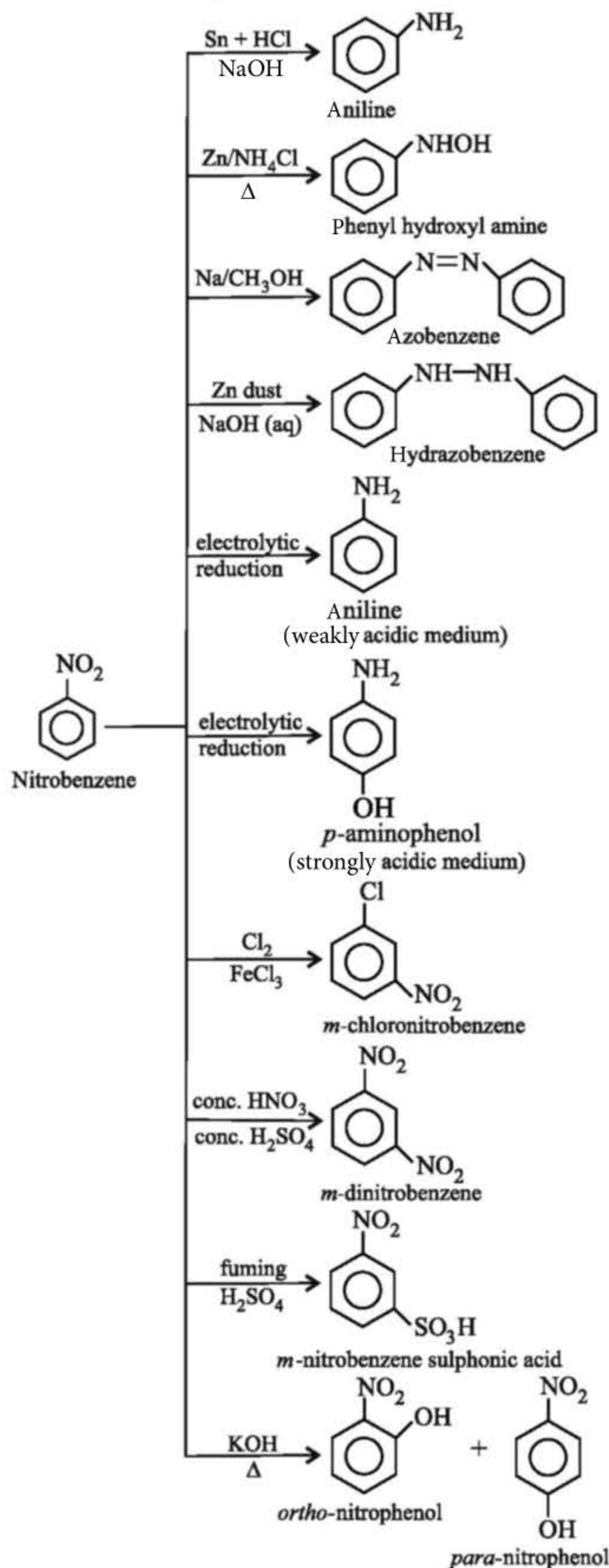
Chemical Properties



Preparation of aromatic nitro compound



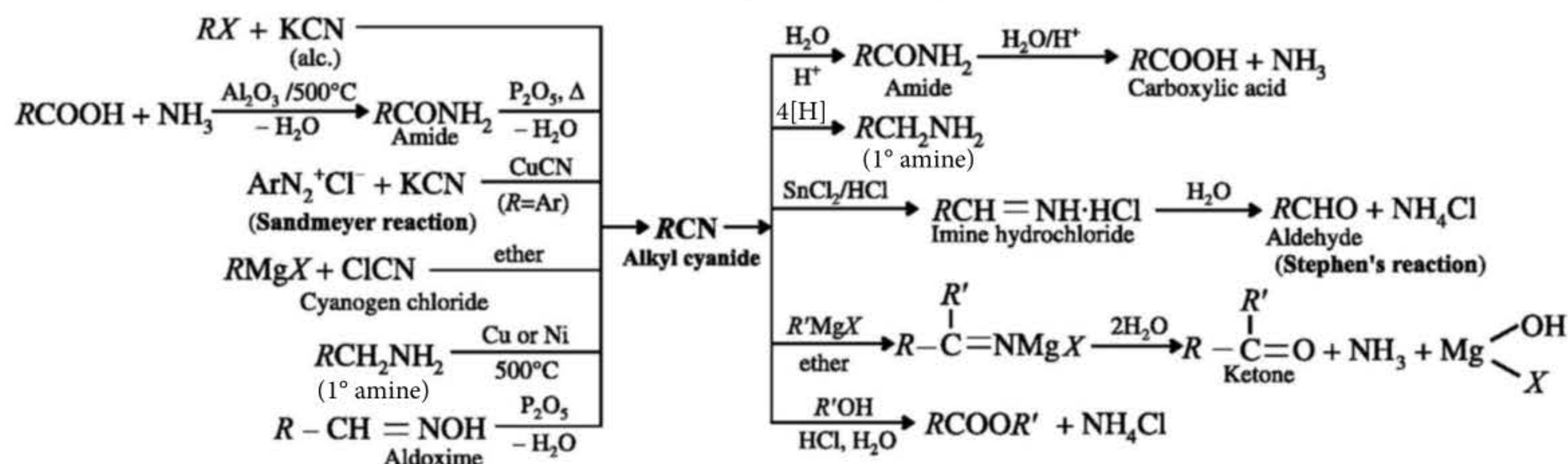
Chemical Properties



CYANIDES

- These are represented as $R-C\equiv N$.
- Alkyl cyanides are also known as *nitriles* or carbonitriles.

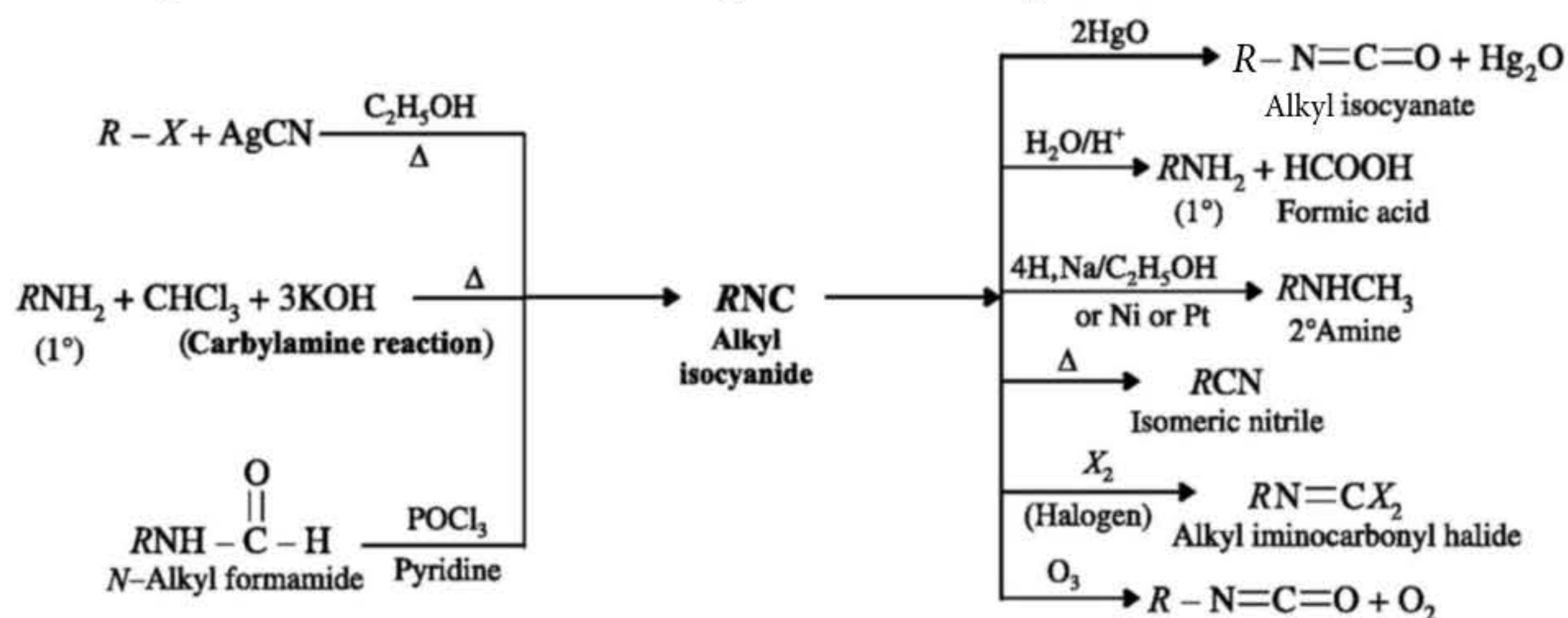
Methods of Preparation and Chemical Properties of Cyanides



ISOCYANIDES

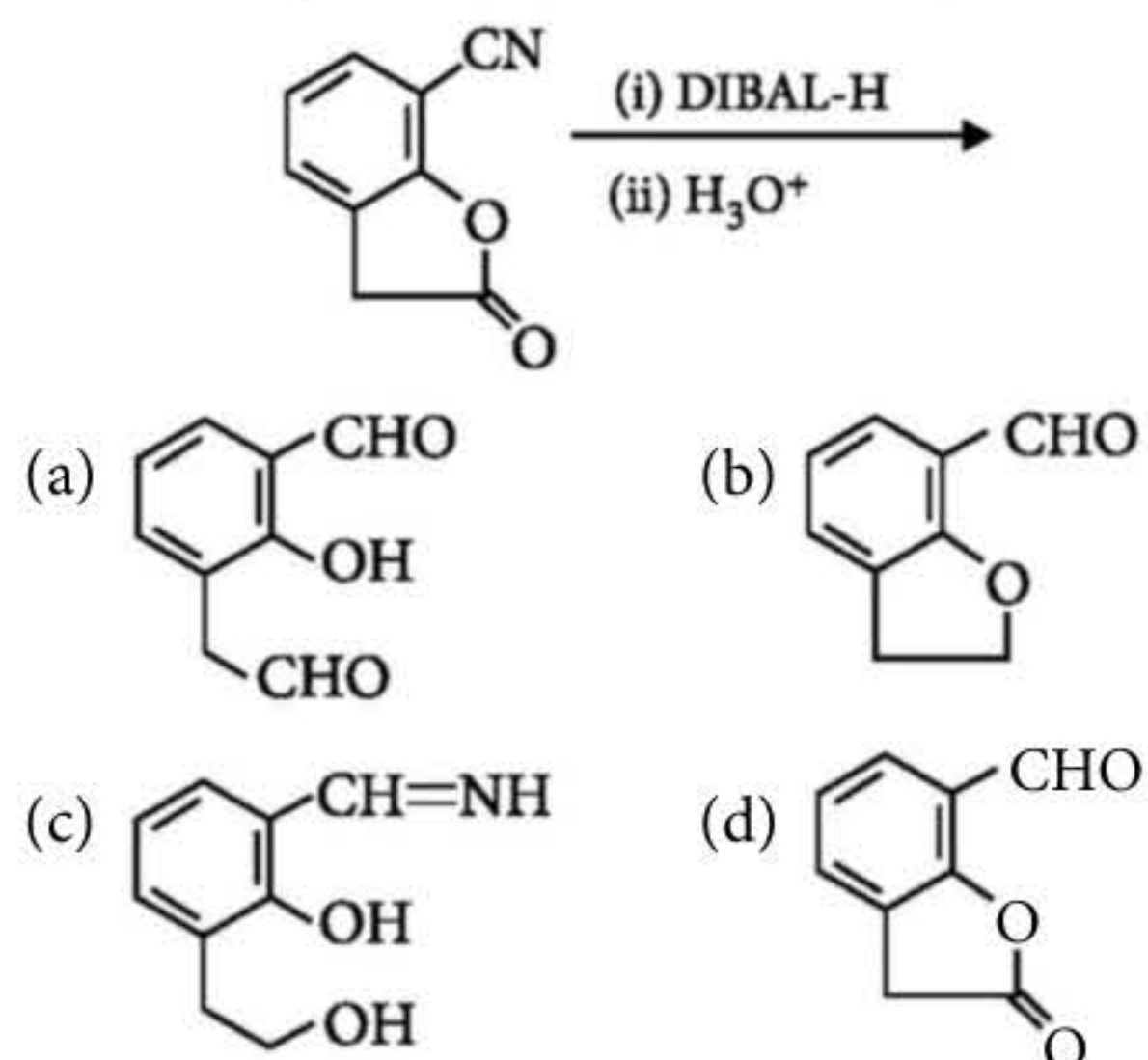
- These are represented as $RN \equiv C$
- Alkyl isocyanides are also known as isonitriles or carbylamines.

Methods of Preparation and Chemical Properties of Isocyanides



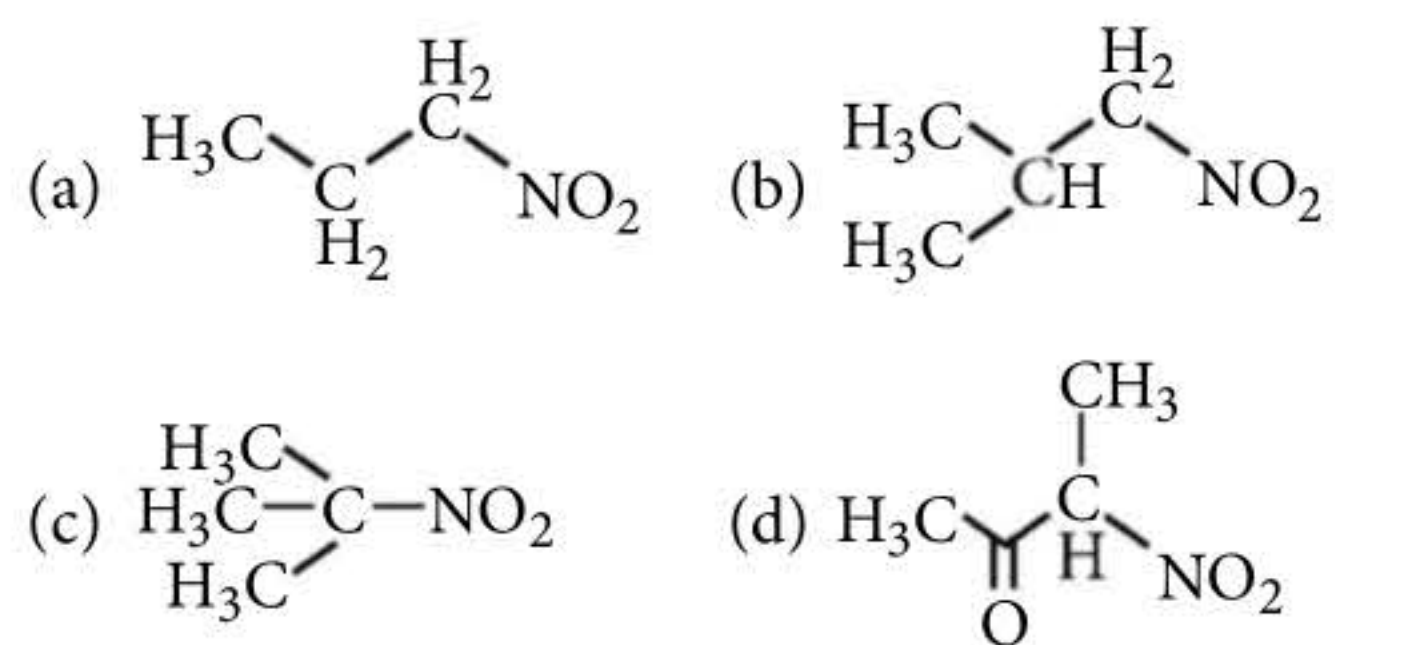
PEEP INTO PREVIOUS YEARS

4. The main product of the following reaction is



(JEE Main 2019)

5. Which one of the following nitro-compounds does not react with nitrous acid?



(NEET-II 2016)

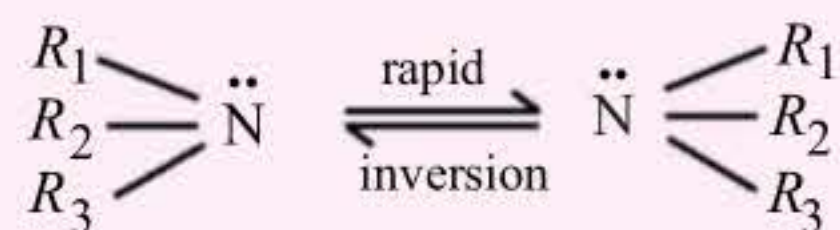
Quotable Quote

"If you want to live a happy life, tie it to a goal. Not to people or things."

ALBERT EINSTEIN

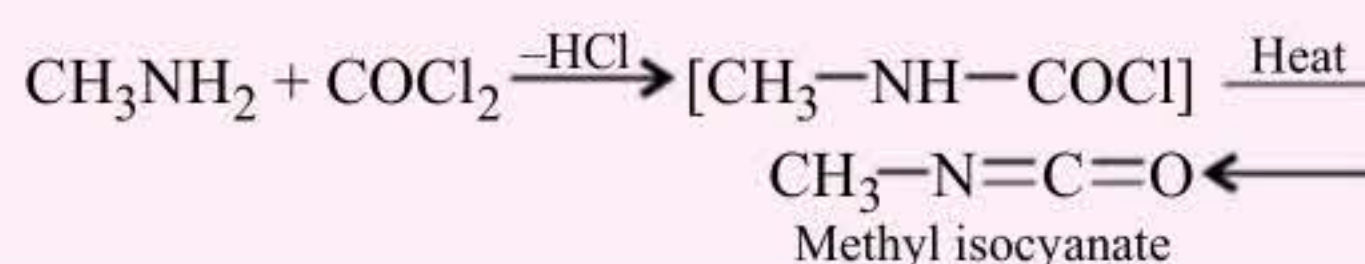
POINTS FOR EXTRA SCORING

- The mixed tertiary amines undergo a phenomenon known as *flipping* or *amine inversion*, whereby the amines exist as a racemic mixture which cannot be resolved into the enantiomeric forms by virtue of this phenomenon.



- Elimination in alkyl-trimethyl ammonium hydroxide proceeds in the direction that gives less substituted alkene. It is less sterically hindered β -hydrogen that is removed by the base in Hoffmann reaction.

- Aliphatic amines are stronger bases than ammonia due to the +I effect of alkyl groups present in amines.
- Aromatic amines are weaker bases than ammonia due to -I effect of aryl group.
- In gaseous phase, the order of basicity of amines is 3° amine > 2° amine > 1° amine > NH_3 .
- The famous Bhopal gas tragedy in Dec., 1984 was caused by extremely poisonous methyl isocyanate (MIC). Methyl isocyanate is industrially prepared by the action of methylamine with phosgene.



Biomolecules

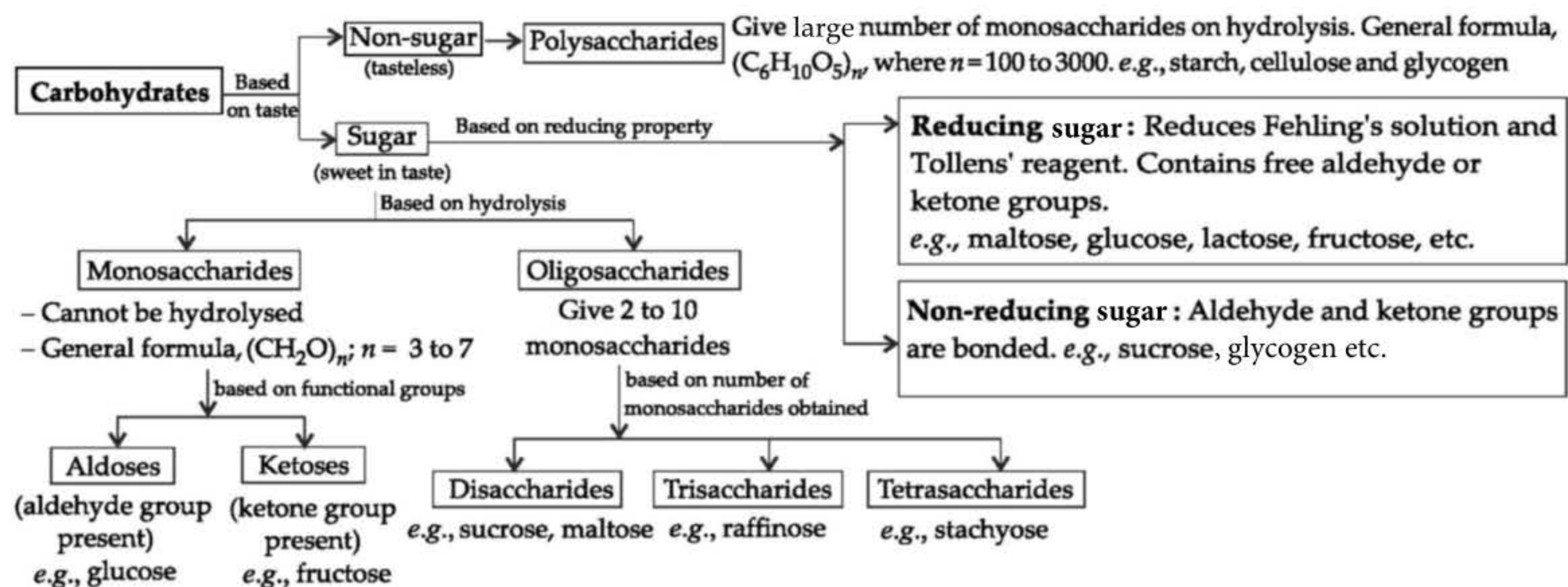
The complex chemical substances which form the basis of life, *i.e.*, they not only build up living systems (creatures) but are also responsible for their growth, maintenance and their ability to reproduce are called biomolecules.

Examples : Carbohydrates, Hormones, Proteins, Vitamins, Enzymes, Nucleic acids, etc.

CARBOHYDRATES

Carbohydrates are defined as optically active polyhydroxy aldehydes or ketones or substances which give these on hydrolysis and contain at least one chiral carbon. 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 of Carbohydrates

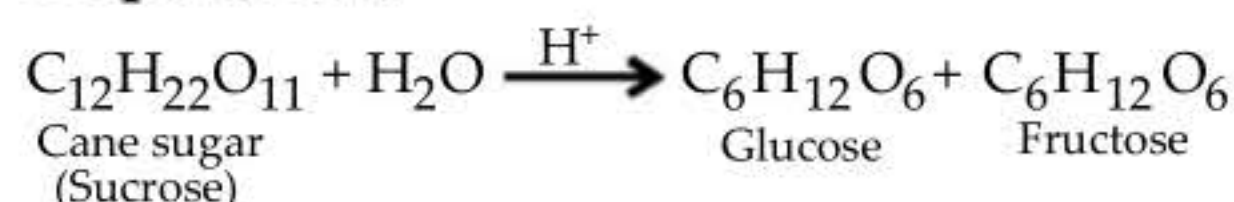


MONOSACCHARIDES

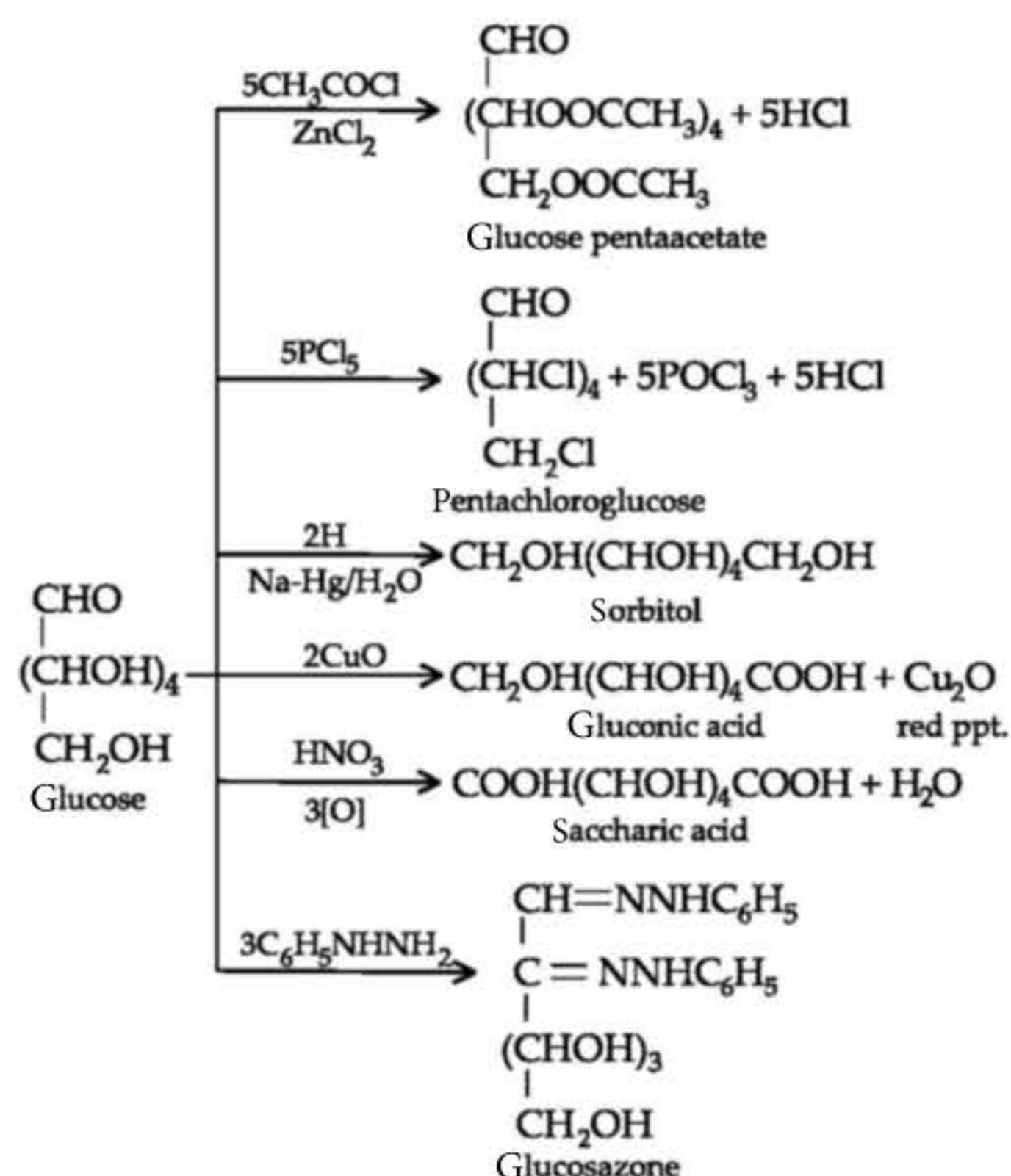
Glucose (C₆H₁₂O₆)

- Glucose is known as *dextrose* because it occurs in nature as an optically active dextrorotatory isomer.

- **Preparation :**

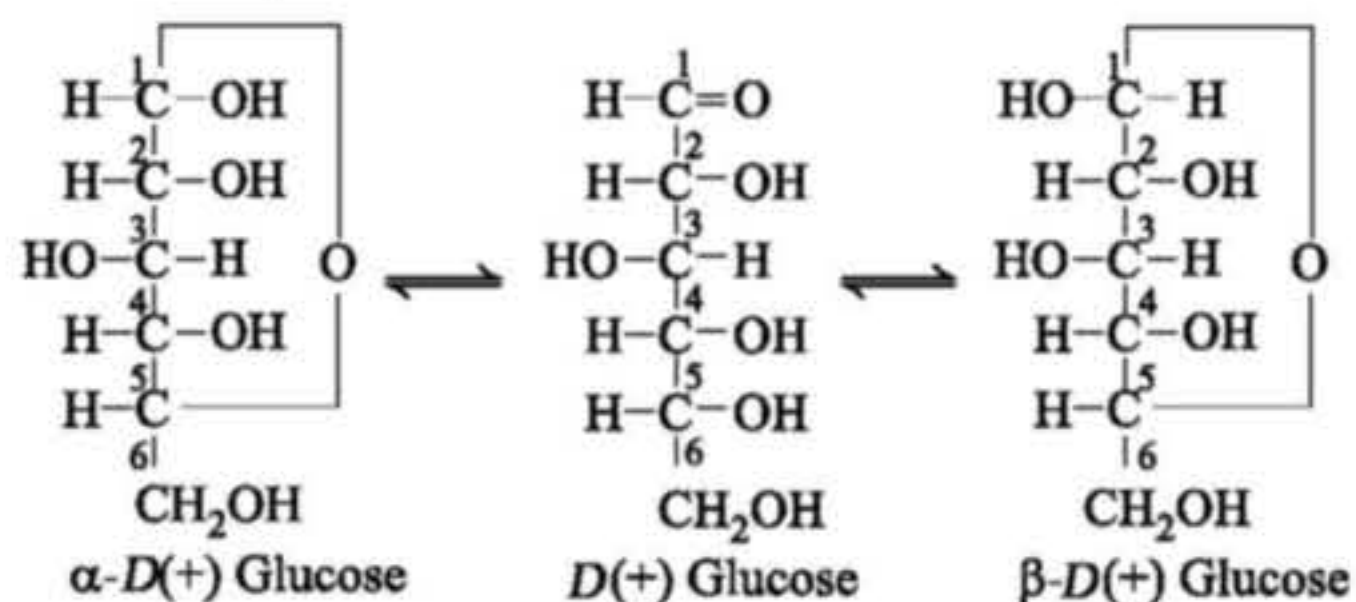


- **Chemical reactions :**



Structure of glucose

- The straight chain form of glucose explained most of its properties but could not explain a few reactions and observations like
 - No reaction with 2,4-DNP and NaHSO₃.
 - No reaction of its pentaacetate with NH₂OH.
 - Existence of α and β-forms of glucose.
- These could however be explained by the cyclic structure of glucose which exists in equilibrium with the open chain form.



Anomers

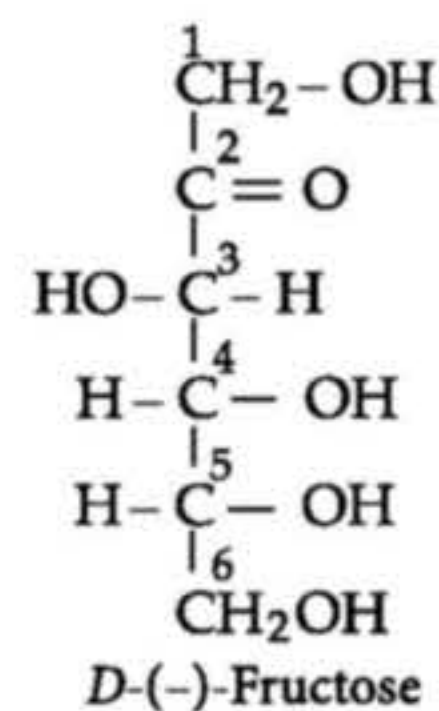
- Due to ring formation, hemiacetal or hemiketal carbon C₁ becomes chiral and hence, the monosaccharide exists in two stereoisomeric forms, the α and the β-forms. If the -OH group attached to hemiacetal or hemiketal carbon is towards right it is called an α-form and if the -OH group is towards left it is called β-form. Such a pair of stereoisomers which differ in configuration only around hemiacetal or hemiketal carbon (C₁) are called anomers and the carbon is called anomeric carbon or glycosidic carbon.

Mutarotation

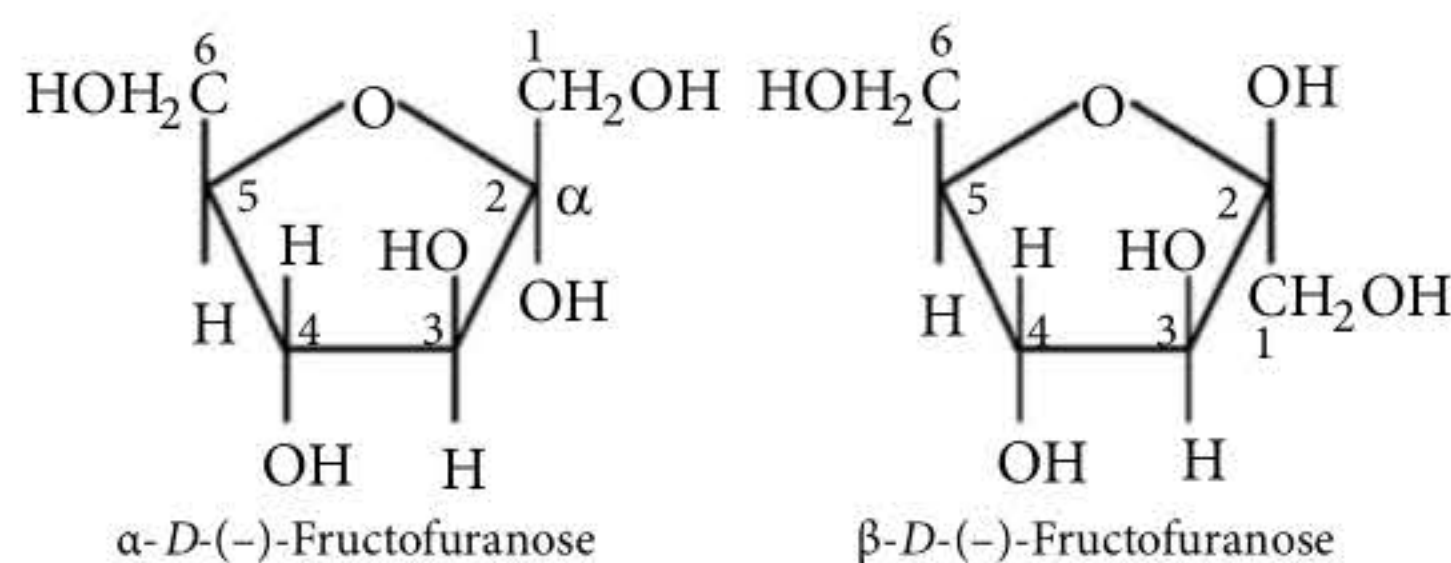
- A freshly prepared aqueous solution of α-D-(+)-glucose has a specific rotation of +111°. When this solution is allowed to stand, specific rotation falls to +52.5° and remains constant at this value. On the other hand, specific rotation of β-D-(+)-glucose increases from +19.2° to 52.5° with time. This change in specific rotation of an optically active compound in solution with time, to an equilibrium value is known as mutarotation. All the reducing sugars undergo mutarotation.

Fructose (C₆H₁₂O₆)

- It is present in abundance in sweet fruits. Since naturally occurring fructose is laevorotatory, it is known as laevulose.



- The cyclic structures of two anomers of fructose are represented by Haworth structures as given :



DISACCHARIDES

Sucrose (C ₁₂ H ₂₂ O ₁₁)	Maltose (C ₁₂ H ₂₂ O ₁₁)	Lactose (C ₁₂ H ₂₂ O ₁₁)
<ul style="list-style-type: none"> - Cane sugar - Non-reducing sugar - Dextrorotatory 	<ul style="list-style-type: none"> - Malt sugar - Reducing sugar - Dextrorotatory 	<ul style="list-style-type: none"> - Milk sugar - Reducing sugar - Epimeric in nature
<p>Chemical structure of Sucrose showing α-D-Glucose and β-D-Fructose linked by a Glycosidic linkage.</p>	<p>Chemical structure of Maltose showing α-D-Glucose (Non-reducing unit) and α-D-Glucose (Reducing unit) linked by a 1,4-α-Glycosidic linkage.</p>	<p>Chemical structure of Lactose showing β-D-Galactose (Non-reducing unit) and β-D-Glucose (Reducing unit) linked by a glycosidic linkage.</p>

POLYSACCHARIDES

- **Starch** (C₆H₁₀O₅)_n is the main storage polysaccharide of plants. It is a polymer of α -D-glucose units and consists of two components : amylose and amylopectin.

Amylose is water soluble component which constitutes about 15-20% of starch. Chemically, amylose is a long unbranched chain with 200-1000 α -D-(+)-glucose units held by 1,4- α -glycosidic linkage.

Amylopectin is insoluble in water and constitutes about 80-85% of starch. 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.

- **Cellulose**, (C₆H₁₀O₅)_n is a straight chain polysaccharide composed only of β -D-glucose units which are joined together by 1,4- β -glycosidic linkages *i.e.*, the β -glycosidic linkages between C-1 of one glucose and C-4 of the next glucose unit.
- **Glycogen (animal starch)** (C₆H₁₀O₅)_n is a major constituent of liver, muscles and brain and when the body needs glucose, enzymes break the glycogen down to glucose.

PEEP INTO PREVIOUS YEARS

6. Which of the following statement(s) is(are) true?
- The two six-membered cyclic hemiacetal forms of D-(+)-glucose are called anomers.
 - Hydrolysis of sucrose gives dextrorotatory glucose and laevorotatory fructose.

(c) Monosaccharides cannot be hydrolysed to give polyhydroxy aldehydes and ketones.

(d) Oxidation of glucose with bromine water gives glutamic acid. **(JEE Advanced 2019)**

7. The difference between amylose and amylopectin is

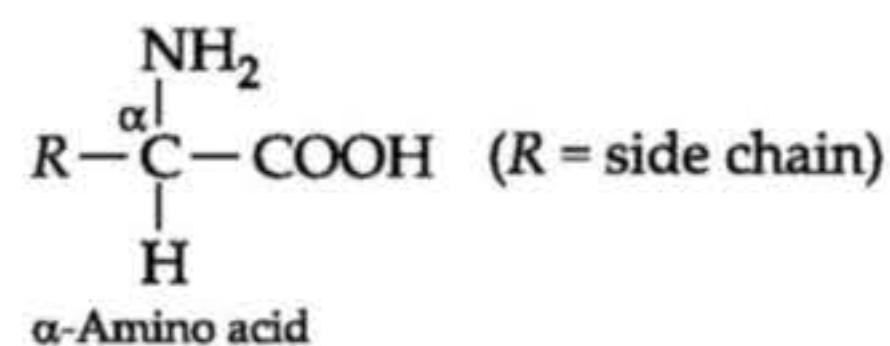
- amylopectin have 1 \rightarrow 4 α -linkage and 1 \rightarrow 6 α -linkage
- amylose have 1 \rightarrow 4 α -linkage and 1 \rightarrow 6 β -linkage
- amylopectin have 1 \rightarrow 4 α -linkage and 1 \rightarrow 6 β -linkage
- amylose is made up of glucose and galactose. **(NEET 2018)**

PROTEINS

- **Proteins** : They are the biomolecules of the living system made up of nitrogenous organic compounds by condensation polymerisation of α -amino acids.

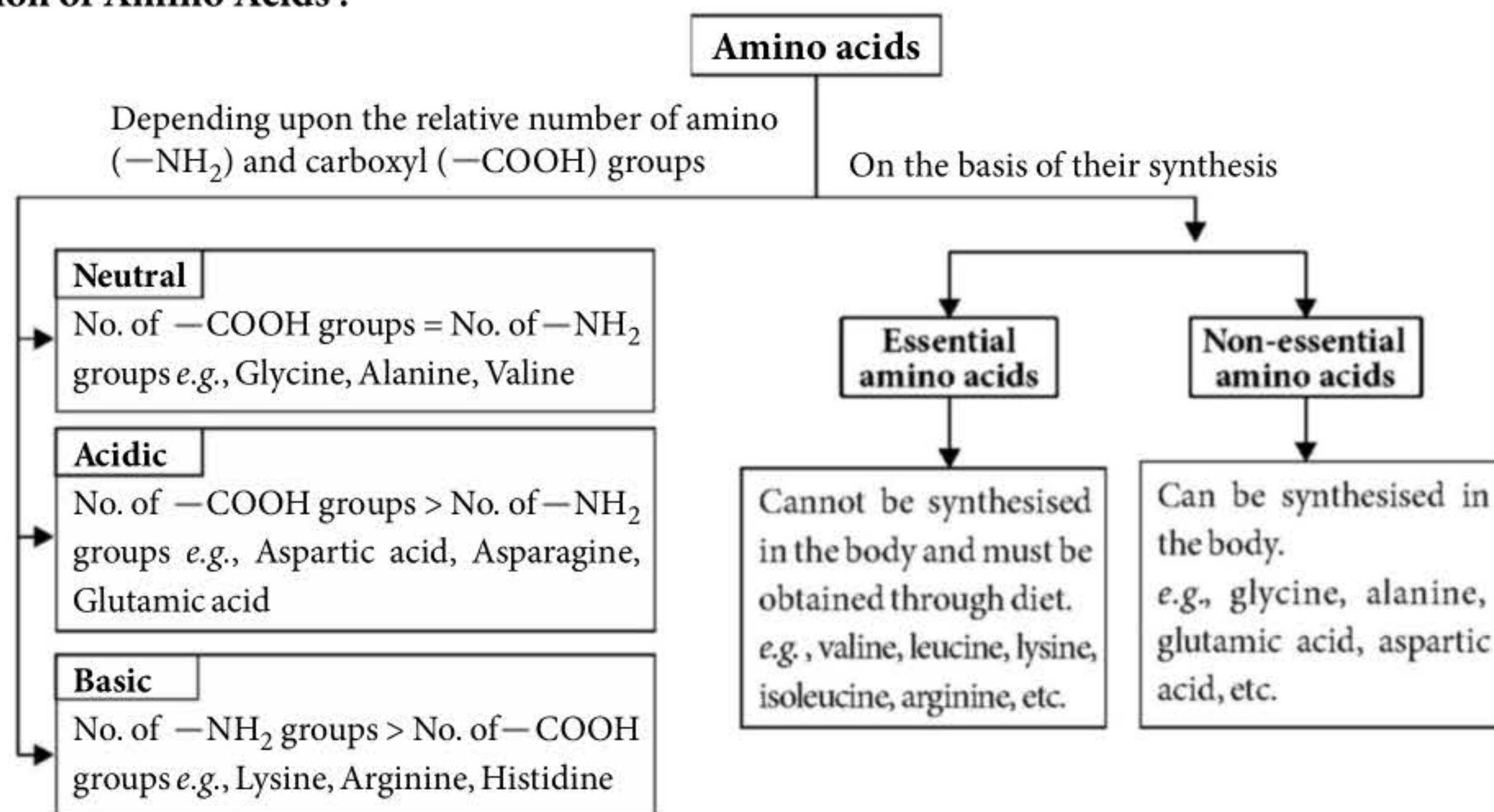
Amino Acids

- Amino acids are the bifunctional molecules with both acidic carboxylic group ($-\text{COOH}$) and basic amino group ($-\text{NH}_2$) and in α -amino acids, the amino ($-\text{NH}_2$) group is at α -position *w.r.t.* carboxylic ($-\text{COOH}$) group. *i.e.*, both amino and carboxylic groups are attached to the same carbon atom.



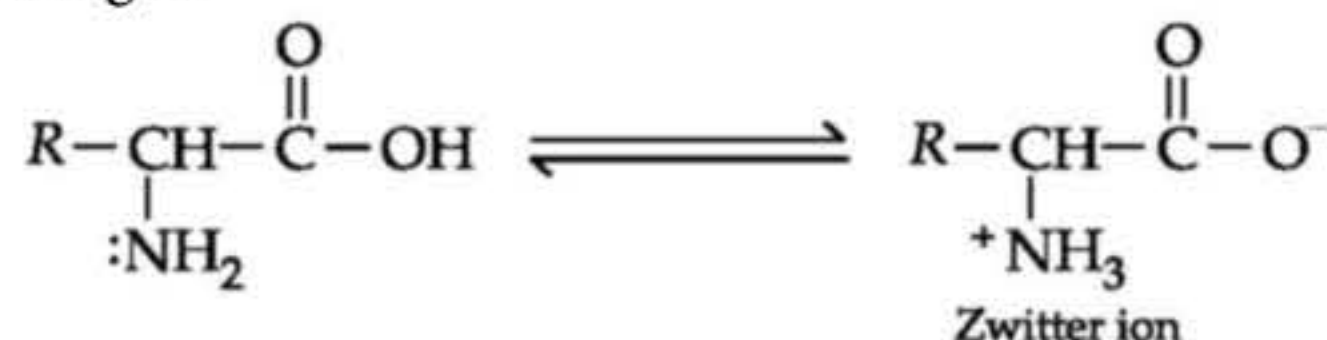
- They are very important as they are the building blocks of proteins.

Classification of Amino Acids :



Properties of Amino Acids

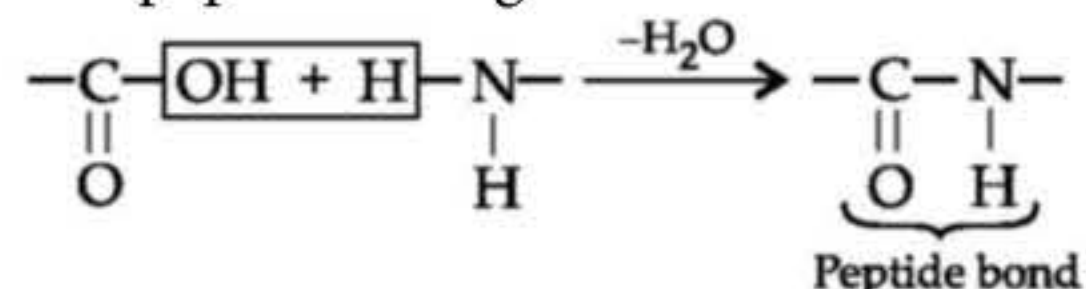
- Amino acids are usually colourless, crystalline, water soluble and high melting solids.
- They behave like salts due to presence of basic amino group ($-\text{NH}_2$) and acidic carboxylic group ($-\text{COOH}$) in the same molecule.
- In aqueous solution, the carboxylic group can lose a proton and amino group can accept a proton giving rise to a dipolar ion known as Zwitter ion. This is neutral but contains both positive and negative charges.



- **Isoelectric point** : The pH at which dipolar ion (zwitter ion) exists as neutral ion, *i.e.*, it does not migrate to either electrode, is called isoelectric point. The amino acids have least solubility at isoelectric point which helps in their separation.

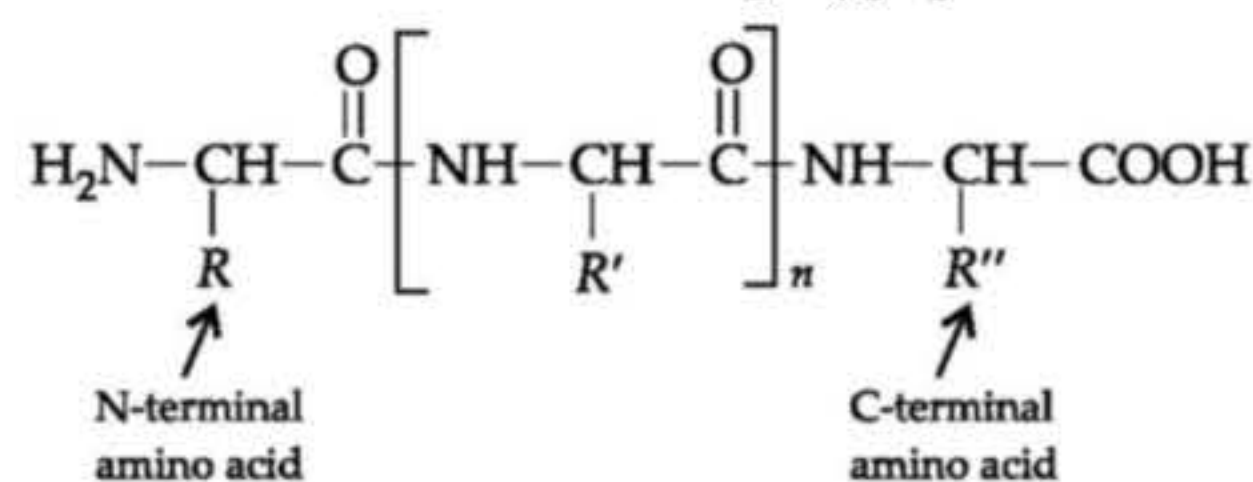
Peptides and their classification

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



- The products formed by the linking of amino acids by peptide linkage are known as peptides.

- Peptides are further divided into *di*, *tri*, *tetra* depending upon the number of amino acids combined.
- **Polypeptides** : Structures with more than ten amino acids are known as polypeptides.



where, R, R', R'' may be same or different alkyl group.

- 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** : Fibrous proteins consist of linear thread-like polypeptide chains which lie side by side to form fibres. These polypeptide chains are held together at many points by hydrogen bonds. These are insoluble in water and are stable to moderate changes in pH and temperature, *e.g.*, keratin in skin, hair, nails and wool, collagen in tendons, fibroin in silk and myosin in muscles.
- **Globular Proteins** : In these proteins, polypeptide chains are folded around itself forming spheroidal shape and the peptide chains are stabilised by intramolecular hydrogen bonds. Globular proteins are soluble in water and sensitive to small changes in temperature and pH. Examples are hormones (insulin), antibodies, haemoglobin, fibrinogen, albumin, etc.

Structure of Proteins

- **Primary Structure** : Primary structure refers to sequence of amino acids present in a protein molecule.
- **Secondary Structure** : Secondary structure refers to the conformation which the polypeptide chains assume as a result of H-bonding. There are two types of secondary structures :
 - **α -Helix** : In this type of protein, polypeptide chains coil up to form a spiral-like structure. There occurs extensive intermolecular hydrogen bonding between two adjacent turns so that the helix is rigid.
 - **β -pleated sheet structure** : In this structure polypeptide chains are extended and held together by intermolecular hydrogen bond.
- **Tertiary Structure** : Tertiary structure refers to the three dimensional structure of proteins.
- **Quaternary Structure** : It describes the arrangement and ways in which different sub-units are held together.

Denaturation of Protein

- In denaturation, three dimensional structure of proteins changes by change in pH, temperature, presence of salts or certain chemical compounds. Denaturation does not change primary structure but changes secondary and tertiary structures of proteins, e.g., coagulation of albumin present in white part of egg when egg is boiled.

ENZYMES

- The enzymes are biocatalysts produced by living cells which catalyse biochemical reactions in living organisms.
- **Some Common Enzymes :**

Enzymes	Reactions which is catalysed
Amylase	Starch $\rightarrow n \times$ Glucose
Maltase	Maltose $\rightarrow 2 \times$ Glucose
Lactase	Lactose \rightarrow Glucose + galactose
Invertase	Sucrose \rightarrow Glucose + fructose
Pepsin	Proteins \rightarrow Amino acid
Trypsin	Polypeptides \rightarrow Amino acid
Nucleases	DNA, RNA \rightarrow Nucleotides
Urease	Urea \rightarrow $\text{NH}_3 + \text{CO}_2$
Carbonic anhydrase	$\text{H}_2\text{CO}_3 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$

VITAMINS

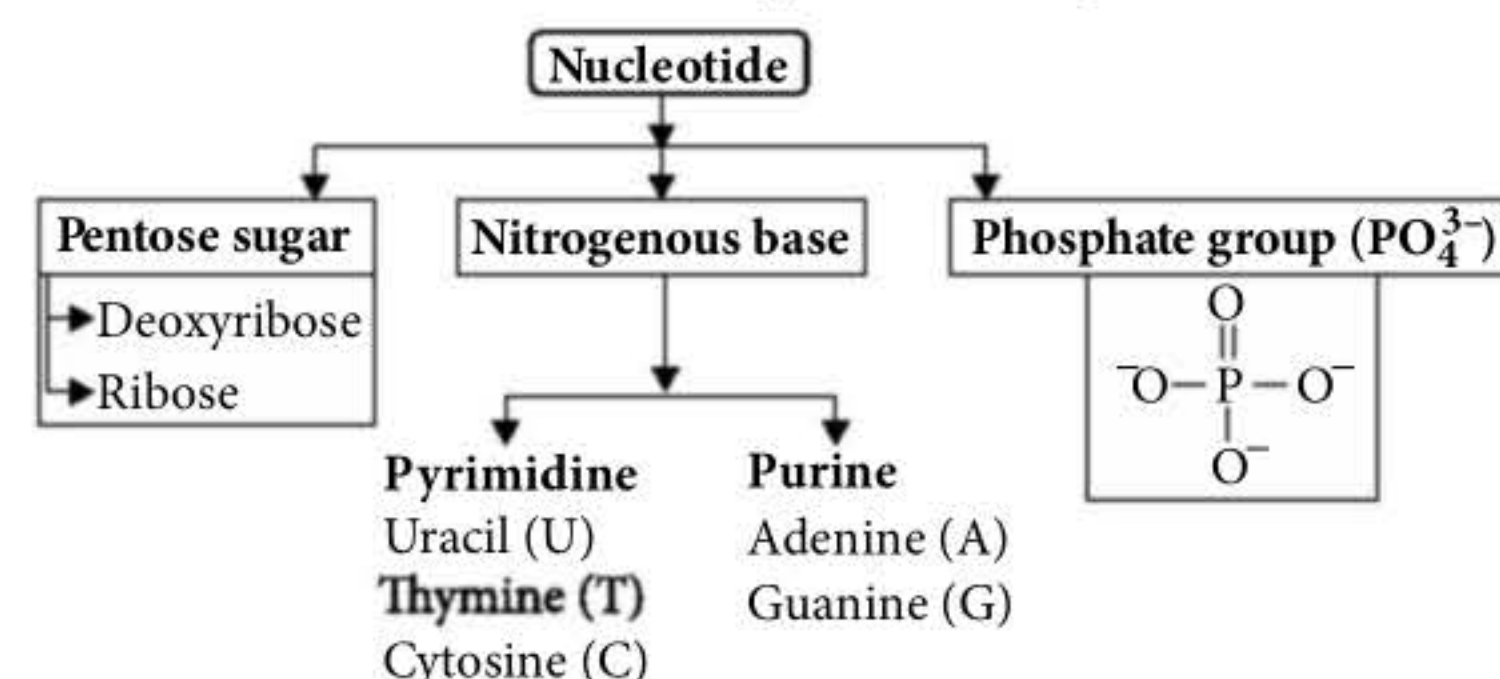
These are biomolecules which cannot be produced by the body and must be supplied in small amounts in diet to carry out essential metabolic reactions which are required for normal growth and maintenance of the body.

Classification

- **Water soluble vitamins** : Must be supplied regularly in diet as they are regularly excreted in urine (except vitamin B_{12}) e.g., Vitamin- $\text{B}_1, \text{B}_2, \text{B}_6, \text{B}_{12}$ and C.
- **Fat soluble vitamins** : Stored in liver and adipose tissues e.g., Vitamin - A, D, E and K.
- Biotin (vitamin H), is however neither soluble in water nor in fat.

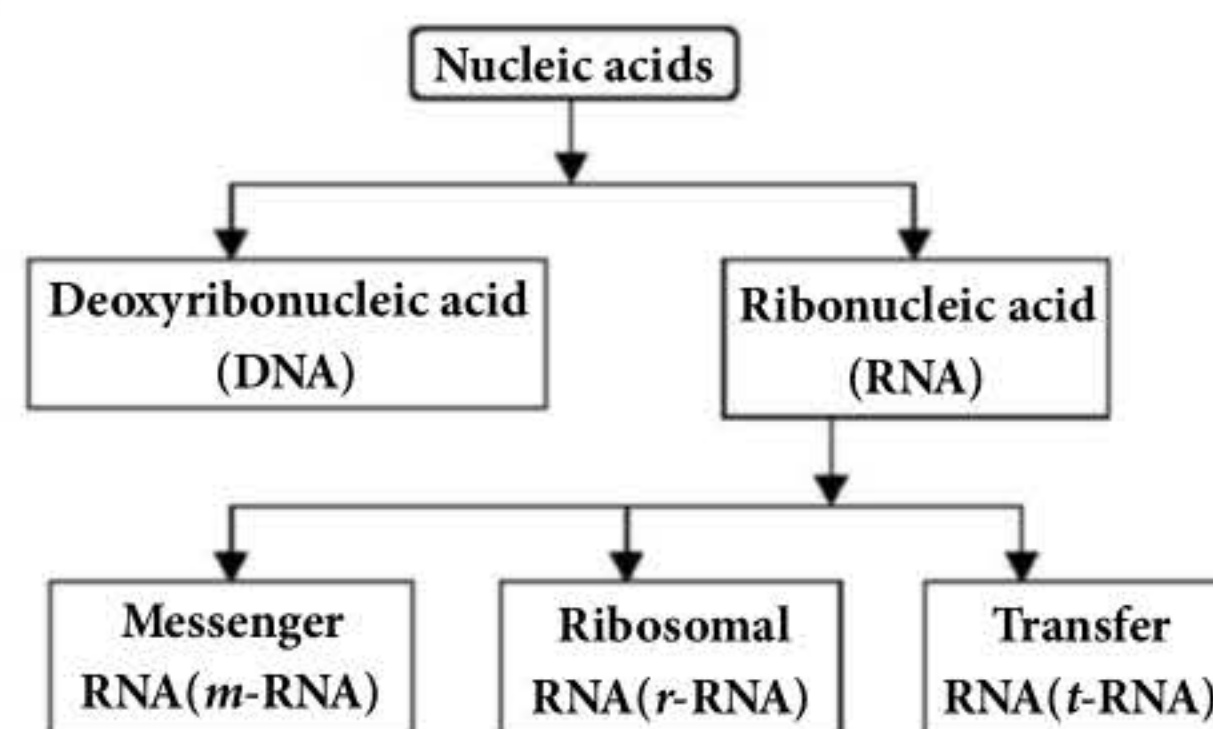
NUCLEIC ACIDS

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



- **Nucleoside** : Pentose sugar + a nitrogenous base.

Types of Nucleic Acids



Differences between DNA and RNA

	Deoxyribonucleic acid (DNA)	Ribonucleic acid (RNA)
1.	Occurs in the nucleus of the cell.	Occurs in the cytoplasm.
2.	Sugar present is 2-deoxy-D-(-)-ribose.	Sugar present is D-(-)-ribose.

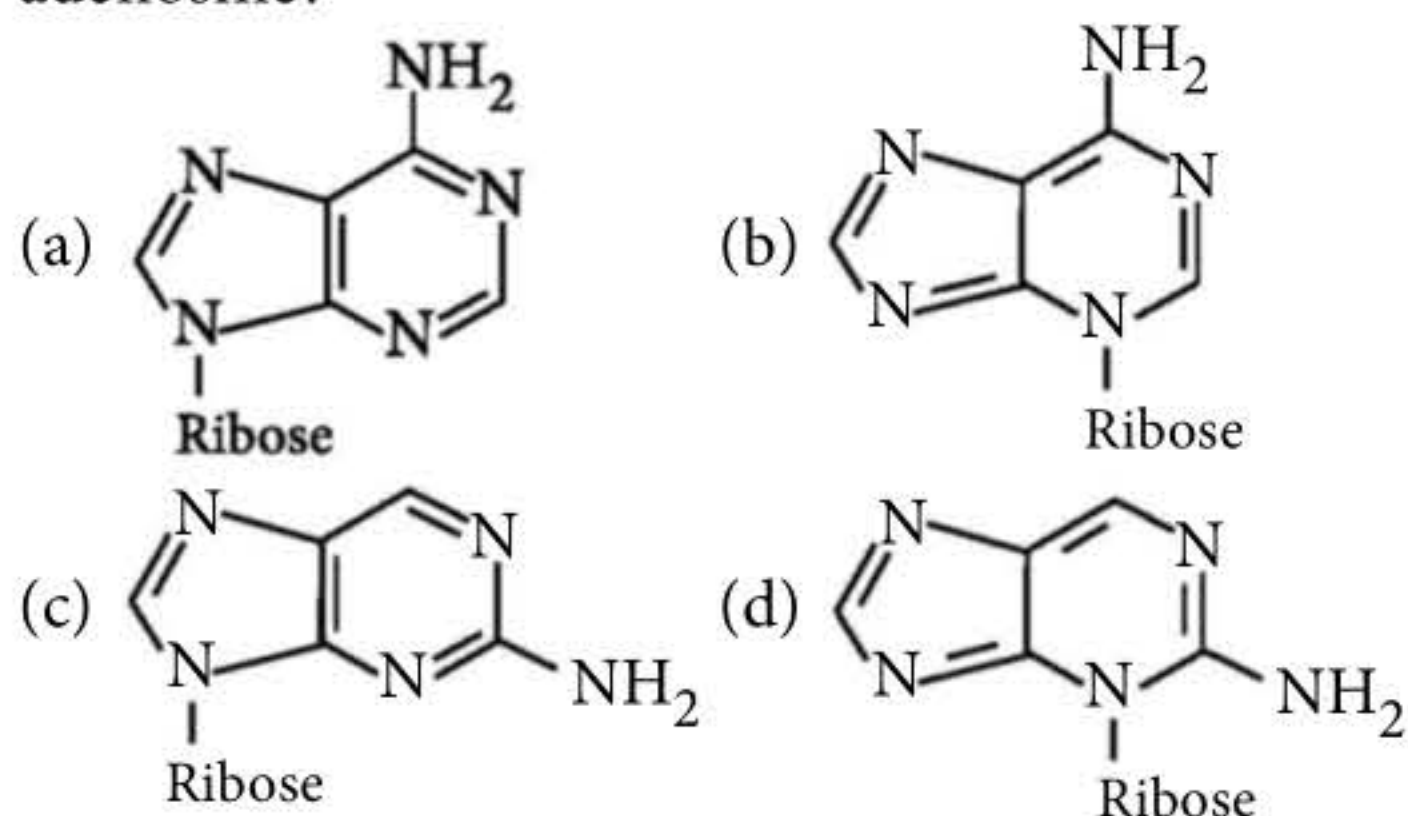
3.	Contains cytosine and thymine as pyrimidine bases, guanine, adenine as purine bases.	Contains cytosine and uracil as pyrimidine bases and guanine and adenine as purine bases.
4.	Double-stranded α -helix structure.	Single-stranded α -helix structure.
5.	Undergoes replication.	Does not undergo replication.

HORMONES

- **Hormones** : They are the molecules that act as intercellular messengers and are poured directly in the blood stream by endocrine glands.
- **Types of hormones** :
 - **Steroids** : Estrogens and androgens
 - **Polypeptides** : Insulin and endorphins
 - **Amino acid derivatives** : Epinephrine and norepinephrine.

PEEP INTO PREVIOUS YEARS

8. The increasing order of pK_a of the following amino acids in aqueous solution is Gly, Asp, Lys, Arg
- (a) Arg < Lys < Gly < Asp
 (b) Asp < Gly < Lys < Arg
 (c) Asp < Gly < Arg < Lys
 (d) Gly < Asp < Arg < Lys (JEE Main 2019)
9. Which of the following is the correct structure of adenosine?



(JEE Main Online 2018)

10. The correct statement regarding RNA and DNA, respectively is
- (a) the sugar component in RNA is arabinose and the sugar component in DNA is ribose

- (b) the sugar component in RNA is 2'-deoxyribose and the sugar component in DNA is arabinose
 (c) the sugar component in RNA is arabinose and the sugar component in DNA is 2'-deoxyribose
 (d) the sugar component in RNA is ribose and the sugar component in DNA is 2'-deoxyribose.

(NEET-I 2016)

POINTS FOR EXTRA SCORING

- **Biuret Test** : On adding few drops of copper sulphate solution to an alkaline solution of protein, a bluish violet colour develops. This test is basically for peptide linkage.
- **Millon's Test** : Proteins give a white precipitate with Millon's base which changes to red upon heating. Millon's reagent is prepared by dissolving an equal amount of mercuric and mercurous nitrate in distilled water.
- **Ninhydrin Test** : Protein and α -amino acids give a blue or violet colour with ninhydrin (indane-1,2,3-trione).
- When cellulose is treated with concentrated NaOH solution, it forms a gelatinous semi-transparent mass which imparts lustre to cotton (mercerised) and this process is called mercerisation.
- The most widely used method for determining the N-terminal amino acid residue in a protein or a polypeptide molecule is called the DNP-method or Sanger's method.
- The most widely used method for determining the C-terminal amino acid residue in a protein or a polypeptide is called hydrazinolysis.
- Sequence of three bases in *t*-RNA molecule is known as anticodon and useful during protein synthesis.
- Separation of DNA strands on heating known as melting and hybridisation again on cooling is known as annealing.

Answer Key For Peep Into Previous Years

1. (b) 2. (b) 3. (d) 4. (a) 5. (c) 6. (a, b, c)
 7. (a) 8. (b) 9. (a) 10. (d)