Chapter 1 Basic Organic Chemistry

Day – 1

Introduction To Organic Chemistry

Definition of Organic Chemistry (Historical Background)

Old Concept:- The word 'organic' signifies life. Therefore, all substances which were obtained directly or indirectly from living organisms, plants and animals, were called organic compounds and the branch of chemistry which deals with these compounds was called organic chemistry. Although, a large number of organic compounds such as sugar, starch, alcohol, oils, indigo, resins, etc., had been known from earliest times, very little information was known regarding their chemistry until the beginning of eighteenth century.

In 1675, Lemery published his famous Cours de Chymie, in which he classified the natural substances into three classes according to their respective origin:

(i):- Mineral substances obtained from the mineral kingdom.

(ii):- Vegetable substances obtained from the vegetable kingdom.

(iii):- Animal substances obtained from the animal kingdom.

This classification was accepted quickly but it was Lavoisier (father of chemistry) who first showed, in 1785, that all compounds obtained from vegetables and animal sources always contained carbon and hydrogen, and frequently nitrogen and phosphorus. It was also realized that some organic compounds occurred both in plants and animals. This led to the re-classification of natural substances into two categories.

(i):- All those which could be obtained from vegetables or animals, *i.e.*, the substances which were produced by living organisms. These substances were produced by living organisms. These substances were classified as organic compounds.

(ii):- All those which were not obtained from the living organisms. These substances were classified as inorganic compounds.

Quite a large number of organic compounds have been discovered and isolated from natural sources by the first quarter of nineteenth century but till then none of the organic compounds could be prepared in laboratory. This led to believe that organic compounds followed laws of formations different from inorganic compounds. Berzelius assumed that some vital force (life force) was necessary to produce organic compounds and synthesis of these compounds in the laboratory was impossible due to the absence of this vital force which only existed in living organisms.

The vital force theory suffered the first death blow, in 1828, when wohler synthesised first organic compound, urea, in the laboratory by heating ammonium cyanate (an inorganic compound).

$$\underset{\text{Ammonium cyanate}}{NH_4CNO} \xrightarrow{\text{Heat}} \underset{\text{Urea}}{NH_2CONH_2}$$

Ammonium cynate is prepared by one of the following methods

$$[(NH_4)_2SO_4 + 2KCNO \xrightarrow{\text{Heat}} 2NH_4CNO + K_2SO_4]$$

$$[PB(CNO)_2 + 2NH_4OH \xrightarrow{\text{Heat}} 2NH_4CNO + PB(OH)_2]$$

$$[NH_4Cl + KCNO \xrightarrow{\text{Heat}} NH_4CNO + KCl]$$

A further blow to vital force theory was given by Kolbe, in 1845, when he synthesized acetic acid, the first organic compound, in laboratory from its elements and later by Berthelot, in 1856, who synthesized methane.

$$2C + H_2 \xrightarrow[\text{are}]{\text{Electric}} \underset{\text{Acetylene}}{HC \equiv CH} \xrightarrow[HgSO_4]{\text{Dil.}H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{\text{Oxidation}} \underset{\text{Acetic acid}}{CH_3COOH}$$

Since then a large number of organic compounds have been synthesised and their formation is governed by simple laws of formation as applicable to inorganic compounds and does not depend on special vital force. Inspite of the fact that there was no fundamental difference between organic and inorganic compounds but a superficial distinction was maintained between organic and inorganic chemistry and this distinction is still followed.

Modern Definition of Organic Chemistry

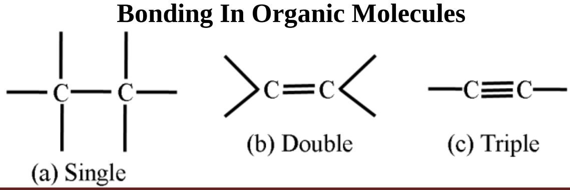
Since carbon is an essential constituent of all organic compounds, organic chemistry is defined as the chemistry of carbon compounds. In fact, out of millions of organic compounds now known, there is not a single compound which does not contain carbon. However, there are compounds of carbon such as carbon monoxide, carbon dioxide, metal carbonates and bicarbonates, metal cyanides, metal carbides, etc., which are studied in inorganic chemistry because of their properties. Simplest organic compounds are those which are composed of carbon and hydrogen only and are called hydrocarbons. Other organic compounds may be regarded as derivatives of hydrocarbons obtained by replacement of hydrogen by any other element or group. Thus, organic chemistry may also be defined as the chemistry of hydrocarbons and their derivatives.

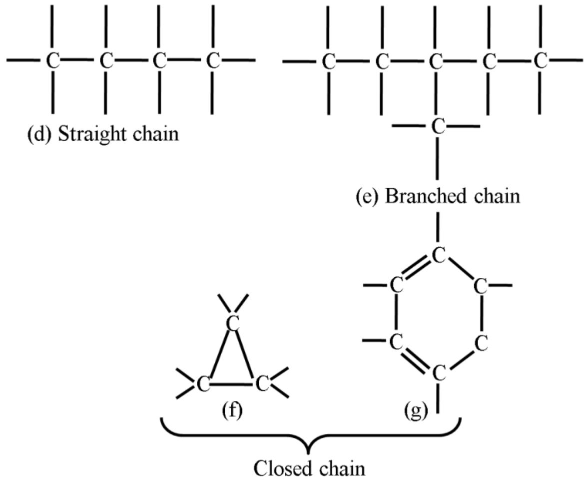
Reasons for Large Number of Organic Compounds

(I) Catenation:-

The tendency of an element to form chains of identical atoms is called catenation. This tendency is observed in the case of non-metals showing covalency of two or more. However, this property is maximum in carbon as it can combine with other carbon atoms by single, double or triple covalent bonds. The bonding can be extended to form long open chains (straight or branched) or closed ones.

Bonding In Organic Molecules





Catenation property depends upon the value of bond energy which is maximum in the case of carbon.

Bond	C — C	Si — Si	S — S	P — P	N —N	O — O
Bond energy (kcal mol^{-1})	83	54	54	50	39	35

The stability or strength of the bond decreases as the bond energy decreases. Hence, the tendency of catenation decreases in the following manner:

$$C > Si \approx S > P > N > O$$

(II) Tendency to combine with other non-metals:-

Carbon has the ability to form strong covalent bonds with many other atoms such as H, O, S, N, Cl, Br, I, etc. The C — C bond energy is approximately equal to the magnitude of bond energies between carbon and various other atoms,

Bond	C — C	C — H	C — O	C — Cl	C — N	C — Br
Bond energy (kcal mol^{-1})	83.0	97.0	86.0	81.0	73.0	68.0

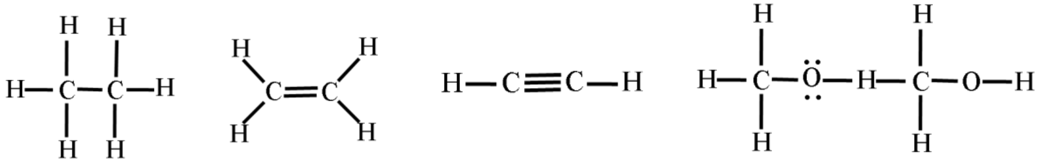
(III) Isomerism:-

The phenomenon of isomerism shown by organic compounds is also responsible for large number of organic compounds. The compounds are said to be isomers if they have same compounds, *i.e.*, same chemical formula but different properties. The phenomenon of isomerism is due to the different arrangement of atoms in the molecules of the isomers. In contrast to this, in inorganic chemistry, one molecular formula stands for only one compounds, *e.g.*, HNO_3 stands for nitric acid and nothing else. A detailed discussion on isomerism has been taken in a subsequent chapter.

Condensed and Bond-line Structural Formulas

Structures of organic compounds are represented in several ways. (i)The Lewis structure or (ii)Dot structure, dash structure, (iii)Condensed structure and (iv)Bond line structural formulas are some of the specific types. The Lewis structures, however, can be simplified by representing the two-electron covalent bond by a dash (–). Such a structural formula focuses on the electrons involved in bond formatting. A single dash represents a single bond, double dash is used for double bond and a triple dash represents triple bond. Lone-pairs of electrons on heteroatoms (*e.g.*, oxygen, nitrogen, sulphur, halogens etc.) may or may not be shown. Thus, ethane (C_2H_6), ethene (C_2H_4), ethyne (C_2H_2) and methanol (CH_3OH) can be represented by the following structural formulas. Such structural representations are called complete structural formulas.

Lewis Structure



Ethane Ethene Ethyne Methanol

Condensed Formula

These structural formulas can be further abbreviated by omitting some or all of the dashes representing covalent bonds and by indicating the number of identical groups attached to an atom by a subscript. The resulting expression of the compound is called a condensed structural formula. Thus, ethane, ethene, ethyne and methanol can be written as:

CH_3CH_3	$H_2C = CH_2$	$HC \equiv CH$	CH_3OH
Ethane	Ethene	Ethyne	Methanol

Similarly, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ can be further condensed to $CH_3\,(CH_2)_6CH_3$.

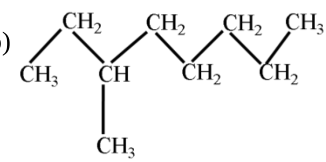
Bond Line Formula

For further simplification, 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. The only atoms specifically written are oxygen, chlorine, nitrogen etc. The terminals denote methyl ($–CH_3$) groups (unless indicated otherwise by a functional group), while the line junctions denote carbon atoms bonded to appropriate number of hydrogens required to satisfy the valency of the carbon atoms. Some of the examples are represented as follows:

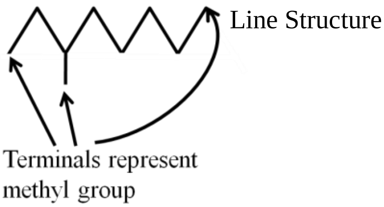
 **$\equiv CH_3 – CH_2 – CH_2 – CH_3$ = Butane**

comparing all three notations

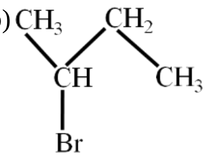
(a) $CH_3CH_2CHCH_2CH_2CH_2CH_2CH_3$ (with CH_3 on the third carbon) Condensed

(b) 

Lewis Structure

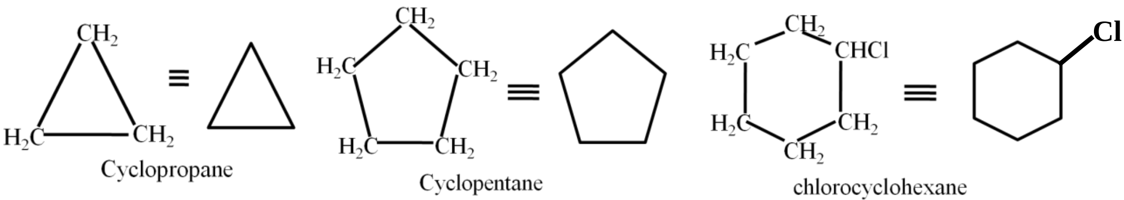
(c) 

(ii) Various ways of representing 2-bromo butane are:

(a) $CH_2CHBrCH_2CH_3$ (b) 

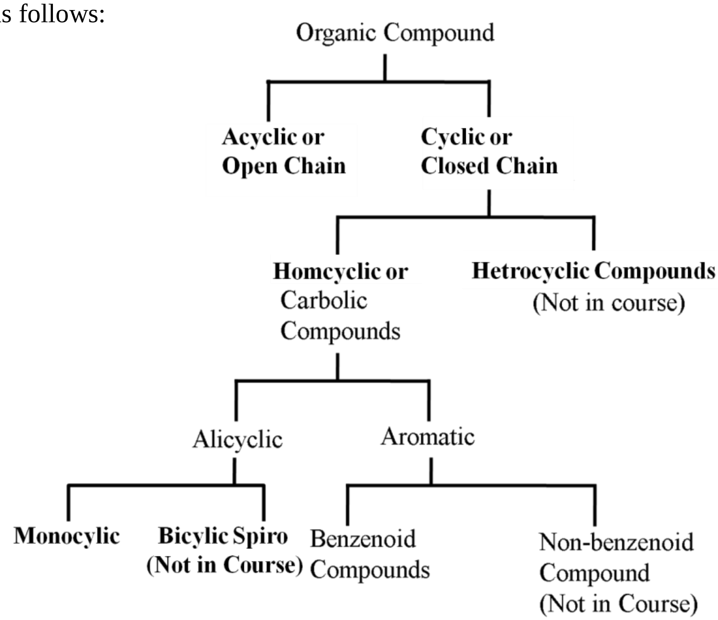
(c) 

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



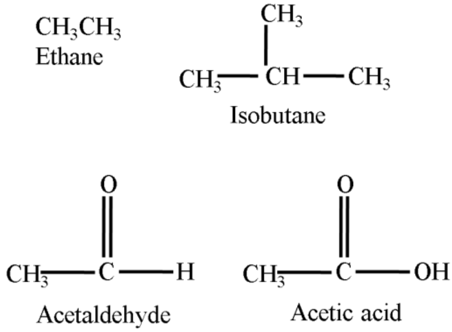
Classification of Organic Compounds

The exiting large number of organic compounds and their ever-increasing numbers has made it necessary to classify them on the basis of their structures. Organic compounds are broadly classified as follows:



I. Acyclic or open chain compounds

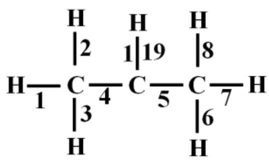
These compounds are also called as aliphatic compounds and consist of straight or branched chain compounds, for example:



Example:-

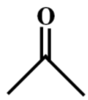
Draw the Lewis structure of Acetone and find number of sigma σ and pie π bond.

Acetone CH_3COCH_3



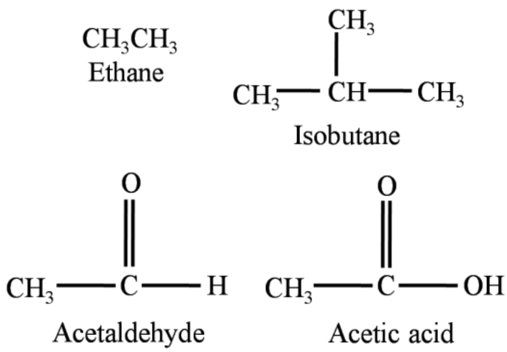
σ – 9 Bond
π – 1 Bond

Line diagram of Acetone



I. Acyclic or Open Chain Compounds

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

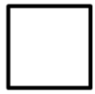


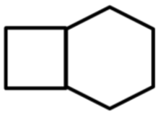
II. Alicyclic or Closed Chain or Ring Compounds

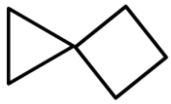
Alicyclic (aliphatic cyclic) compounds contain carbon atoms joined in the form of a ring (homocyclic). Sometimes atoms other than carbon are also present in the ring (heterocylin). Some example of this type of compounds are:


Cyclopropane

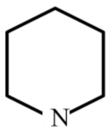

Cyclohexane

Monocyclic

Cyclobutane

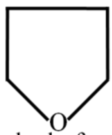
Bicyclic

Bicyclio (4, 2, 0) octane
(Not in course)

Spiro

Spiro (2, 3) Hexane
(Not in course)

Heterocyclic



Piperidine



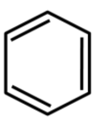
Tetrahydrofuran

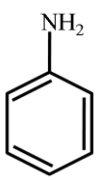
These exhibit some of the properties similar to those of aliphatic compounds.

Aromatic compounds

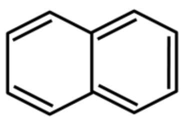
Aromatic compounds are special types of compounds. You will learn about these compounds later. These include benzene and other related ring compounds (benzenoid). Like alicyclic compounds, aromatic compounds may also have hetero atom in the ring. Such compounds are called hetrocyclic aromatic compounds. Some of the examples of various types of aromatic compounds are:

Benzenoid aromatic compounds


benzene

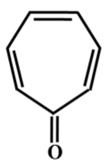


Aniline


Nephthalene

Non-benzenoid compound

Homocyclic



Tropolone

Heterocyclic aromatic compounds

Organic compounds can also be classified on the basis of functional groups. Into families or homologous series.

Functional Group

The functional group may be defined as an atom or group of atoms joined in a specific manner which is responsible for the characteristic chemical propertied of the organic compounds. The examples are hydroxyl group (–OH), aldehyde group (–CHO) and carboxylic acid group (–COOH) etc.

Homologous Series

A group or a series of organic compounds each containing a characteristic functional group forms a homologous series and the members of the series are called homologues. The member of a homologous series can be represented by general molecular formula and the successive members differ from each other in molecular formula by a $–CH_2$ unit. There are a number of homologous series of organic compounds. Some of these are alkanes, alkenes, alkynes, haloalkanes, alkanols, alkanals, alkanones, alkanoic acids, amines etc.