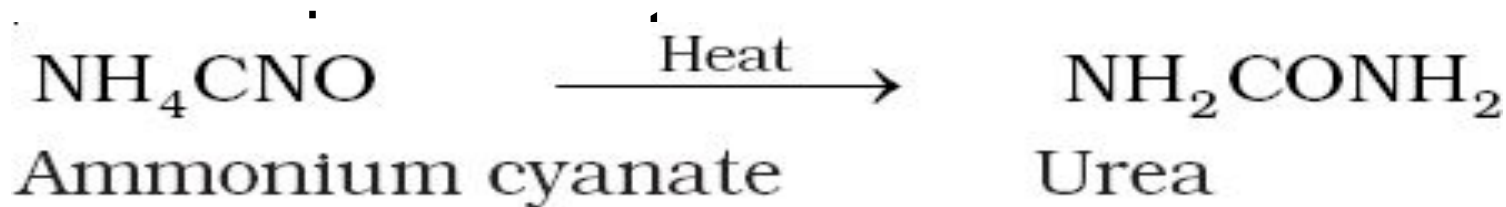


UNIT 12

ORGANIC CHEMISTRY – SOME BASIC PRINCIPLES AND TECHNIQUES

Introduction

1. Organic chemicals compounds appear in materials like clothing, fuels, polymers dyes and medicines.
2. F. Wohler synthesised an organic compound, urea from an inorganic compound,



STRUCTURAL REPRESENTATION OF ORGANIC COMPOUNDS

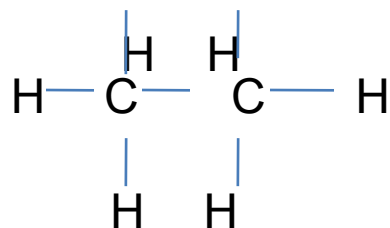
Complete, condensed and bond line structural formulas

□ Organic compounds structures are represented in several ways.

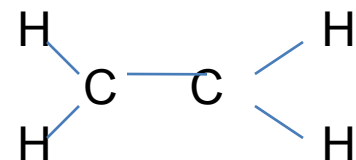
1. The *Lewis structure or dot structure, dash structure, condensed structure and bond line structural formulas* are some of the specific types.
2. The Lewis structures, however, can be simplified by representing the two-electron covalent bond by a dash (—).

Thus, ethane (C_2H_6), ethene (C_2H_4),
ethyne (C_2H_2)

Such structural representations are
called
complete structural formula



Ethane



Ethene



Ethyne

$$\text{way 5: } \text{CH}_3 - \text{CH}_3 - \text{H}_2\text{C} = \text{H}_2\text{C} \equiv \text{HC}$$

Ethyn

Ethane

Ethene

Ethane Ethene

organic chemists use another way of representing the structures, in which only lines are used. In this bond-line structural representation of organic compounds, carbon and hydrogen atoms are not shown and the lines representing carbon-carbon bonds are drawn in a zig-zag fashion.

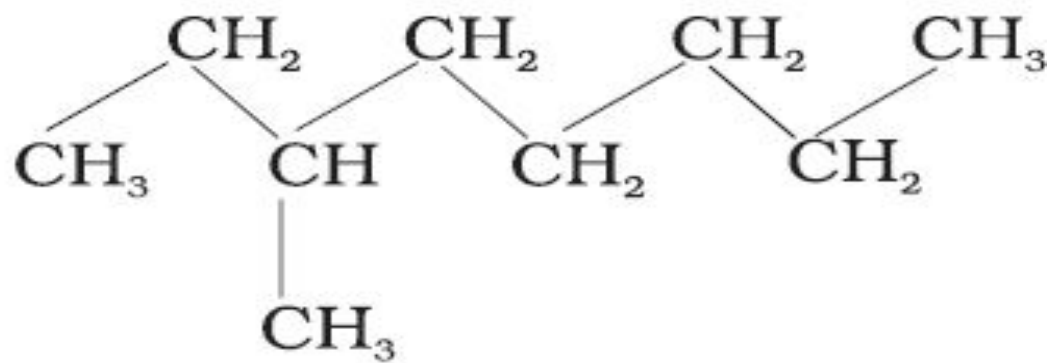
For example

3-Methyloctane can be represented in various forms as:

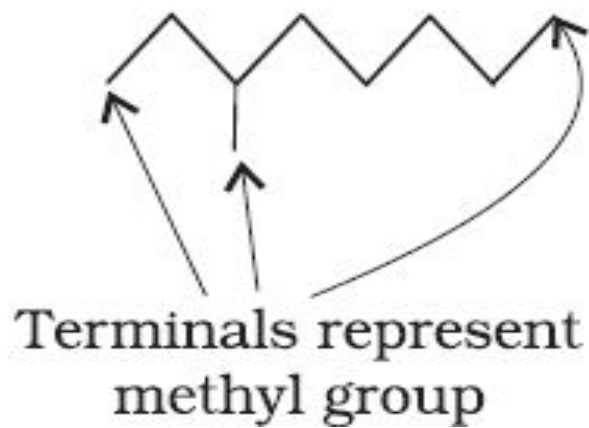
i) $\text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

1

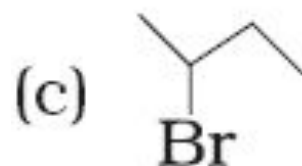
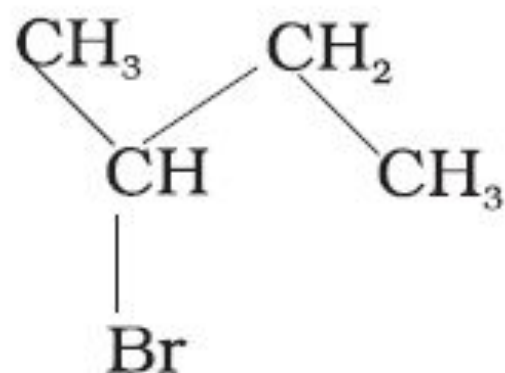
(b)



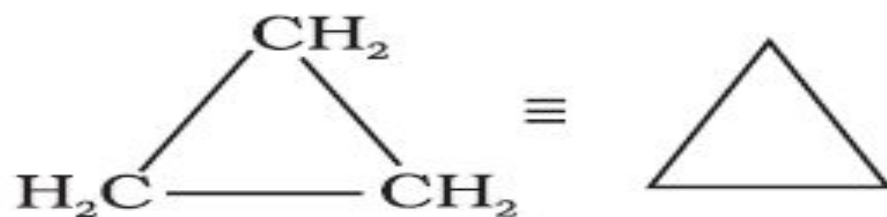
(c)



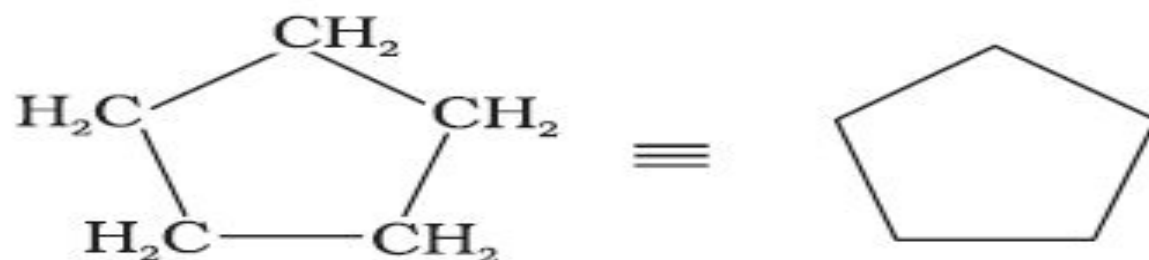
(ii) Various ways of representing 2-bromobutane are:



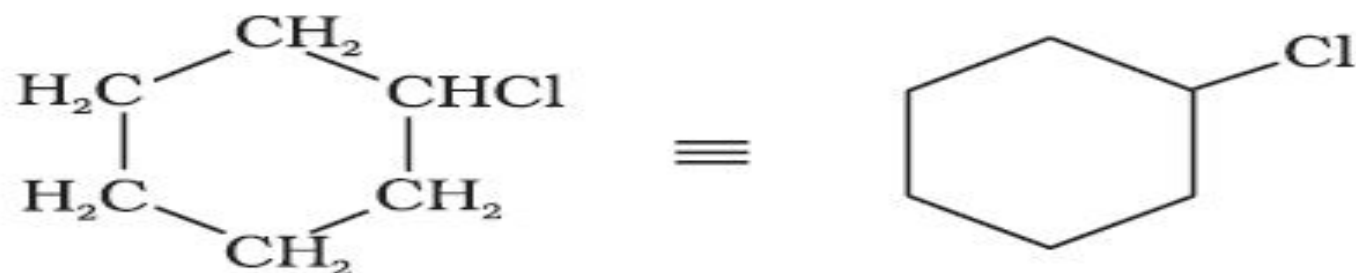
In cyclic compounds, the bond-line formulas may be given as follows:



Cyclopropane



Cyclopentane



chlorocyclohexane

Three-Dimensional Representation of Organic Molecules

The three-dimensional (3-D) structure of organic molecules can be represented on paper by using certain conventions. For example, by using solid and dashed wedge formula, the 3-D image of a molecule from a two-dimensional picture can be perceived.



solid-wedge is used to indicate a bond projecting out of the plane of paper, towards the observer.

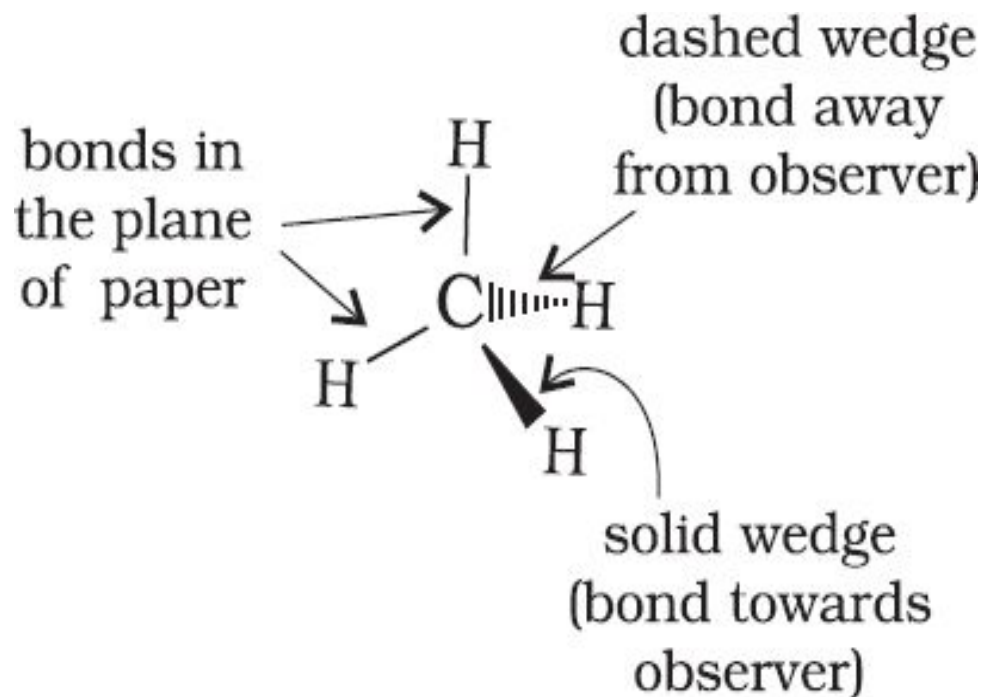


The dashed-wedge is used to depict the bond projecting out of the plane of the paper and away from the observer.

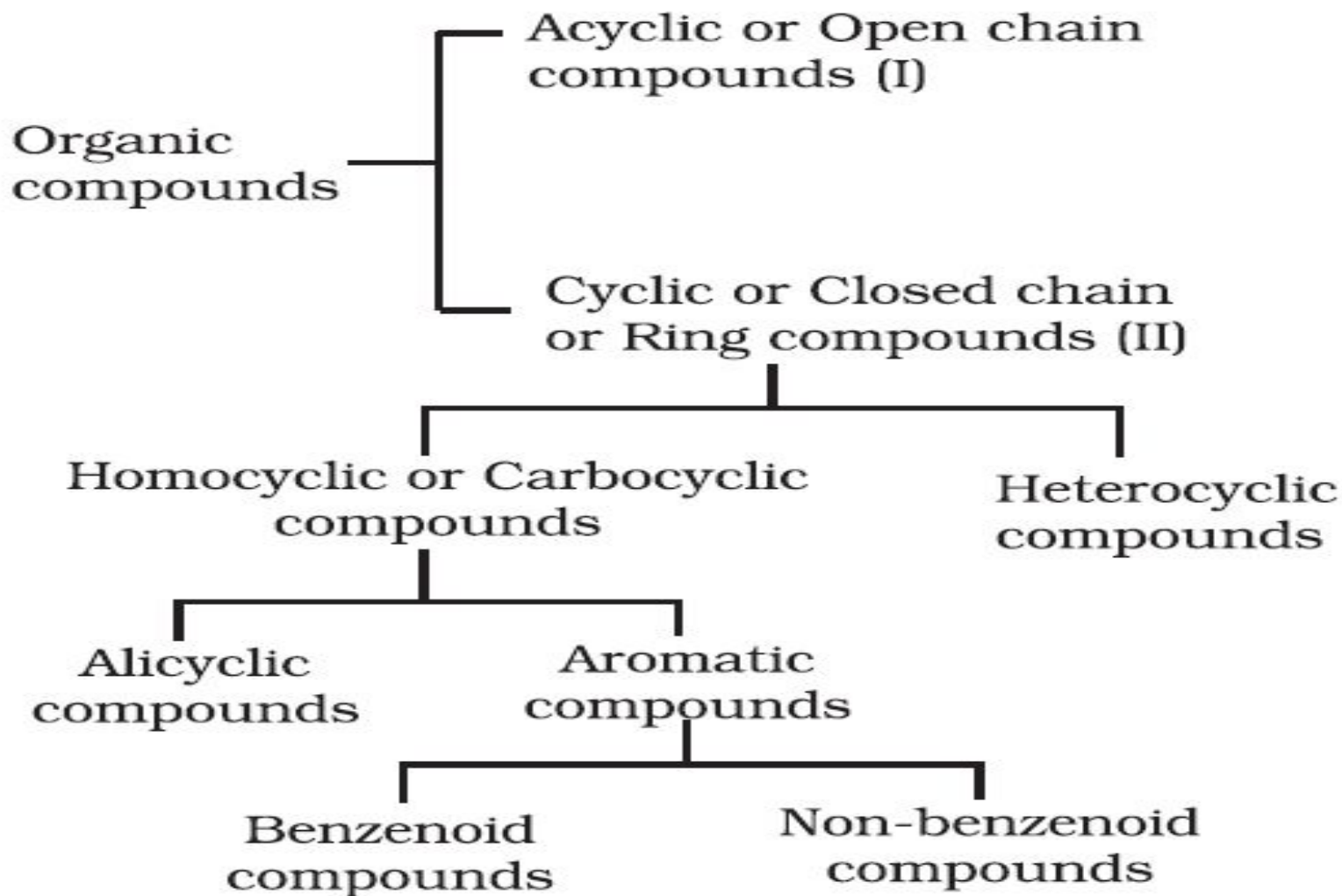


The bonds lying in plane of the paper are depicted by using a normal line (—).

Wedge-and-dash representation of CH₄

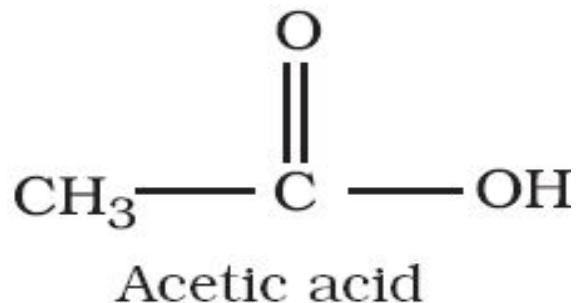
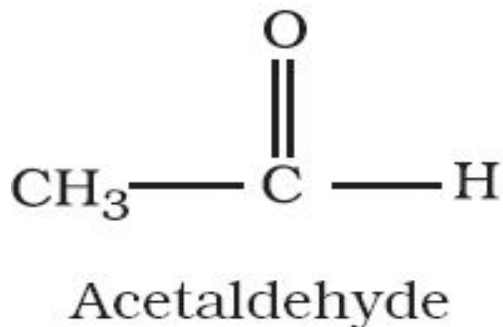
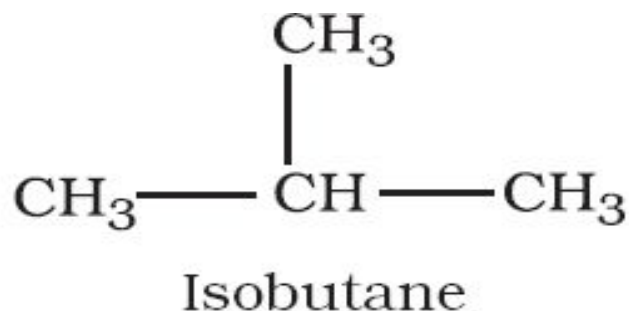


CLASSIFICATION OF ORGANIC COMPOUNDS



Acyclic or open chain compounds

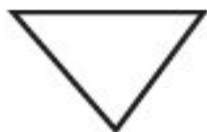
These compounds are also called as **aliphatic** compounds and consist of straight or branched chain compounds, for example:



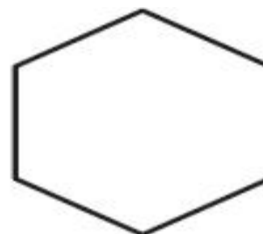
Alicyclic or closed chain or ring compounds

Alicyclic (aliphatic cyclic) compounds contain carbon atoms joined in the form of a ring (homocyclic). Sometimes atoms other than carbon are also present in the ring (heterocyclic).

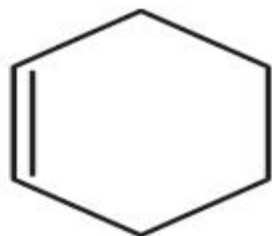
Some examples are



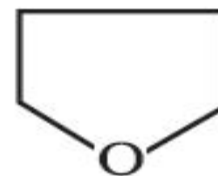
Cyclopropane



Cyclohexane



Cyclohexene

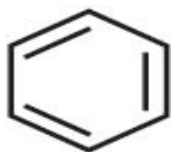


Tetrahydrofuran

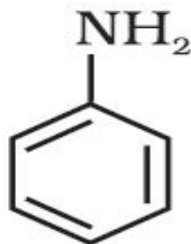
Aromatic

compounds are special types of compounds.

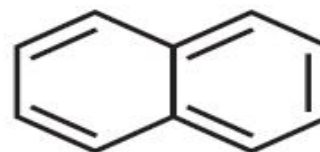
These include benzene and other related ring **Benzenoid aromatic compounds**



Benzene

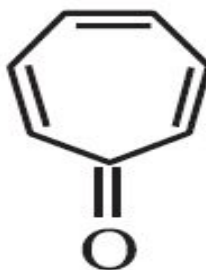


Aniline



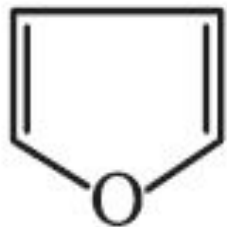
Naphthalene

Non-benzenoid compound



Tropolone

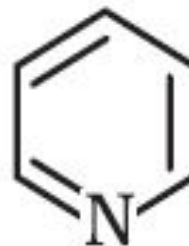
Heterocyclic aromatic compounds



Furan



Thiophene



Pyridine

NOMENCLATURE OF ORGANIC COMPOUNDS

In order to clearly identify compound, a systematic method of naming has been developed and is known as the **IUPAC (International Union of Pure and Applied Chemistry) system of nomenclature**.

The names are correlated with the structure such that the

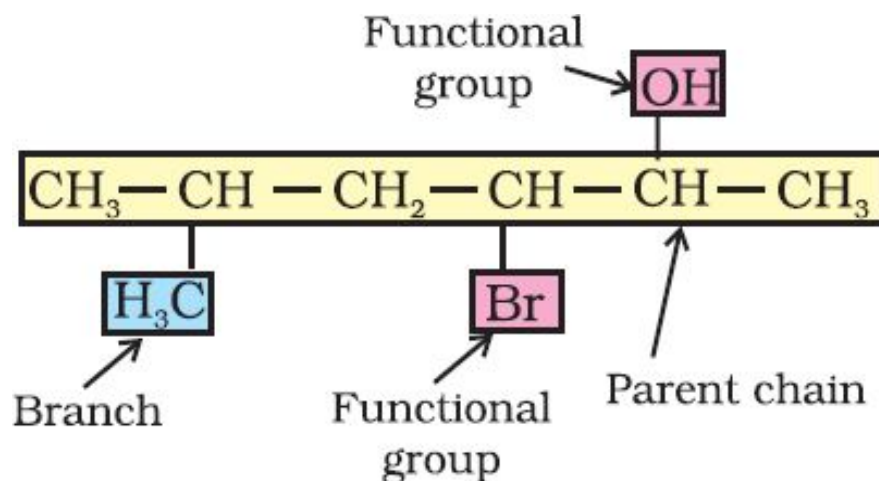
reader or listener can deduce the structure from the name.

The traditional names are considered a *trivial or common names*.

Common or Trivial Names of Some Organic Compounds

Compound	Common name
CH_4	Methane
$\text{H}_3\text{CCH}_2\text{CH}_2\text{CH}_3$	<i>n</i> -Butane
$(\text{H}_3\text{C})_2\text{CHCH}_3$	Isobutane
$(\text{H}_3\text{C})_4\text{C}$	Neopentane
$\text{H}_3\text{CCH}_2\text{CH}_2\text{OH}$	<i>n</i> -Propyl alcohol
HCHO	Formaldehyde
$(\text{H}_3\text{C})_2\text{CO}$	Acetone
CHCl_3	Chloroform
CH_3COOH	Acetic acid
C_6H_6	Benzene
$\text{C}_6\text{H}_5\text{OCH}_3$	Anisole
$\text{C}_6\text{H}_5\text{NH}_2$	Aniline
$\text{C}_6\text{H}_5\text{COCH}_3$	Acetophenone
$\text{CH}_3\text{OCH}_2\text{CH}_3$	Ethyl methyl ether

The IUPAC System of Nomenclature



Hydrocarbons Compounds containing carbon and only are called hydrogen hydrocarbons.

Hydrocarbons

```
graph TD; A[Hydrocarbons] --> B[Saturated]; A --> C[unsaturated]; B --> D["A hydrocarbon is termed saturated if it contains only carbon-carbon single bonds."]; C --> E["Unsaturated hydrocarbons are those, which contain at least one carbon-carbon double or triple bond."];
```

Saturated

A hydrocarbon is termed saturated if it contains only carbon-carbon single bonds.

unsaturated

Unsaturated hydrocarbons are those, which contain at least one carbon-carbon double or triple bond.

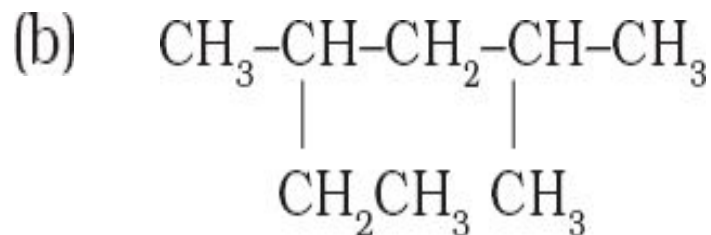
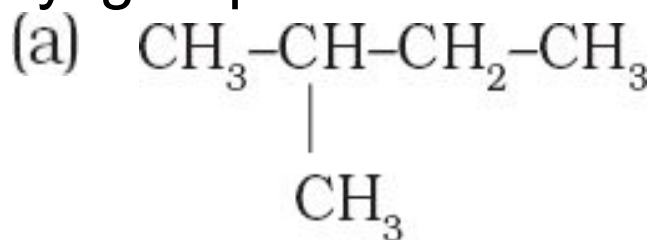
IUPAC Nomenclature of Alkanes

Straight chain hydrocarbons: The names of such compounds are based on their chain structure, and end with suffix '*-ane*' and carry a prefix indicating the number of carbon atoms present in the chain (except from CH₄ to C₄H₁₀, where the prefixes are derived from trivial names).

IUPAC Names of Some Unbranched Saturated Hydrocarbons

Name	Molecular formula	Name	Molecular formula
Methane	CH ₄	Heptane	C ₇ H ₁₆
Ethane	C ₂ H ₆	Octane	C ₈ H ₁₈
Propane	C ₃ H ₈	Nonane	C ₉ H ₂₀
Butane	C ₄ H ₁₀	Decane	C ₁₀ H ₂₂
Pentane	C ₅ H ₁₂	Icosane	C ₂₀ H ₄₂
Hexane	C ₆ H ₁₄	Triacontane	C ₃₀ H ₆₂

Branched chain hydrocarbons: In a branched chain compound small chains of carbon atoms are attached at one or more carbon atoms of the parent chain. The small carbon chains (branches) are called alkyl groups.



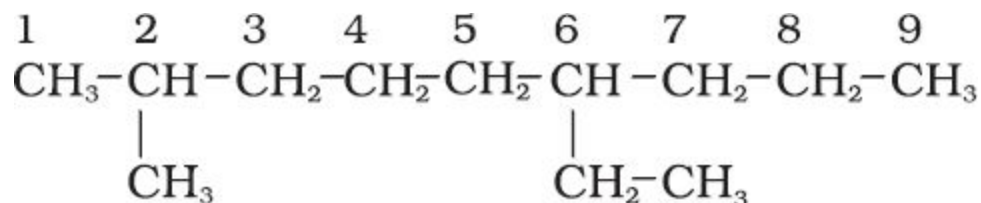
In order to name such compounds, the names of alkyl groups are prefixed to the name of parent alkane. An alkyl group is derived from a saturated hydrocarbon by removing a hydrogen atom from carbon. Thus, CH₄ becomes -CH₃ and is called *methyl group*.

Alkane		Alkyl group	
Molecular formula	Name of alkane	Structural formula	Name of alkyl group
CH ₄	Methane	-CH ₃	Methyl
C ₂ H ₆	Ethane	-CH ₂ CH ₃	Ethyl
C ₃ H ₈	Propane	-CH ₂ CH ₂ CH ₃	Propyl
C ₄ H ₁₀	Butane	-CH ₂ CH ₂ CH ₂ CH ₃	Butyl
C ₁₀ H ₂₂	Decane	-CH ₂ (CH ₂) ₈ CH ₃	Decyl

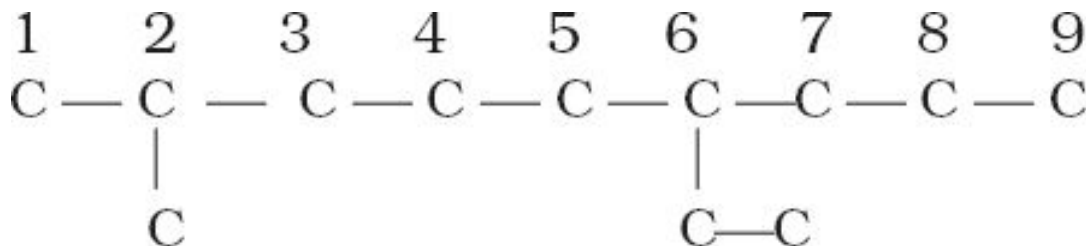
Nomenclature of branched chain alkanes

1. First of all, the **longest carbon chain in the molecule is identified.**

Example



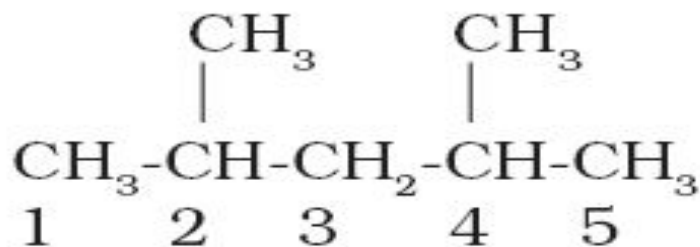
2 . The numbering is done in such a way that the branched carbon atoms get the lowest possible numbers.



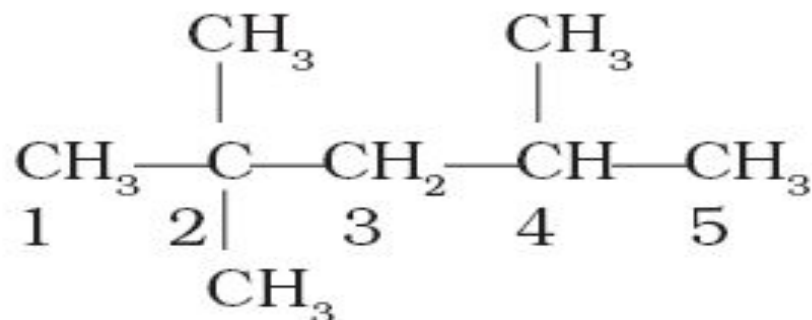
3. If different alkyl groups are present, they are listed in alphabetical order. Thus, name for the compound shown above is: 6-ethyl-2- methylnonane.

[Note: the numbers are separated from the groups by hyphens and there is no break between methyl and nonane.]

4. If two or more identical substituent groups are present then the numbers are separated by commas. The names of identical substituents are not repeated, instead prefixes such as di (for 2), tri (for 3), tetra (for 4), penta (for 5), hexa (for 6) etc. are used.

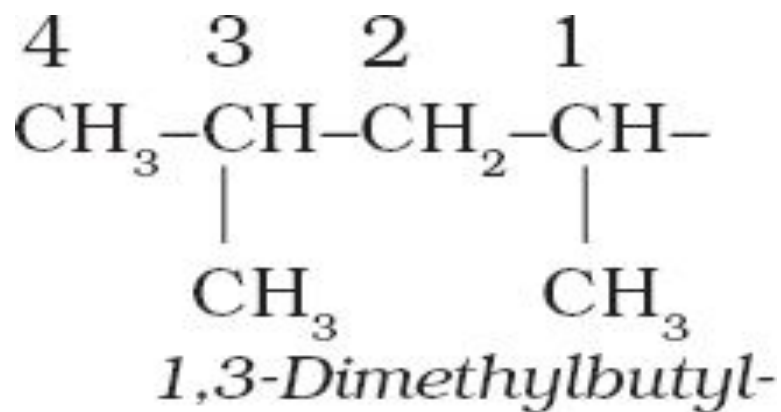


2,4-Dimethylpentane



2,2,4-Trimethylpentane

5. If the two substituents are found in equivalent positions, the **lower number is given to the one coming first in the alphabetical listing.**
6. The branched alkyl groups can be named by following the above mentioned procedures. **carbon atom of the branch that attaches to the root alkane is numbered 1 as exemplified below.**

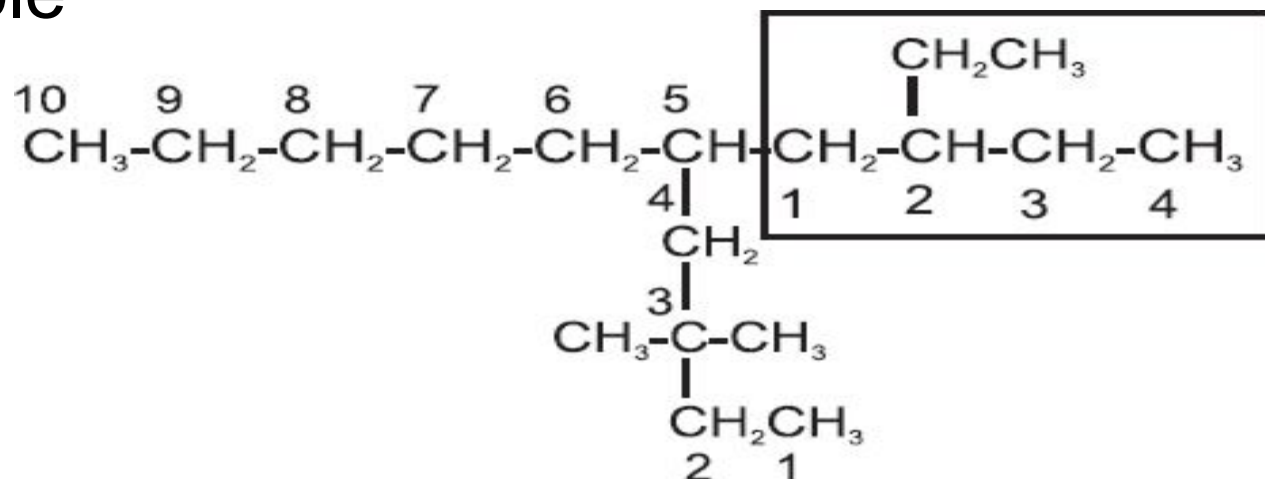


While writing the trivial names of substituents' in **alphabetical order**, the prefixes **iso-** and **neo-** are considered to be the part of the fundamental name of alkyl group. The prefixes ***sec-*** and ***tert-*** are not considered to be the part of the fundamental name.

□ In multi-substituted compounds, the following rules may also be remembered:

- If there happens to be two chains of equal size, then that chain is to be selected which contains more number of side chains.
- After selection of the chain, numbering is to be done from the end closer to the substituent.

For
example



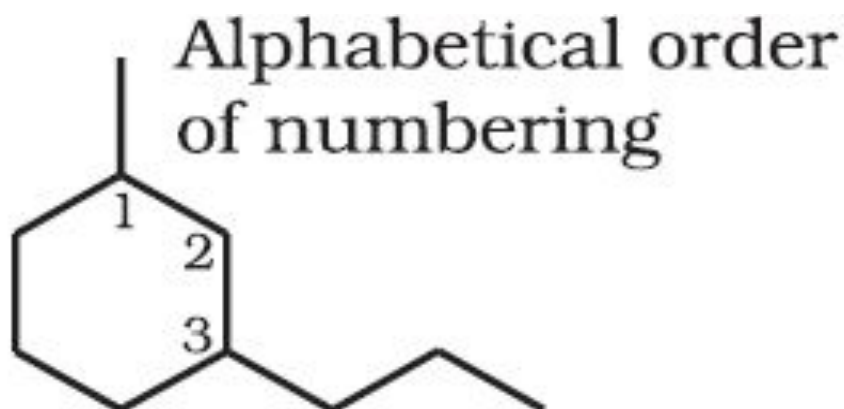
5-(2-Ethylbutyl)-3,3-dimethyldecane
[and not 5-(2,2-Dimethylbutyl)-3-ethyldecane]

Cyclic Compounds: A saturated monocyclic :

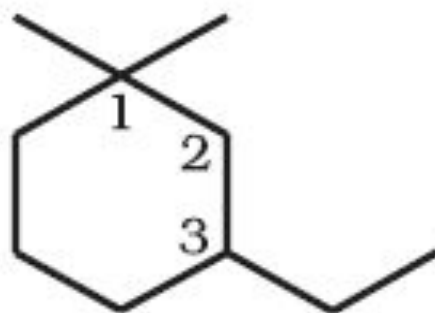
Compound is named by prefixing 'cyclo' to the corresponding straight chain alkane. If side chains are present, then the rules given above are applied. Names of some cyclic compounds are given below.



Cyclopentane



1-Methyl-3-propylcyclohexane



More branched
carbon gets lower
number

3-Ethyl-1,1-dimethylcyclohexane
(not 1-ethyl-3,3-dimethylcyclohexane)

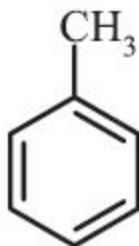
Nomenclature of Organic Compounds having Functional Group(s)

- ✓ A functional group, as defined earlier, is an atom or a group of atoms bonded together in a unique manner which is usually the site of chemical reactivity in an organic molecule.
- ✓ For example, CH_3OH , $\text{CH}_3\text{CH}_2\text{OH}$, and $(\text{CH}_3)_2\text{CHOH}$ — all having $-\text{OH}$ functional group liberate hydrogen on reaction with sodium metal.
- ✓ First of all, the functional group present in the molecule is identified which determines the choice of appropriate suffix.

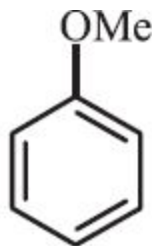
- ✓ The longest chain of carbon atoms containing the functional group is numbered in such a way that the functional group is attached at the carbon atom possessing lowest possible number in the chain.
- ✓ In the case of poly functional compounds, one of the functional groups is chosen as the *principal functional group* and the compound is then named on that basis.
- ✓ The choice of principal functional group is made on the basis of order of preference. **The order of decreasing priority for some functional groups is: -COOH, -SO₃H, -COOR (R=alkyl group), COCl, -CONH₂, -CN, -HC=O, >C=O, -OH, -NH₂, >C=C<, -C≡C- .**

Nomenclature of Substituted Benzene Compounds

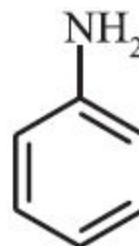
For IUPAC nomenclature of substituted benzene compounds, the substituent is placed as prefix to the word *benzene* as shown in the following examples.



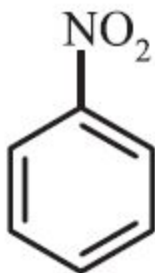
Methylbenzene
(Toluene)



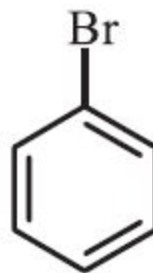
Methoxybenzene
(Anisole)



Aminobenzene
(Aniline)

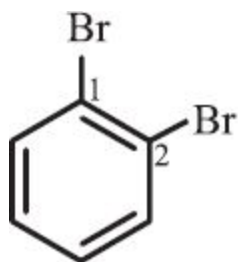


Nitrobenzene



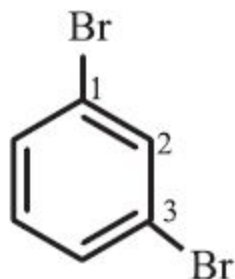
Bromobenzene

If benzene ring is disubstituted, the position of substituents is defined by numbering the carbon atoms of the ring such that the substituents are located at the lowest numbers possible.



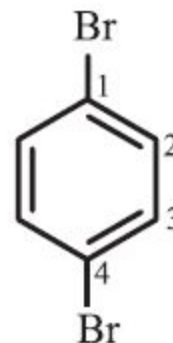
(a)

1,2-Dibromo-
benzene



(b)

1,3-Dibromo-
benzene



(c)

1,4-Dibromo-
benzene

In the trivial system of nomenclature the terms *ortho* (*o*), *meta* (*m*) and *para* (*p*) are used as prefixes to indicate the relative positions 1,2- ;1,3- and 1,4- respectively.

ISOMERIS

M

Isomerism

Structural isomerism

Stereoisomerism

Chain
isomerism

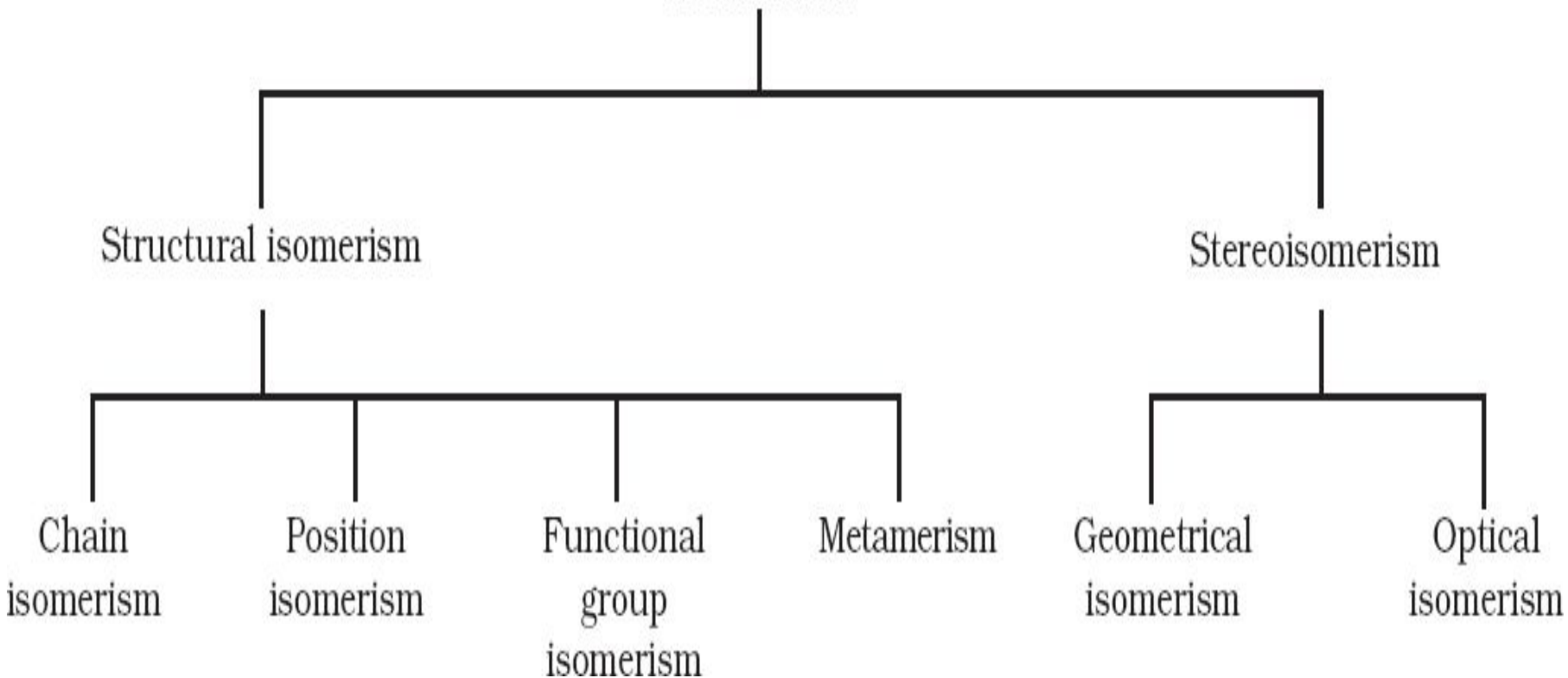
Position
isomerism

Functional
group
isomerism

Metamerism

Geometrical
isomerism

Optical
isomerism



Structural Isomerism

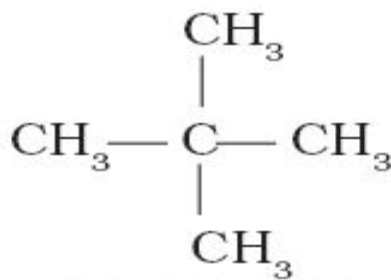
(i) Chain isomerism: When two or more compounds have similar molecular formula but different carbon skeletons, these are referred to as chain isomers and the phenomenon is termed as *example, C₅H₁₂* n.



Pentane

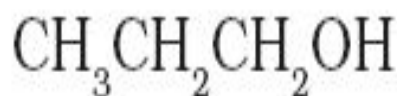


Isopentane
(2-Methylbutane)

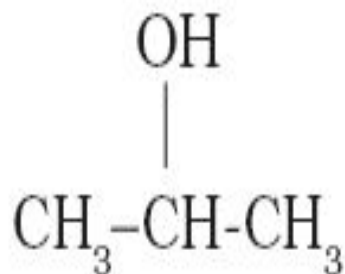


Neopentane
(2,2-Dimethylpropane)

(ii) Position isomerism: When two or more compounds differ in the position of substituent atom or functional group on the carbon skeleton, they are called position isomers and this phenomenon is termed as position isomerism.

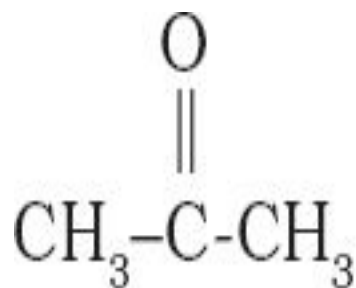
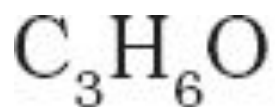


Propan-1-ol

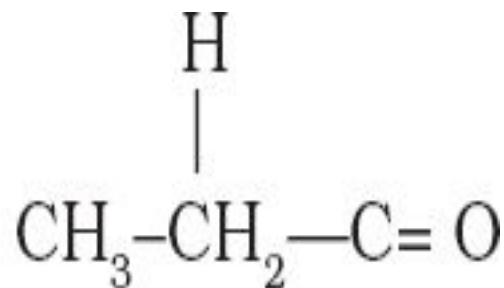


Propan-2-ol

(iii) Functional group isomerism: Two or more compounds having the same molecular formula but different functional groups are called functional isomers and this phenomenon is termed as functional group isomerism.



Propanone



Propanal

(iv) Metamerism: It arises due to different alkyl chains on

methoxypropane ($\text{CH}_3\text{OC}_3\text{H}_7$) and ethoxyethane ($\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$). i.e.

Stereoisomeris

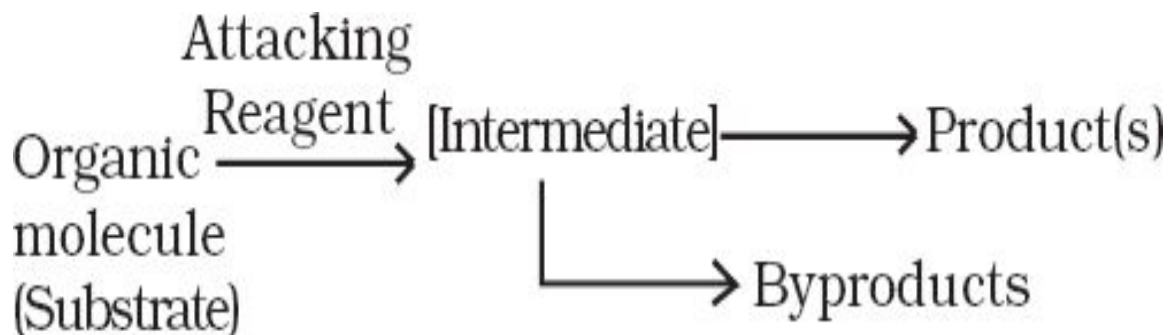
m

The compounds that have the same constitution and sequence of covalent bonds but differ in relative positions of their atoms or groups in space are called stereoisomers. This special type of isomerism is called as stereoisomerism and can be classified as *geometrical and optical isomerism*.

FUNDAMENTAL CONCEPTS IN ORGANIC REACTION MECHANISM

In an organic reaction, the organic molecule (also referred as a substrate) reacts with an appropriate attacking reagent and leads to the formation of one or more intermediate(s) and finally product(s)

The general reaction is depicted as follows :



- ✓ Substrate is that reactant which supplies carbon to the new bond and the other reactant is called reagent.
- ✓ If both the reactants supply carbon to the new bond then choice is arbitrary and in that case the molecule on which attention is focused is called *substrate*.

Reaction mechanism: A sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products (kinetics) is referred to as

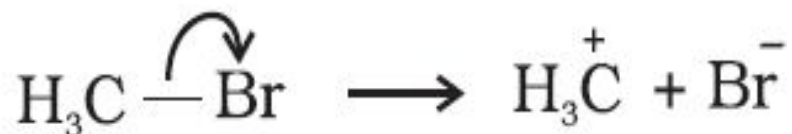
Fission of a Covalent Bond

Cleavages of covalent bonds

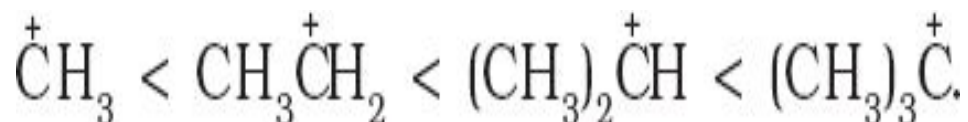
(i) **Heterolytic cleavage:** In **heterolytic cleavage**, the bond breaks in such a fashion that the shared pair of electrons remains with one of the fragments.

- ✓ one atom has a sextet electronic structure and a positive charge and the other, a valence octet with at least one lone pair and a negative charge.

CH_3^+ and Br^- as shown below.



- ✓ A species having a carbon atom possessing sextet of electrons and a positive charge is called a *carbocation* (earlier called *carbonium ion*).
- ✓ The observed order of carbocation stability is:

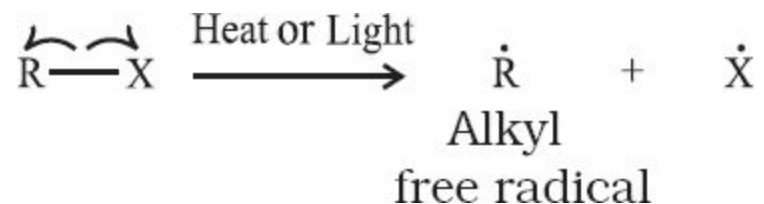


- ✓ The organic reactions which proceed through heterolytic bond cleavage are called **ionic or heteropolar or just polar** reactions.

(ii) Homolytic cleavage: In *homolytic cleavage*, **one of the** electrons of the shared pair in a covalent bond goes with each of the bonded atoms. Thus in homolytic cleavage, the movement of a single electron takes place instead of an electron pair.

✓ Such cleavage results in the formation of neutral species (atom or group) which contains an unpaired electron. These species are called *free radicals*.

✓ A homolytic cleavage can be shown as:



✓ Organic reactions, which proceed by homolytic fission are called *free radical or homopolar or nonpolar reactions*.

Nucleophiles and Electrophiles

Nucleophile (Nu) : A reagent that brings an electron pair i.e., nucleus seeking and the reaction is then called **nucleophilic**.

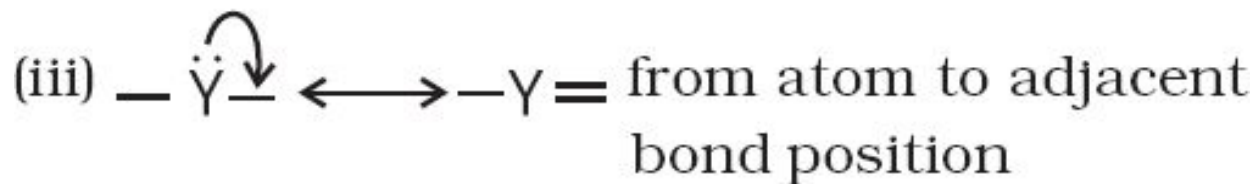
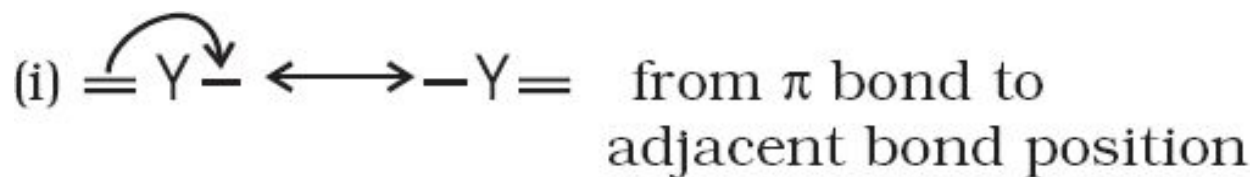
Electrophile (E⁺): A reagent that takes away an electron pair i.e., electron seeking and the reaction is called **electrophilic**.

- ✓ During a polar organic reaction, a nucleophile attacks an electrophilic centre of the substrate which is that specific atom or part of the electrophile that is electron deficient.
- ✓ Similarly, the electrophiles attack at nucleophilic centre, which is the electron rich centre of the substrate

Electron Movement in Organic Reactions

The movement of electrons in organic reactions can be shown by curved-arrow notation.

Presentation of shifting of electron pair is given below :



- ✓ Movement of single electron is indicated by a single barbed 'fish hooks' (i.e. half headed curved arrow).

Electron Displacement Effects in Covalent Bonds

The electron displacement in an organic molecule may take place either in the ground state under the influence of an atom or a substituent group or in the presence of an appropriate attacking reagent.

examples of this type of electron displacements are:

- resonance effects
- Inductive effect

Resonance Structure: A single Lewis structure cannot explain all the property of the molecule hence many Lewis structure are proposed for a some molecule to explain the properties.

Different Lewis structure proposed are called as resonance Lewis structure or canonical form of contributing structure the phenomenon is called resonance and the structures proposed are called resonance structure.

- ✓ The resonance structures (canonical structures or contributing structures) are hypothetical and individually do not represent any real molecule.
- ✓ The difference in energy between the actual structure and the lowest energy resonance structure is called the ***resonance stabilisation energy or simply the resonance energy.***

The following rules are applied while writing resonance structures:

The resonance structures have

- (i) the same positions of nuclei
- (ii) the same number of unpaired electrons.

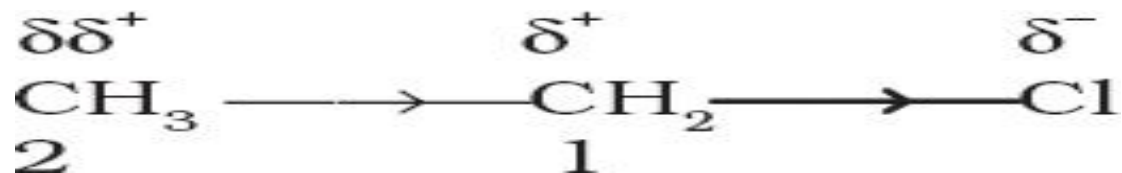
Resonance Effect: The resonance effect is defined as 'the polarity produced in the molecule by the interaction of two π -bonds or between a π -bond and lone pair of electrons present on an adjacent atom'.

There are two types of resonance effect

- (i) **Positive Resonance Effect (+R effect)** : In this effect, the transfer of electrons is away from an atom or substituent group attached to the conjugated system.
- (ii) **Negative Resonance Effect (- R effect)**: This effect is observed when the transfer of electrons is towards the atom or substituent group attached to the conjugated system.

Inductive Effect: The process of electron displacement of electrons along the chain of carbon atoms due to the presence of a polar covalent bond at one end of the chain.

This is a permanent effect and is generally represented by an arrow as shown on the next slide.



It may be noted that this effect decreases sharply as we move away from the atom involved in the initial polar bond and becomes negligible from the fourth atom onwards.

It arises whenever an electron withdrawing group is attached to end of a carbon chain.

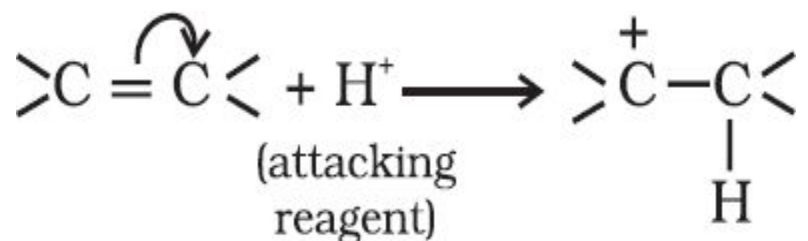
Electromeric Effect (E effect)

It is defined as the complete transfer of a shared pair of π - electrons to one of the atoms joined by a multiple bond on the demand of an attacking reagent.

□ There are two distinct types of electromeric effect.

(i) Positive Electromeric Effect (+E effect)

In this effect the π -electrons of the multiple bond are transferred to that atom to which the reagent gets attached. For example :



(ii) Negative Electromeric Effect (–E effect)

In this effect the π - electrons of the multiple bond are transferred to that atom to which the attacking reagent does not get attached.

Hyperconjugati on

Hyperconjugation is a general stabilising interaction. It involves delocalisation of σ electrons of C—H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared *p orbital*. Hyperconjugation is a permanent effect.

Example:

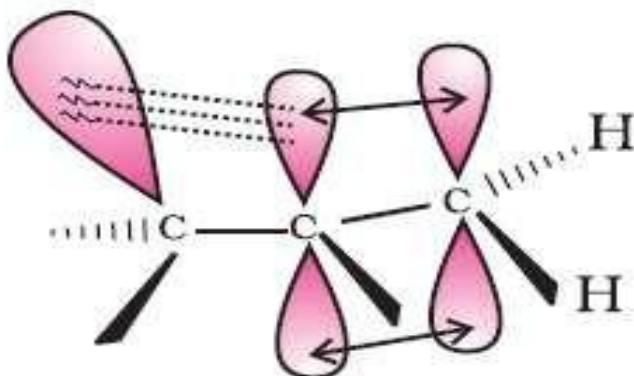


Fig. 12.4(b) Orbital diagram showing hyperconjugation in propene

METHODS OF PURIFICATION OF ORGANIC COMPOUNDS

Once an organic compound is extracted from a natural source or synthesised in the laboratory, it is essential to purify it. Various methods used for the purification of organic compounds are based on the nature of the compound and the impurity present in it.

The common techniques used for purification are as follows :

- (i) Sublimation
- (ii) Crystallisation
- (iii) Distillation
- (iv) Differential extraction and
- (v) Chromatography

❑ Sublimation: In this process the solid substance changes from solid to vapour form without going to the liquid state it is used to separate sublimable compound from non-sublimable impurities.

❑ Crystallisation: It is based on the difference in the solubilities of the compound and the impurities in a suitable solvent.

❑ Distillation: This important method is used to separate:-

- (i) Volatile liquids from nonvolatile impurities
- (ii) And the liquids having sufficient difference in their boiling points.

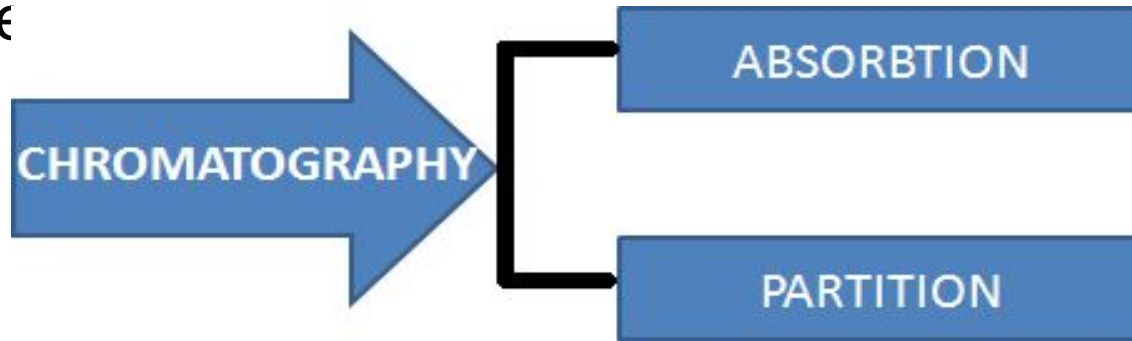
Distillation is further divided in
to :

i) **Fractional distillation**: If the difference in boiling points of two liquids is not much, simple distillation cannot be used to separate them. The technique of fractional distillation is used in such cases.

ii) **Steam distillation** : This technique is applied to separate substances which are steam volatile and are immiscible with water.

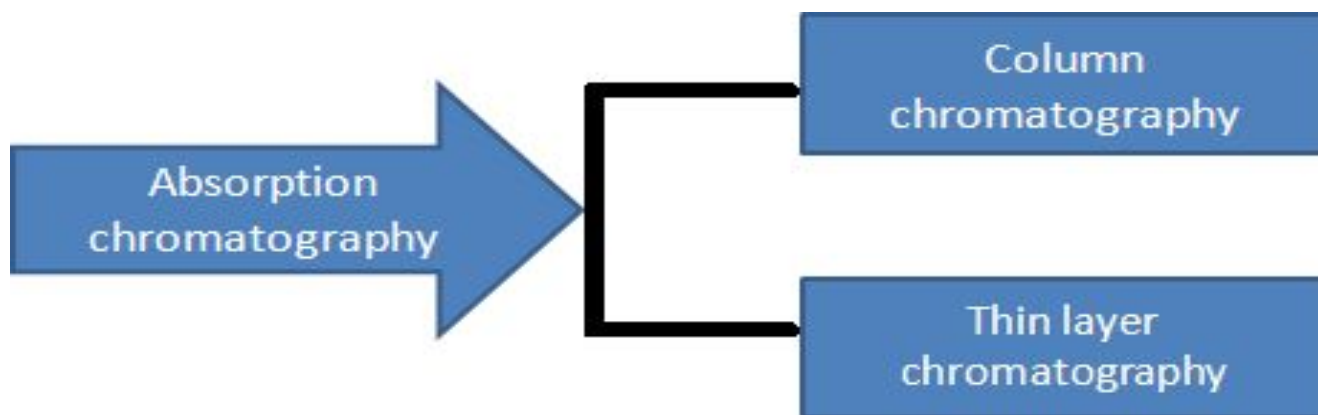
❑ **Differential Extraction**: The organic solvent and the aqueous solution should be immiscible with each other so that they form two distinct layers which can be separated by separatory funnel.

❑ **Chromatography:** In this technique, the mixture of substances is applied onto a stationary phase, which may be a solid or a liquid. A pure solvent, a mixture of solvents, or a gas is allowed to move slowly over the stationary phase



Adsorption chromatography : Is based on the fact that different compounds are adsorbed on an adsorbent to different degrees.

❑ Commonly used adsorbents are silica gel and alumina.



Column chromatography: It involves separation of a mixture over a column of adsorbent (stationary phase) packed in a glass tube.

Thin layer chromatography (TLC): Is another type of adsorption chromatography, which involves separation of substances of a mixture over a thin layer of an adsorbent coated on glass plate.

The relative adsorption of each component of the mixture is expressed in terms of its **retardation factor**.

$$R_f = \frac{\text{Distance moved by the substance from base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$$

Partition
chromatograph

Continuous differential
partitioning of component
of a mixture between
stationary and mobile
phases

QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

The elements present in organic compounds are carbon and hydrogen. In addition to these, they may also contain oxygen, nitrogen, sulphur, halogens and phosphorus.

Detection of Carbon and Hydrogen

Carbon and hydrogen are detected by heating the compound with copper(II) oxide.

Carbon present in the compound is oxidised to carbon dioxide which develops turbidity)

$$\text{CO}_2 + \text{Ca(OH)}_2 \longrightarrow \text{CaCO}_3\downarrow + \text{H}_2\text{O}$$

Hydrogen to water (tested with anhydrous copper sulphate,

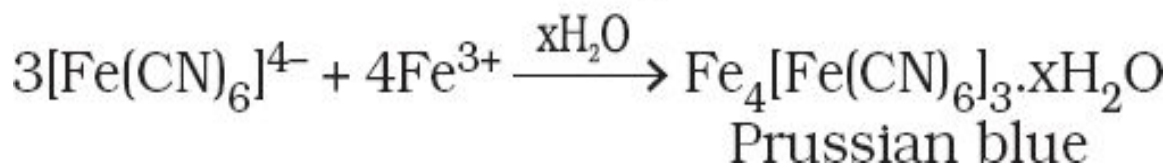
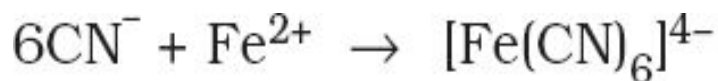


Detection of Other Elements: Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by “**Lassaigne’s test**”.

(A) Test for Nitrogen: The sodium fusion extract is boiled with iron(II) sulphate and then acidified with concentrated sulphuric acid. The formation of Prussian blue colour confirms the presence of nitrogen.

✓ Sodium cyanide first reacts with iron(II) sulphate and forms sodium hexacyanoferrate(II).

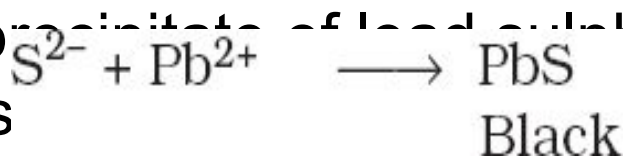
✓ On heating with concentrated sulphuric acid some iron(II) ions are oxidised to iron(III) ions which react with sodium hexacyanoferrate(II) to produce iron(III) hexacyanoferrate(II) (ferriferrocyanide) which is Prussian blue in colour.



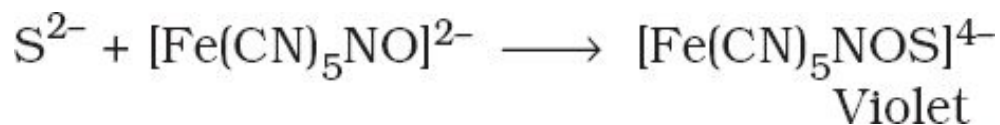
(B) Test for Sulphur:

(a) The sodium fusion extract is acidified with acetic acid and lead acetate is added

to it. A black precipitate is formed which indicates the presence of S



(b) On treating sodium fusion extract with sodium nitroprusside, appearance of a violet colour further indicates the presence of sulphur.



(C) Test for Halogens: The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate. **Results:**

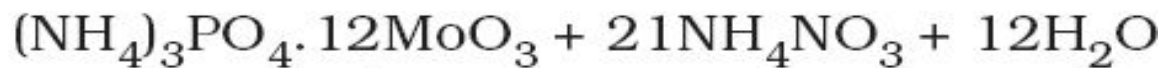
- ✓ A white precipitate, soluble in ammonium hydroxide shows the presence of chlorine.
 - ✓ A yellowish precipitate, sparingly soluble in ammonium hydroxide shows the presence of bromine.
 - ✓ A yellow precipitate, insoluble in ammonium hydroxide
- $$\text{X}^- + \text{Ag}^+ \longrightarrow \text{AgX}$$
- X represents a halogen – Cl, Br or I.

(D) Test for Phosphorus: The compound is heated with an oxidising agent (sodium peroxide). The phosphorus present in the compound is oxidised to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate.

Result: A yellow colouration or precipitate indicates the presence of phosphorus.



Ammonium
molybdate



Ammonium
phosphomolybdate

QUANTITATIVE ANALYSIS

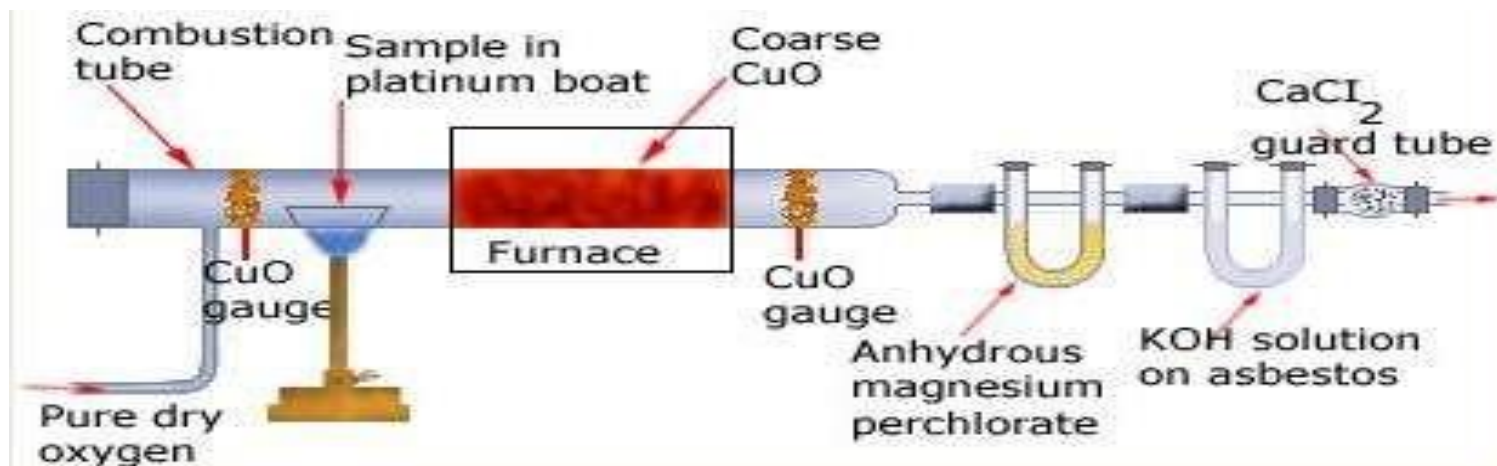
Carbon and Hydrogen: A known mass of an organic compound is burnt in the presence of excess of oxygen and copper(II) oxide.

- ✓ Carbon and hydrogen in the compound are oxidised to carbon dioxide and water respectively.



Observation

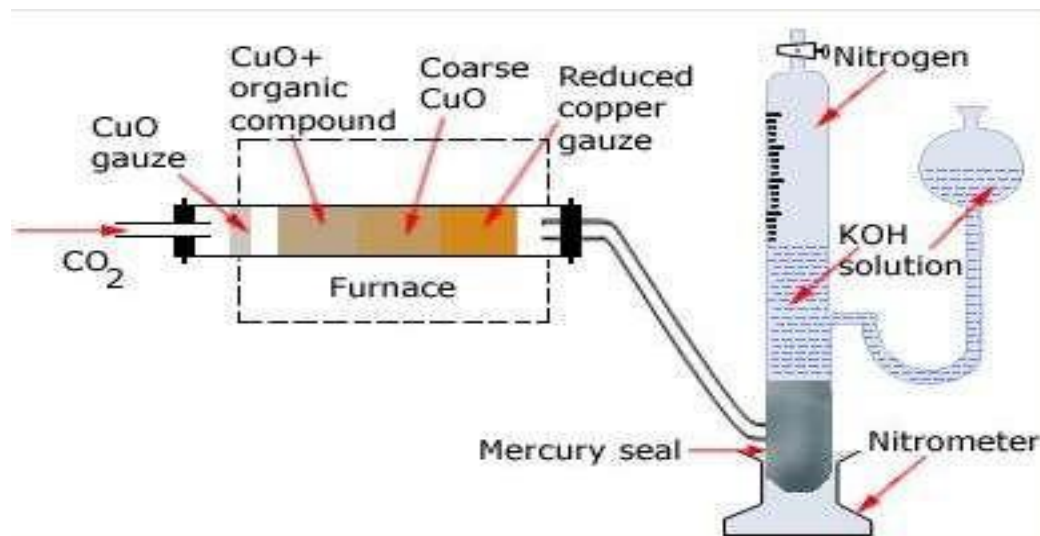
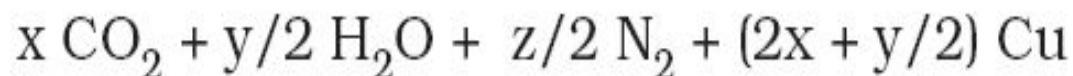
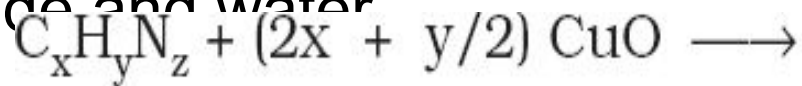
- ✓ The mass of water produced is determined by passing the mixture through a weighed U-tube containing anhydrous calcium chloride.
- ✓ Carbon dioxide is absorbed in another U-tube containing concentrated solution of potassium hydroxide



The increase in masses of calcium chloride and potassium hydroxide gives the amounts of water and carbon dioxide from which the percentages of carbon and hydrogen are calculated.

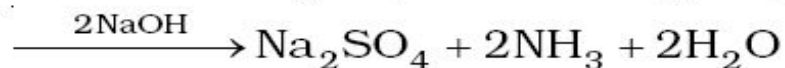
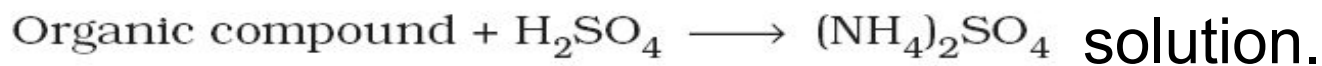
❑ **Nitrogen:** There are two methods for estimation of nitrogen: (i) Dumas method (ii) Kjeldahl's method.

(i) Dumas method: The nitrogen containing organic compound, when heated with copper oxide in an atmosphere of carbon dioxide, yields free nitrogen in addition to carbon dioxide and water.



(ii) Kjeldahl's method: The compound containing nitrogen is heated with concentrated sulphuric acid. Nitrogen in the compound gets converted to ammonium sulphate.

- ✓ The liberated ammonia gas is absorbed in an excess of standard solution of sulphuric acid.
- ✓ The amount of ammonia produced is determined by estimating unreacted sulphuric acid left after the absorption of ammonia.

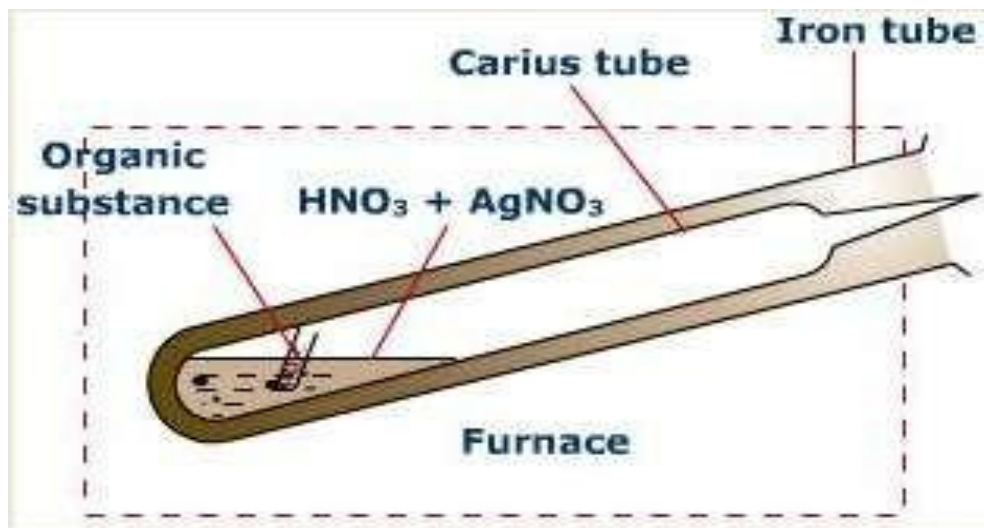


Drawbacks of this method: It is not applicable to compounds containing nitrogen in nitro and azo groups and nitrogen present in the ring (e.g. pyridine) as nitrogen of these compounds does not change to ammonium sulphate under these conditions.

❑ Halogens

Carius method: A known mass of an organic compound is heated with fuming nitric acid in the presence of silver nitrate contained in a hard glass tube known as Carius tube, in a furnace.

- ✓ Carbon and hydrogen present in the compound are oxidised to carbon dioxide and water.
- ✓ The halogen present forms the corresponding silver halide (AgX). It is filtered, washed, dried and weighed.



Sulphur: A known mass of an organic compound is heated in a Carius tube with sodium peroxide or fuming nitric acid. Sulphur present in the compound is oxidised to sulphuric acid.

- ✓ It is precipitated as barium sulphate by adding excess of barium chloride solution in water.
- ✓ The precipitate is filtered, washed, dried and weighed. The percentage of sulphur can be calculated from the mass of barium sulphate.

Phosphorus: A known mass of an organic compound is heated with fuming nitric acid where upon phosphorus present in the compound is oxidised to phosphoric acid.

- ✓ It is precipitated as ammonium phosphomolybdate, by adding ammonia and ammonium molybdate.

Oxygen: A definite mass of an organic compound is decomposed by heating in a stream of nitrogen gas.

- ✓ The mixture of gaseous products containing oxygen is passed over red-hot coke when all the oxygen is converted to carbon monoxide.
- ✓ This mixture is passed through warm iodine pentoxide when carbon monoxide is oxidised to carbon dioxide producing iodine.
- ✓ The percentage of oxygen can be derived from the amount of carbon dioxide or iodine produced.