industrial organic Chemistry

Chapter I: Basics of organic chemistry

I. Introduction to organic chemistry

I.1. Historical Background of Organic Chemistry

Organic chemistry is the area of chemistry that involves the study of **carbon and its compounds**. Carbon is now known to form a seemingly unlimited number of compounds. The uses of organic compounds impact our lives daily in medicine, agriculture, and general life.

In theory (Oparin, 1923) organic chemistry may have its beginnings with the **big bang** when the components of ammonia, nitrogen, carbon dioxide and methane combined to form amino acids, an experiment that has been verified in the laboratory (Miller, 1950). Organic chemicals were used in ancient times by Romans and Egyptians as dyes, medicines and poisons from natural sources, but the chemical composition of the substances was unknown.

In the **16th** century organic compounds were **isolated from nature** in the pure state (**Scheele, 1769**) and analytical methods were developed for determination of elemental composition (**Lavoisier, 1784**).

Scientists believed (**Berzelius, 1807**) that organic chemicals found in nature contained a special "vital force" that directed their natural synthesis, and therefore, it would be impossible to accomplish a laboratory synthesis of the chemicals. Fortunately, later in the century **Frederich Wöhler (1828)** discovered that **urea**, a natural component in **urine**, could be synthesized in the laboratory by heating **ammonium cyanate**. His discovery meant that the natural "vital force" was not required to synthesis organic compounds, and paved the way for many chemists to synthesize organic compounds.

By the middle of the **nineteenth** century many advances had been made into the discovery, analysis and synthesis of many **new organic compounds**. Understanding about the structures of organic chemistry began with a theory of bonding called valence theory (**Kekule, Couper, 1858).**

Organic chemistry developed into a productive and exciting science in the nineteenth century. Many new synthetic methods, reaction mechanisms, analytical techniques and structural theories have been developed. Toward the end of the century much of the knowledge of organic chemistry has been expanded to the study of biological systems such as proteins and **DNA**. Volumes of information are published monthly in journals, books and electronic media about organic and biological chemistry.

The vast information available today means that for new students of organic chemistry a great deal of study is required. Students must learn about organic reactions, mechanism, synthesis, analysis, and biological function. The study of organic chemistry, although complex, is very interesting, and begins here with an introduction of the theory of chemical bonding.

The carbon atom is the basis of any organic structure. Carbon atoms can join together to form chains or rings. Organic chemistry creates long and often complex molecules for which it seems very complicated to give a name or to build the molecule from its name. A few rules make it possible to quickly find the link name molecules and without ambiguity, that is to say that everyone must name the same molecule with the same name.

I.2. Study of the carbon atom

I.2.1. Definition

The carbon atom: carbon gives covalent bonds with hydrogen, oxygen, nitrogen and non-metals. Organic compounds are essentially covalent compounds. Because each carbon is identical, they all have four valence electrons, so they can easily bond with other carbon atoms to form long chains or rings.

I.2.2. The nucleus

The nucleus, that dense central core of the atom, contains both protons and neutrons. Electrons are outside the nucleus in energy levels. Protons have a positive charge, neutrons have no charge, and electrons have a negative charge.

(nucleus = protons) + neutrons) and electron cloud

I.2.3. Structure

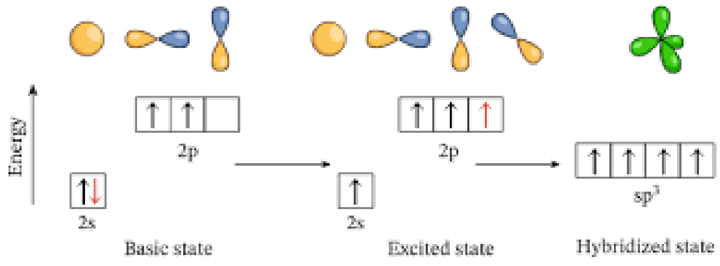
Atomic Number and Symbol: Carbon has the atomic number 6 and is represented by the symbol "C".

Electron Configuration: In its ground state, carbon has an electron configuration of $1s^2$ $2s^2$ $2p^2$. This configuration means it has two electrons in its first shell and four electrons in its second shell.

I.2.4. Orbitals

s-orbitals: The first energy level contains one s-orbital, which can hold up to 2 electrons.

p-orbitals: The second energy level contains three p-orbitals, which can collectively hold up to 6 electrons. Carbon has 2 of these p-orbitals occupied with 2 electrons each.



I.3. Properties of the carbon atom

I.3.1. Ionization energies

1 st : 11,26030 eV	4 th : 64,4939 eV
2 nd : 24,3833 eV	5 th : 392,087 eV
3 rd : 47,8878 eV	6 th : 489,99334 eV

VARIOUS

Electronegativity (Pauling)	2.55
Massic heat	710 J·kg^{-1}·K^{-1}
Electrical conductivity	61×10^{3} S·m^{-1}
Thermal conductivity	129 W·m^{-1}·K^{-1}

I.3.2. Isotopes of carbon characteristics

Carbon has several isotopes, each with distinct characteristics. The most common isotopes of carbon are:

Isotope	**N**	**Mass (u)**	**abundance**	**Period**	**Decay mode**	**Ed**	**radioactive reaction**	**Nuclear spin**
^{12}C	6	12	99.9 %	5730 years	Stable with 6 neutrons	0.156		0+
^{13}C	7	13.003355	1.1 %		Stable with 7 neutrons			½-
^{14}C	8	14.0003242	trace		ray β-		^{14}N	0+

I.3.3. Applications and Significance of isotope of carbon

- **Carbon-12**: It is the reference isotope against which atomic masses of all elements are measured.
- **Carbon-13**: Provides insights into molecular structures and dynamics through NMR. Its presence in molecules can be used to study metabolic pathways and the source of carbon in different compounds.
- **Carbon-14**: Essential for archaeological and geological dating, as well as in some scientific research to trace biochemical processes.

Each isotope of carbon plays a unique role in scientific research and practical applications, underlining the importance of carbon in various fields.

I.4. Electronic structure of the carbon atom

- **hybridization:** The mixing of the atomic orbitals in an atom to produce a set of hybrid orbitals.

- **hybrid orbitals:** The atomic orbitals obtained when two or more nonequivalent orbitals form the same atom combine in preparation for bond formation.

Carbon state	Electronic configuration	Valence number
Fundamental excited	$^{6}C: 1s^2\ 2s^2\ 2p^2$ $1s^2\ 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$	2 only 4

I.4.1. Atomic orbital

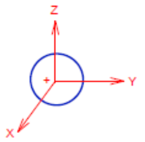
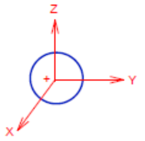
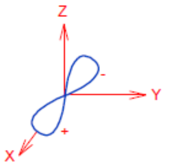
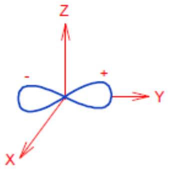
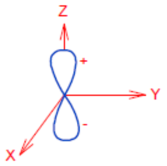
The orbital of an electron in an atom is the geometric location in space where there is a very high probability of finding it. Each atomic orbital is characterized by four quantum numbers:

- The principal quantum number **n** (n = 1, 2, 3…) denotes a shell, with each shell containing one or more subshells called atomic orbitals (A.O.) defined by the triplet (n, *l*, m).

- The azimuthal quantum number ***l*** (l = 0, 1, 2, ..., n−1) defines the shape of the orbital, with each value of ***l*** corresponding to a type of orbital (s, p, d, f…).

- The magnetic quantum number ***m*** $(-l \le m \le +l)$ defines the position of the atomic orbital in space.

- The spin quantum number **s** accounts for the electron's intrinsic angular momentum; it can only take two values: **+1/2** (α state, denoted ↑) and **−1/2** (β state, denoted ↓). Electrons with the same spin are said to be parallel, while electrons with opposite spins are said to be antiparallel or paired.

Orbital		*n*	*l*	*m*	**Orbital Form**
1s		1	0	0	
2s		2	0	0	
2p	2px	2	1	-1	
	2py	2	1	0	
	2pz	2	1	1	

I.5. The Chemical Bond

Carbon is the basic element in organic chemistry. Covalent bond, in chemistry, the interatomic linkage that results from the sharing of an electron pair between two atoms. The binding arises from the electrostatic attraction of their nuclei for the same electrons. A covalent bond forms when the bonded atoms have a lower total energy than that of widely separated atoms.

I.5.1. Types of Chemical Bonds

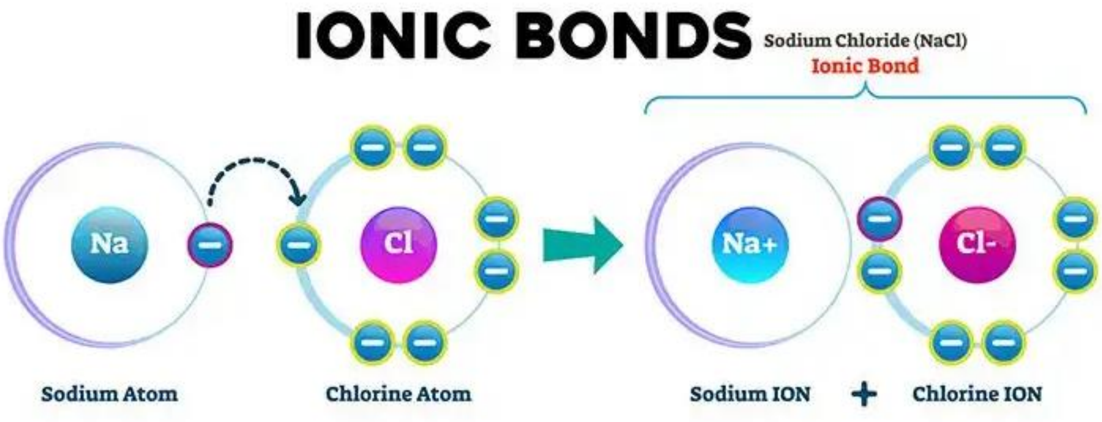
When substances participate in chemical bonding and yield compounds, the stability of the resulting compound can be gauged by the type of chemical bonds it contains.
The type of chemical bonds formed varies in strength and properties. There are **4 primary types** of chemical bonds which are formed by atoms or molecules to yield compounds. These types of chemical bonds include:

- **Ionic Bonds**
- **Covalent Bonds**
- **Hydrogen Bonds**
- **Polar Bonds**

These types of bonds in chemical bonding are formed from the **loss**, **gain** or **sharing** of electrons between two atoms/molecules.

I.5.1.1. Ionic Bonds

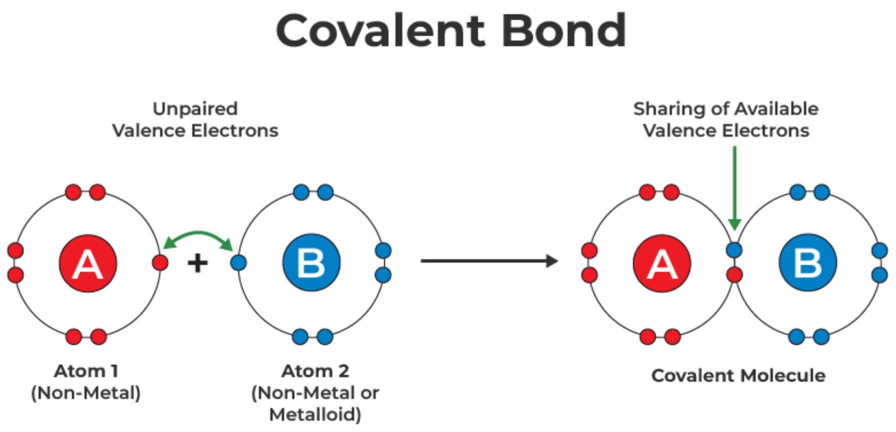
- **Formation**: Ionic bonds form when electrons are transferred from one atom to another. Typically, this occurs between metals and nonmetals. The metal atom loses one or more electrons to become a positively charged ion (cation), while the nonmetal atom gains those electrons to become a negatively charged ion (anion).
- **Example**: Sodium chloride (NaCl) is formed when sodium (Na) donates an electron to chlorine (Cl). Sodium becomes Na^+ , and chlorine becomes Cl^- , creating an ionic bond due to the electrostatic attraction between these oppositely charged ions.
- **Properties**: Ionic compounds generally have high melting and boiling points, and they conduct electricity when melted or dissolved in water due to the mobility of the ions.



I.5.1.2. Covalent Bonds

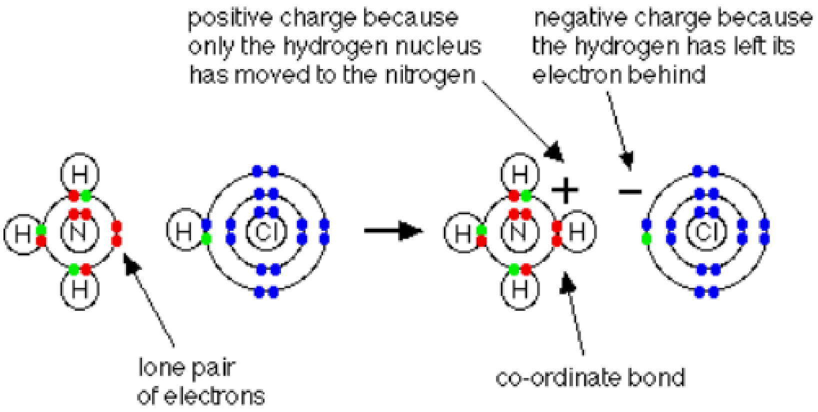
- **Formation**: Covalent bonds form when two atoms share one or more pairs of electrons. This type of bonding usually occurs between nonmetals.
- **Example**: In a water molecule (H_2 O), oxygen shares electrons with hydrogen atoms. Each hydrogen atom shares one electron with oxygen, resulting in a covalent bond.

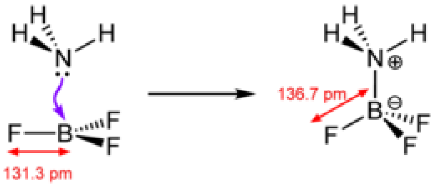
- **Types**:
  - **Single Covalent Bond**: One pair of electrons is shared (e.g., H_2).
  - **Double Covalent Bond**: Two pairs of electrons are shared (e.g., O_2).
  - **Triple Covalent Bond**: Three pairs of electrons are shared (e.g., N_2).
- **Properties**: Covalent compounds can have varying melting and boiling points, often lower than ionic compounds. They may not conduct electricity in any state.



I.5.1.3. Coordinate covalent bond (dative bond)

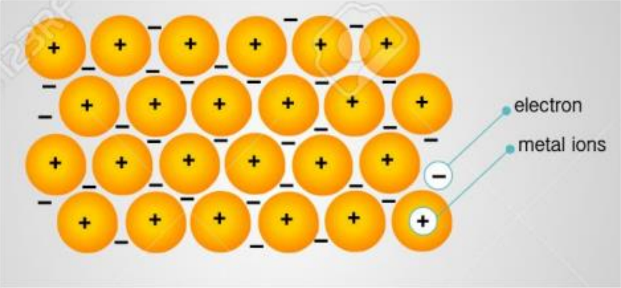
A coordinate bond (also called a dative covalent bond) is a covalent bond (a shared pair of electrons) in which **both** electrons come from the same atom. A covalent bond is formed by two atoms sharing a pair of electrons. The atoms are held together because the electron pair is attracted by both of the nuclei. In the formation of a simple covalent bond, each atom supplies one electron to the bond - but that does not have to be the case.





I.5.1.4. Metallic Bonds

- **Formation**: Metallic bonds occur between metal atoms. In this bond, electrons are not shared or transferred but instead form a "sea of electrons" that are free to move around. The metal atoms lose their outer electrons, which become delocalized and create a bond through electrostatic attraction between the positively charged metal ions and the free electrons.
- **Example**: In copper (Cu), metal atoms share their outer electrons with many other atoms, creating a conductive structure.
- **Properties**: Metallic compounds are typically good conductors of heat and electricity, and they have high melting and boiling points. They are also malleable and ductile.



I.5.1.5. Polar and Nonpolar Covalent Bonds

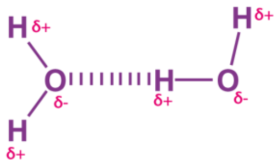
- **Nonpolar Covalent Bond**: Electrons are shared equally between the two atoms. This usually occurs when two identical nonmetal atoms bond (e.g., H_2, O_2).

- **Polar Covalent Bond**: Electrons are shared unequally between the two atoms due to a difference in electronegativity. The atom with higher electronegativity attracts the shared electrons more strongly, creating a dipole moment (e.g., in H_2O, oxygen is more electronegative than hydrogen).

I.5.1.6. Hydrogen Bonding

Compared to ionic and covalent bonding, Hydrogen bonding is a weaker form of chemical bonding. It is a type of polar covalent bonding between oxygen and hydrogen, wherein the hydrogen develops a partial positive charge. This implies that the electrons are pulled closer to the more electronegative oxygen atom.

This creates a tendency for the hydrogen to be attracted towards the negative charges of any neighbouring atom. This type of chemical bonding is called a hydrogen bond and is responsible for many of the properties exhibited by water.



The valence shell (S.V.) of an element corresponds to the last unsaturated electron shell (S.E.). Only this valence shell is involved in the formation of chemical bonds. The valence of an element is the number of single electrons

- The Atomic Orbitals are (s, p, d, f)

I.5.2. Hybridizations

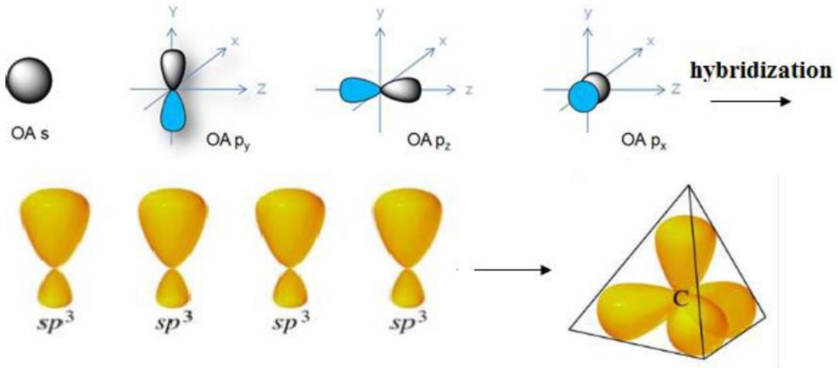
There are various types of hybridizations, we have:

I.5.2.1. sp3 hybridization Tetrahedral (tetragonal)

When the carbon atom is bonded to four other atoms the hybridization is said to be sp3 type. Here **1 s** orbital and **3 p** orbitals in the same shell of an atom combine to form four new equivalent orbitals. The arrangement is tetrahedral with a bond angle of **109.5°.**

The new orbitals formed are called **sp^3 hybrid orbitals.**

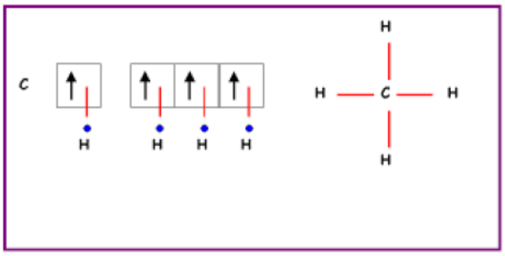
$$\mathbf{1\ S\ orbital\ +\ 3\ P\ orbitals\ \rightarrow\ 4\ sp3\ hybrid\ orbitals}$$



4 sp3 hybrid orbitals

Spatial layout

Example: carbon hybridization in the **CH$_4$** molecule the 4 bonds are identical and indistinguishable



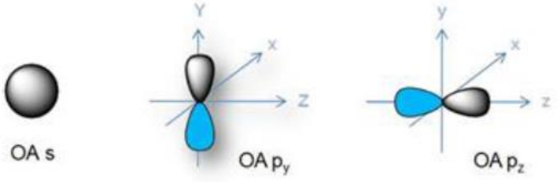
Important Points Tto Remember

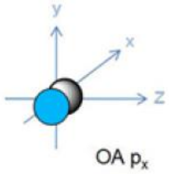
- The different types of hybridization (sp3, sp2, sp) in carbon determines the structure and reactivity of carbon compounds that are formed.
- Hybridized orbitals are formed by the mixing of orbitals where electrons are mostly in an excited state.
- The different types of hybridization influence the bond strength and structure of the molecules.

I.5.2.2. sp2 hybridization (trigonal)

sp2 hybridization is observed when one **s** and two **p** orbitals of the same shell of an atom mix to form **3** equivalent orbitals. The new orbitals formed are called **sp2** hybrid orbitals.

$$\mathbf{1\ S\ orbital\ +\ 2\ P\ orbital\ \rightarrow 3\ sp2\ hybrid\ orbitals + 1\ pure\ P\ orbital}$$





Combination of the 2s orbital and the $2p_x$ and $2p_y$ orbitals of carbon

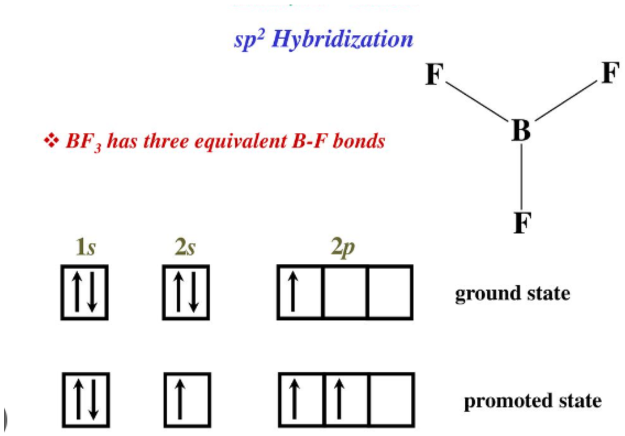
Orbital untouched
By hybridization

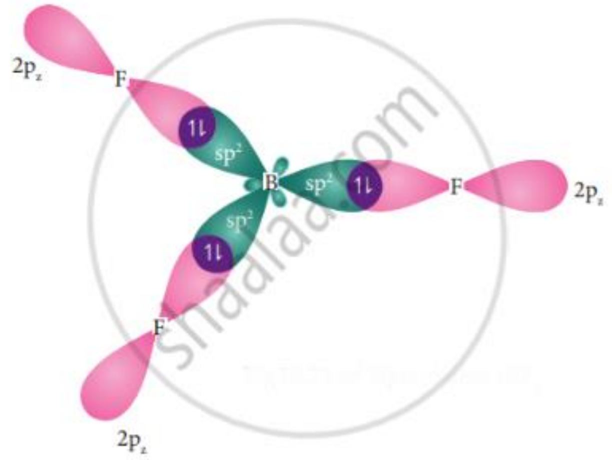
- **sp2** hybridization is also called trigonal hybridization.
- It involves the mixing of one '**s**' orbital and two '**p**' orbitals of equal energy to give a new hybrid orbital known as **sp2**.
- A mixture of s and p orbital formed in trigonal symmetry and is maintained at **120^0**.
- All three hybrid orbitals remain in one plane and make an angle of **120°** with one another. Each of the hybrid orbitals formed has a **33.33%** '**s**' character and **66.66%** '**p**' character.
- The molecules in which the central atom is linked to **3** atoms and is **sp2** hybridized have a triangular planar shape.

Examples of sp2 Hybridization

- All the compounds of Boron, i.e., BF_3 and BH_3
- All the compounds of carbon, containing a carbon-carbon double bond, Ethylene (C_2H_4)

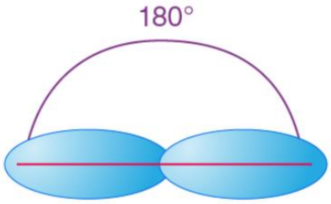
$_5$**B**: $1s^2$ s^2 $2s^2$





1.5.2.3. sp Hybridization (linear)

sp hybridization is observed when one **s** and one **p** orbital in the same main shell of an atom mix to form two new equivalent orbitals. The new orbitals formed are called **sp hybridized orbitals.** It forms linear molecules with an angle of 180°.

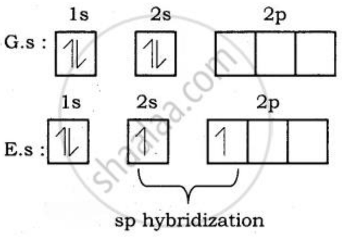


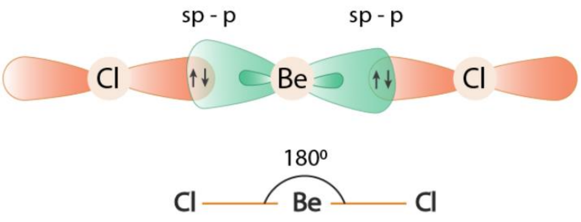
- This type of hybridization involves the mixing of one '**s**' orbital and one '**p**' orbital of equal energy to give a new hybrid orbital known as an **sp** hybridized orbital.
- The **sp** hybridization is also called **diagonal** hybridization.
- Each **sp** hybridized orbital has an equal amount of s and p characters – 50% s and 50% p characters.

Examples of sp Hybridization:

- All compounds of beryllium, like BeF_2, BeH_2, $BeCl_2$
- All compounds of a carbon-containing triple bond, like C_2H_2.

$_{4}$Be: s^2, $2s^2$



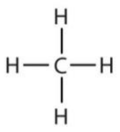


I.6. Structural Formulas

I.6.1. Complete Structural Formula

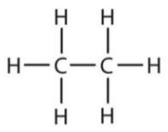
The Lewis dot structure is considered the complete structural formula. In Lewis's structure, the covalent bonds in the compound are denoted by a dash (—). This helps to emphasize the number of bonds formed by the atoms present in the molecule. Every single bond, a double bond, and a triple bond are represented by one dash, double dash, and triple dash respectively. It illustrates every single bond formed between every atom in the compound, thus called the complete structural formula.

For example, the complete structural formula for ethane, ethene and ethyne is shown as below:



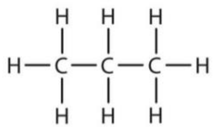
$H-\overset{H}{\underset{H}{C}}-H$

Methane



$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$

Ethane

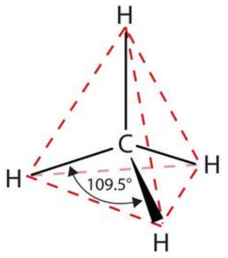


$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$

Propane

The VSEPR theory correctly predicts a tetrahedral shape for the methane molecule

Ex: The Tetrahedral Methane Molecule



1.6.2. Condensed Structural Formula

In condensed structural formulas, the bonds to each carbon are omitted, but each distinct structural unit (group) is written with subscript numbers designating multiple substituents, including the hydrogens.

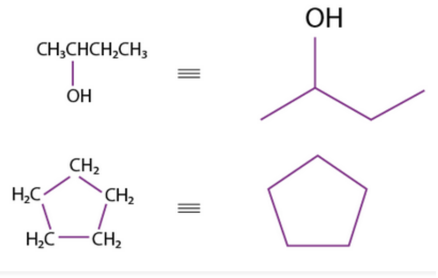
$H_2C=CH_2$ Ethene

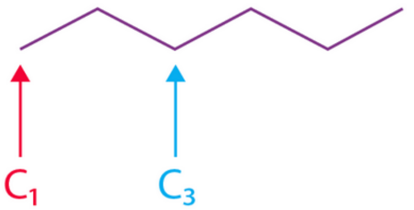
$CH_3\,CH_3$ Ethane

$HC=CH$ Ethyne

1.6.3. Bond Line Structural Formula

A bond line structural formula is another way of structural representation of organic compounds. Here, every bond is represented as a line in a zigzag manner. If not specified, every terminal is assumed to be a methyl (-CH_3) group.

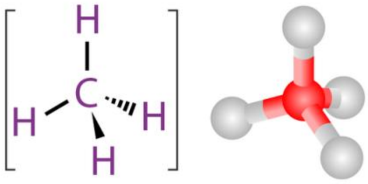




1.6.4. 3-D Representation of Organic Compounds

The organic compounds which were represented using structural formulas in the previous section are three-dimensional compounds. In order to draw the 3-D structure of an organic compound, we can use wedge-dash representation.

In wedge-dash representation, the bond that protrudes out of the plane of paper towards the viewer is denoted by a solid wedge while that project away from the viewer or into the plane of the paper is denoted by a dashed wedge and the bond in the plane of the paper is represented by a line. For example, the wedge-dash representation for methane molecule is shown as below:



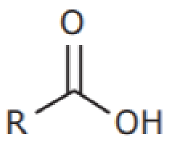
I.7. Functional Group Classification

A systematic study of chemistry or for that matter any other branch of science is not possible without arranging the subject matter in a logical manner when sufficient data has accumulated. In case of inorganic chemistry, formulation of the periodic table stimulated not only the search for missing elements but also led to the understanding of the periodic behavior. In organic chemistry, as the number of known organic compounds runs into millions, it is very difficult to study each and every compound individually. Thus, by grouping similar compounds together in a class or a family, it is easier to understand their properties, reactions etc. One way of such classification is based on the functional groups. A **functional group** can be defined as an atom or a group of atoms in a molecule which exhibits characteristic chemical properties. Such chemical properties exhibited by the functional group are more or less constant for various transformation of the functional group and do not affect the rest of the molecule. The advantage of such a classification based on functional groups is that in addition to logically systematizing the organic compounds, the properties of the compounds can be predicted just by looking at their structures, i.e., by knowing the type of functional group present.

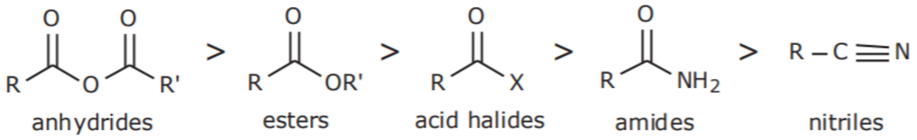
I.7.1. Functional Groups

In the IUPAC nomenclature system, organic molecules are grouped into specific classes of compounds determined by the main functional group present in the structure. A system of priorities is used to determine the main functional group, which determines the identity of the compound. All other functional groups are treated as substituents. The following order of precedence refers to functional groups containing carbon as the central atom. As a rule of thumb, the higher the oxidation state of the central carbon, the higher the priority of the functional group. Thus, carboxylic acids have higher priority than alcohols.

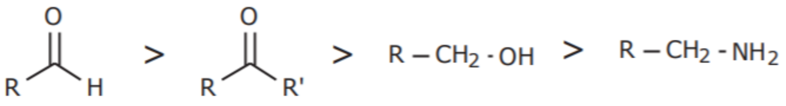
1. **Carboxylic Acids (highest priority among carbon-containing functional groups).**



2. **Carboxylic Acids derivatives**



3. **Other groups containing oxygen or nitrogen**



4. **Alkenes and Alkynes**

$R-CH=CH_2 > R-C\equiv CH$

alkenes alkynes

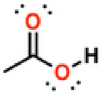
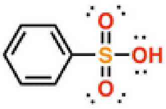
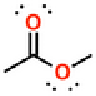
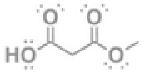
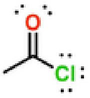
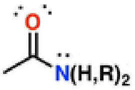
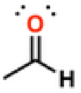
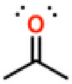
Note: substances containing double and triple bonds are called ***alkenynes.*** (notice that the name ends in *yne*). Chain numbering starts from the end closest to either group, unless they're both equidistant from the chain ends, in which case the *double bond* takes priority and is given the lower number. See examples in the textbook.

5. **Lowest priority**: These groups are usually considered substituents in the main chain.

R— > RO— > X—

alkyl groups alkoxy groups halides

I.7.2. Functional group priorities, highest to lowest

	Group	Prefix	Suffix	Example
1.	 **carboxylic acid**	carboxy-	-carboxylic acid -oic acid	ethanoic acid
2.	 **sulfonic acid**	sulfo-	-sulfonic acid	benzenesulfonic acid
3.	 **ester**	alkoxycarbonyl-  *e.g. 2-(methoxycarbonyl) acetic acid*	-oate	methyl ethanoate
4.	 **acid halide**	halocarbonyl-	-oyl halide	ethanoyl chloride
5.	 **amide**	carbamoyl- (aminocarbonyl-)	-carboxamide -amide	ethanamide
6.	—C≡N: **nitrile**	cyano-	-nitrile	ethanonitrile
7.	 **aldehyde**	formyl-	-al -carbaldehyde	ethanal
8.	 **ketone**	oxo-	-one	2-propanone
9.	 **alcohol**	hydroxy-	-ol	methanol
10.	 **thiol**	mercapto-	-thiol	methanethiol
11.	—N(H, R)$_2$ **amine**	amino-	-amine	methylamine

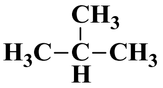
12. Arene (cyclic of arrays of (C=C)	Aryl	ene	Benzene
13. (C=C) **Alkene**	Alkenyl	-ene	Propene
14. (C ≡ C) **alkyne**	Alkynyl	-yne	Ethyne
15. (C-C) **Alkane**	Alkyl	-ane	Methane
16. (C-O-C) **Ether**	Alkoxy	-ane	Methoxymethane
17. R-X **Alkyl halide**	Halo-	-ane	Bromomethane
18. NO_2 **Nitro**	Nitro	-ane	Nitromethane

II. Nomenclature of Organic Compounds

The earliest attempts to name organic compounds were based either on their origin or on their properties. For example, citric acid was named so because of its occurrence in *citrus* fruits. The aromatic compounds were called so because of their characteristic odour (Greek: **aroma,** fragrant smell). Examples are oil of wintergreen and vanillin (a constituent of vanilla also used as a flavouring agent) which were called aromatic due to their characteristic fragrance. With the advancement and growth in the knowledge of chemistry, the number of known organic compounds has increased rapidly. Also, with the increase in the number of carbon atoms, the number of possible isomers for hydrocarbons (without any functional group) becomes very large).

Isomers are the compounds that have identical molecular formulas but differ in the ways in which the atoms are bonded to each other. For example, four carbons in a hydrocarbon having molecular formula C_4H_{10} can be arranged in the two different ways:

Straight chain $H_3C - CH_2 - CH_2 - CH_3$: Common name; normal butane or n-butane

Branched chain 
$H_3C-\overset{\overset{CH_3}{|}}{\underset{H}{C}}-CH_3$
with a common name 150 – butane.

Thus, **n-butane** and isobutene are isomers.

Having learned about the variety of functional groups, you can imagine that the nature and position of functional groups present can raise these numbers many fold. Under such a situation, it is next to impossible to learn the names randomly assigned to the compounds, especially when there is no correlation of the name to the structure of the compound.

This necessitated the need to have **a systematic nomenclature** for which the International Committee of Chemists met at Geneva in 1892.

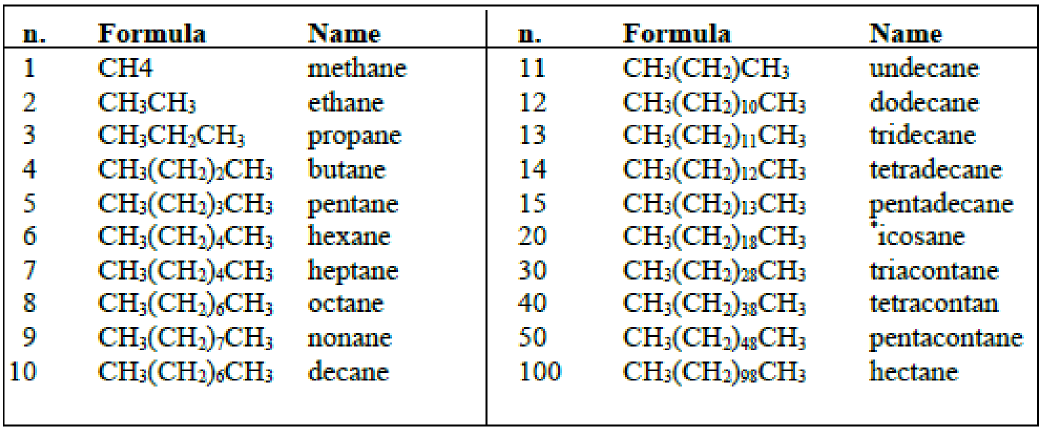
The work was carried on by the **International Union of Chemists (I.U.C.)** which gave its report in 1931, known as the I.U.C. system of nomenclature. As the nomenclature is always undergoing modifications and revisions, the latest rules which are widely accepted were recommended by the Commission on Nomenclature of Organic Chemistry of the **International Union of Pure and Applied Chemistry (I.U.P.A.C)**

Since the nomenclature of other classes of compounds is based on the nomenclature of alkanes. The IUPAC names for various alkanes having different chain lengths are given in Table below. The unbranched alkanes have their common names as normal alkanes or n-alkanes.

Compounds that differ from each other in their molecular formulas by the unit – CH2- are called members of a homologous series. Thus, the compounds listed in the following Table belong to a homologous series.

II.1. Alkane

Table: IUPAC Names of straight chain alkanes having general formula C_nH_{2n+2}

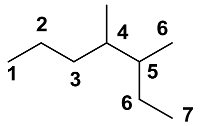


n.	Formula	Name	n.	Formula	Name
1	CH4	methane	11	$CH_3(CH_2)CH_3$	undecane
2	CH_3CH_3	ethane	12	$CH_3(CH_2)_{10}CH_3$	dodecane
3	$CH_3CH_2CH_3$	propane	13	$CH_3(CH_2)_{11}CH_3$	tridecane
4	$CH_3(CH_2)_2CH_3$	butane	14	$CH_3(CH_2)_{12}CH_3$	tetradecane
5	$CH_3(CH_2)_3CH_3$	pentane	15	$CH_3(CH_2)_{13}CH_3$	pentadecane
6	$CH_3(CH_2)_4CH_3$	hexane	20	$CH_3(CH_2)_{18}CH_3$	*icosane
7	$CH_3(CH_2)_4CH_3$	heptane	30	$CH_3(CH_2)_{28}CH_3$	triacontane
8	$CH_3(CH_2)_6CH_3$	octane	40	$CH_3(CH_2)_{38}CH_3$	tetracontan
9	$CH_3(CH_2)_7CH_3$	nonane	50	$CH_3(CH_2)_{48}CH_3$	pentacontane
10	$CH_3(CH_2)_6CH_3$	decane	100	$CH_3(CH_2)_{98}CH_3$	hectane

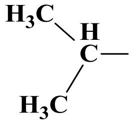
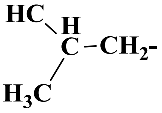
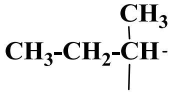
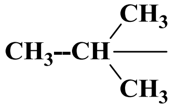
*** Prior to 1979 version of IUPAC rules, icosane was spelled as eicosane.**

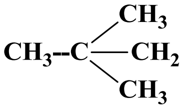
The branched chain alkanes are named by using the following steps:

1. **The longest continuous chain of carbon** atoms is taken as the parent hydrocarbon. For example, in the compound shown below, the parent hydrocarbon is heptane and not the hexane.

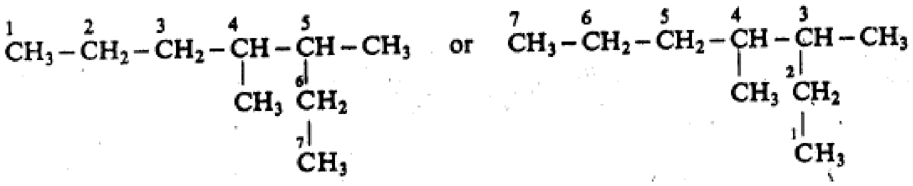


2. Identify the substituent alkyl groups attached to the parent chain. Some common alkyl groups are listed in Table below. You can locate that both the substituents in the example cited above are methyl groups.

Alkyl group	**Common name**	**IUPAC name**
CH_3	methyl	methyl
CH_3CH_2	ethyl	ethyl
$CH_3CH_2CH_2$	*n*-propyl	propyl
	Iso-propyl	1-methylethyl
$CH_3CH_2CH_2CH_2$-	*n*-butyl	butyl
	*Iso*-butyl	2-methylpropyl
 $CH_3\text{-}CH_2\text{-}\overset{CH_3}{CH}\text{-}$	*Sec*-butyl	1-methylpropyl
	*tert*-butyl	1,1-dimethylethyl

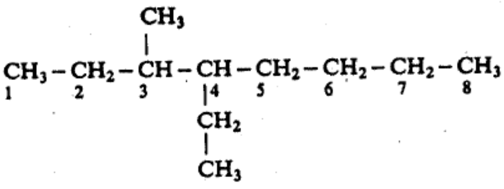
	*neo*-pentyl	2,2-dimethylpropyl

3. The parent carbon chain is then numbered in such a way that the substituents get the lowest possible numbers. The carbon atoms in the above compound can be numbered as:



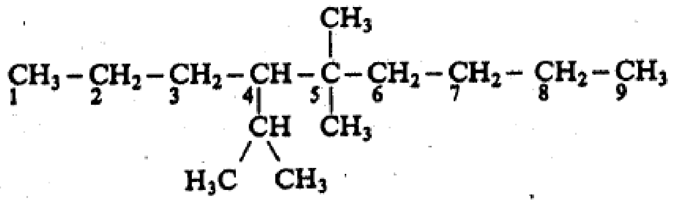
4. Perfixes *di, tri, tetra, penta* etc, are used when the substituents occur more than once. Since in the above compound the methyl substituent is occurring twice, the name is prefixed with *di* for the above compound.
5. The name of the compound is written by writing the location and name of the substituents followed by the name of the parent alkane. Thus, the above compound can be named as 3, 4-dimethylheptane. Note that a comma is used to separate the two numbers and the numbers are separated from names of groups by a hyphen. Also note that there is no blank space between the name of the last substituent and the parent alkane.
6. When more than one type of alkyl groups are present, then they are cited in the name in the alphabetical order, regardless of their location in the principal chain.

The numerical prefixes *di, tri, tetra,* etc. and hyphenated prefixes such as *sec-tert* – are not considered in determining the alphabetical order but prefixes *iso, neo, cyclo* are considered for alphabetizing. To understand it, let us consider the examples given below:



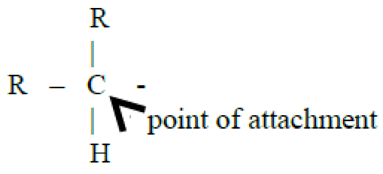
4-ethyl-3-methyloctane

7. The branched chain substituents, such as 1-methylethyl shown in step 6, are numbered starting from the carbon attached directly to the parent chain. Note that the name and numbering of branched substituent is written in brackets in order to separate it from the numbering of the main chain.



can be named as 4-isopropyl-5,5-dimethylnonane or 4-(1-methylethy1)-5, 5-dimethylnonane.

8. The alkyl substituents can be further classified as primary, secondary or tertiary. An alkyl group is called a primary alkyl group if the carbon atom at the point of attachment is bonded to only one other carbon. For example, $R-CH_2-$ is a primary alkyl group. Similarly, a secondary alkyl group has two alkyl groups bonded to the carbon atom taken as the point of attachment to the main chain. Thus, a secondary alkyl group can be written as shown below:

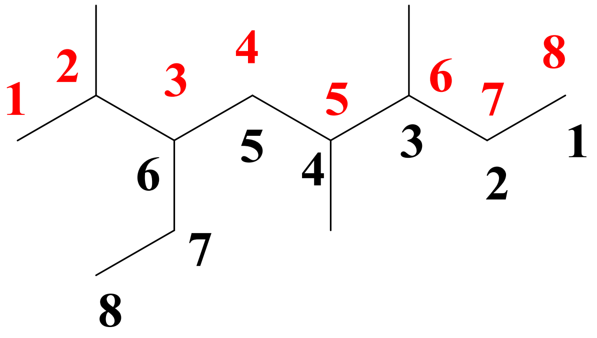


$$R-\overset{R}{\underset{H}{C}}-$$

secondary alkyl group

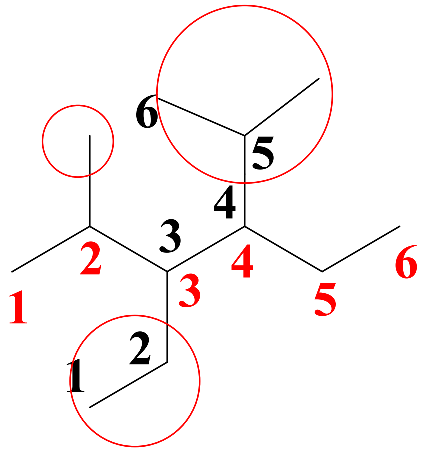
9. When more than one carbon chains of equal length are available, the numbering is done considering the following points:

(a) The principal chain should have the **greatest number of side chains**. For example, in the compound shown below:



The chain having numbering in **red color** has **four side chains** while the chain marked with numbers in **black color** has **three side chains**. So the principal chain is the one which is marked in the red color. Hence, the name is **3-ethyl-2,5,6-trimethyloctane.**

(b) The chain having the lowest number for substituents is chosen as the principal chain. In the compound shown below;



If the numbering is done as shown in **black color**, the name would have substituents at positions **3,4 and 5**. But, if the carbon chain numbered in **red color** is taken as the principal chain, then the substituents get the numbers **2, 3 and 4**, which is obviously the correct choice.

II.2. Alkenes

The suffix ***ane*** of the parent hydrocarbon is changed to ***ene*** and the functional group (a double bond in this case) is given the lowest possible number.

Their general formula: $\mathbf{C_nH_{2n}}$

Some examples are:

$CH_2{=}CH_2$
ethene
(common name: ethylene)

$CH_3CH{=}CH_2$
propene

4 3 2 1
$CH_3\ CH_2\ CH{=}CH_2$
but-l-ene

1 2 3 4 5
$CH_3 - CH = CH - CH_2 - CH_3$
pent-2-ene

II.3. Alkynes

Alkynes are unsaturated, non-cyclic hydrocarbons that have a carbon-carbon $C \equiv C$ trible bond.

Their general formula $\mathbf{C_nH_{2n-2}}$

The ending ***ane*** of the corresponding alkanes is replaced by the ending ***yne***. For the first compound in this series H−C≡C−H, the trivial name acetylene is used instead of ethyne.

When both double and triple bonds are present, then the double bond gets the lower number. Thus, for the compound show below.

1 2 3 4 5
$CH_2 = CH - CH_2 - C \equiv CH$

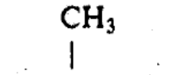
The correct name is pent – l-ene-4-yne

II.4. Alkyl halides

The alkyl halides are the halogen derivatives of alkanes. The halogens present are usually F, Cl, Br and 1. The common names are arrived at by writing the name of alkyl group followed by the name of the halide. Examples are shown below:

$CH_3CH_2CH_2CH_2Cl$

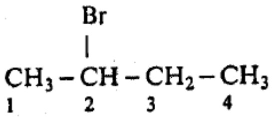
n-butyl chloride



$$CH_3-\overset{\overset{\large CH_3}{|}}{CH}-CH_2Br$$

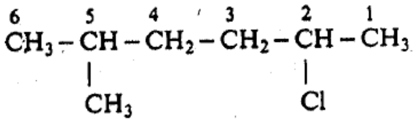
isobutyl bromide

In the IUPAC system of nomenclature, prefix *halo-* (i.e., *fluoro, chloro-, bromo or iodo-*) is used to give the lowest number to the carbon atom to which the halogen is attached. For example, some halogen compounds are named below:



$$\underset{1}{CH_3}-\underset{2}{\overset{\overset{\large Br}{|}}{CH}}-\underset{3}{CH_2}-\underset{4}{CH_3}$$

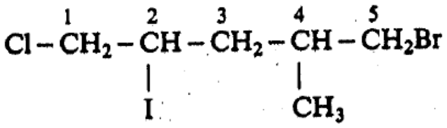
2-bromobutane



$$\overset{6}{CH_3}-\underset{\underset{\large CH_3}{|}}{\overset{5}{CH}}-\overset{4}{CH_2}-\overset{3}{CH_2}-\underset{\underset{\large Cl}{|}}{\overset{2}{CH}}-\overset{1}{CH_3}$$

2-chloro-5-methylhexane

When more than one type of halogen atoms are present, their names are arranged in alphabetical order as shown in the next example,



$$Cl-\overset{1}{CH_2}-\underset{\underset{\large I}{|}}{\overset{2}{CH}}-\overset{3}{CH_2}-\underset{\underset{\large CH_3}{|}}{\overset{4}{CH}}-\overset{5}{CH_2}Br$$

5-bromo-1-chloro-2-iodo-4-methylpentane

II.5. Alcohols

The name for an alcohol uses the ***-ol*** suffix with the name of the parent alkane, together with a number to give the location of the hydroxyl group.

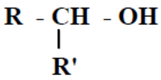
-Name the longest carbon chain that contains the carbon atom bearing the **—OH** group. Drop the final **-e** from the alkane name, and add the suffix **-ol.**

- Number the longest carbon chain starting at the end nearest the —OH group, and use the appropriate number, if necessary, to indicate the position of the **—OH** group.
- Name the substituents, and give their numbers as for an alkane or alkene.
- We distinguish:

Primary alcohol

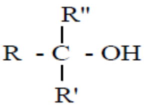
$R-CH_2OH$

Secondary alcohols



$$R-\underset{\underset{\displaystyle R'}{|}}{CH}-OH$$

Tertiary alcohols



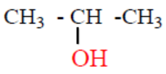
$$R-\overset{\overset{\displaystyle R''}{|}}{\underset{\underset{\displaystyle R'}{|}}{C}}-OH$$

Example

Ethanol

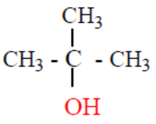
CH_3-CH_2-OH

Propan-2-ol



$$CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_3$$

2-methylpropan-2-ol



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_3$$

II.6. Ethers

The common names for ethers are derived by naming the two alkyl groups in alphabetical order followed by the word ether. This is illustrated in the examples given below:

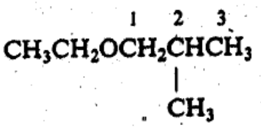
CH_3OCH_3
dimethyl ether

$CH_3OCH_2CH_3$
ethyl methyl ether

In the IUPAC system, ethers are named as alkoxyalkanes. The larger of the two alkyl groups is chosen as the hydrocarbon chain. For example, the compound,

$$CH_3O\overset{1}{CH_2}\,\overset{2}{CH_3}$$

is named as **1-methoxyethane** and not as **ethoxymethane.** Similarly, the compound,

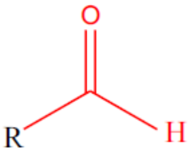


$$CH_3CH_2O\overset{1}{CH_2}\overset{2}{\underset{\underset{\displaystyle CH_3}{|}}{C}H}\overset{3}{CH_3}$$

has the name **1-ethoxy-2-methylpropane.**

II.7. Aldehydes

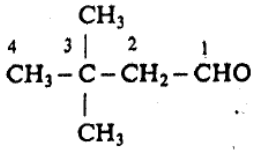
Aldehydes are carbonyl compounds. They have the characteristic group:



aldehydes

Note: Functional carbon is trigonal.

In the IUPAC system of nomenclature, they are named as **alkanals**. The simplest aldehyde is **methanal.** Since the aldehyde group – **CHO**) is always at the end of the chain, it is always numbered as C– 1 in the chain, but this number is not specified in the name, i.e. the compound.

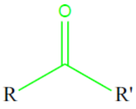


$$\overset{4}{CH_3}-\underset{CH_3}{\overset{CH_3}{\overset{3|}{C}}}-\overset{2}{CH_2}-\overset{1}{CHO}$$

is named as **3, 3-dimethylbutanal**.

II.8. Ketones

ketones are carbonyl compounds. They have the characteristic group:

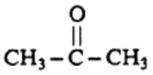


Ketone

The name of a ketone derives from that of the alkane with the same carbon skeleton, by replacing the final **e** by the **one** ending preceded by the position of the carbonyl group in the main chain. The functional carbon cannot be at the end of the chain.

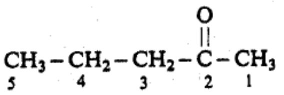
Acetone: propanone is used as a solvent (nail polish remover).

As usual, the position of the carbonyl group is indicated by the lowest possible number. A few examples are



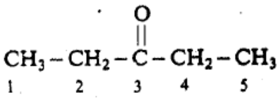
$$CH_3-\overset{\overset{O}{||}}{C}-CH_3$$

propanone



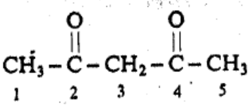
$$\underset{5}{CH_3}-\underset{4}{CH_2}-\underset{3}{CH_2}-\underset{2}{\overset{\overset{O}{||}}{C}}-\underset{1}{CH_3}$$

pentan-2-one



$$\underset{1}{CH_3}-\underset{2}{CH_2}-\underset{3}{\overset{\overset{O}{||}}{C}}-\underset{4}{CH_2}-\underset{5}{CH_3}$$

pentan-3-one



$$\underset{1}{CH_3}-\underset{2}{\overset{\overset{O}{||}}{C}}-\underset{3}{CH_2}-\underset{4}{\overset{\overset{O}{||}}{C}}-\underset{5}{CH_3}$$

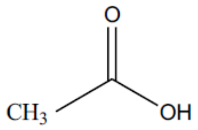
pentan-2, 4-dione

II.9. Carboxylic acids

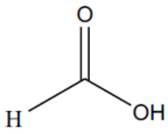
Carboxylic acids have in common the characteristic group: **R – COOH**

- The functional carbon is trigonal and it is bonded to two oxygen atoms.

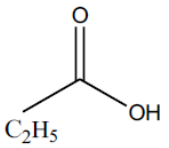
the IUPAC names are derived by replacing ***e*** ending of the alkane by ***oic acid.*** As for aldehydes, the carboxyl carbon is numbered **1**. However, in case of the dicarboxylic acids, the final ***e*** of the hydrocarbon is not dropped.



Ethanoic acid
Acetic acid

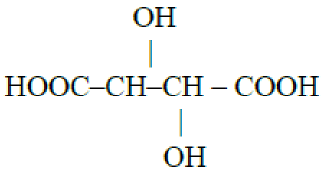


Methanic acid
Formic acid



Propanoic acid

Ex: dicarboxylic acids

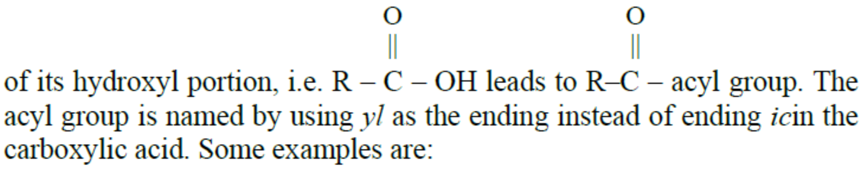


$$\begin{array}{c} \quad\ \ \mathrm{OH} \\ \quad\ \ | \\ \mathrm{HOOC{-}CH{-}CH-COOH} \\ \qquad\qquad | \\ \qquad\qquad \mathrm{OH} \end{array}$$

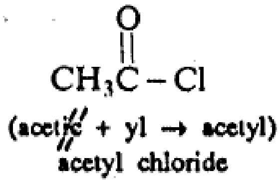
2,3-dihydroxybutanedioic acid (Tartaric acid)

II.10. Acyl halides

Acyl halides are commonly named by placing the names of the halide after the name of the acyl group. The acyl group is obtained from the carboxylic acid by removal

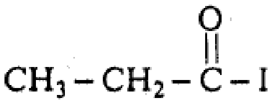


of its hydroxyl portion, i.e. $R - \overset{\overset{O}{||}}{C} - OH$ leads to $R{-}\overset{\overset{O}{||}}{C} -$ acyl group. The acyl group is named by using *yl* as the ending instead of ending *ic*in the carboxylic acid. Some examples are:



$CH_3\overset{\overset{O}{||}}{C} - Cl$

(acet~~ic~~ + yl → acetyl)
acetyl chloride

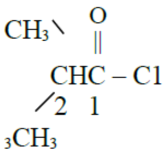


$CH_3 - CH_2 - \overset{\overset{O}{||}}{C} - I$

propanoyl iodide

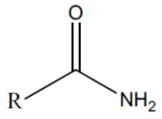
IUPAC names for acyl groups use the ending ***oyl*** instead offending *e* in the name of the corresponding hydrocarbon. The acetyl chloride has the IUPAC name ethanoyl chloride.

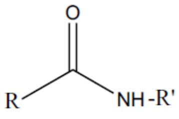
Another example: is named as 2-methylpropanoyl chloride

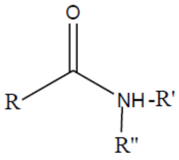


II.11. Amides

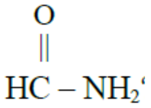
The common names for acid amides are derived by replacing the suffix ***ic*** or ***oic*** of the carboxylic acid by the suffix amide. A distinction is made between primary amides, secondary amides and tertiary amides.


Primary amide:


Secondary amide:

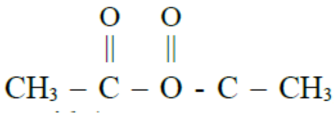

Tertiary amide:

The IUPAC name for an amide is derived by appending the suffix amide to the parent hydrocarbon with the final e dropped. Thus, acetamide has the IUPAC name ethanamide. Having done this, can you give common and IUPAC names for


$\overset{O}{\overset{\|}{HC}} - NH_2$‘ These are formamide and methanamide, respectively.

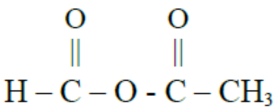
II.12. Acid anhydrides

A symmetrical anhydride is named as anhydride of the parent acid. Thus,


$$CH_3 - \overset{O}{\overset{\|}{C}} - \overset{O}{\overset{\|}{O}} - C - CH_3$$

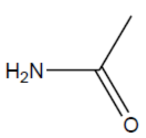
The anhydride which is obtained from ethanic acid (common name: acetic acid) is commonly known as acetic anhydride. The IUPAC name for this anhydride is ethanoic anhydride.

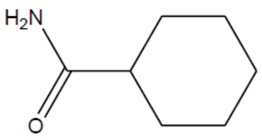
For mixed anhydrides, both the parent carboxylic acids are cited in alphabetical order, followed by the word anhydride, as illustrated below:


$$H - \overset{O}{\overset{\|}{C}} - O - \overset{O}{\overset{\|}{C}} - CH_3$$

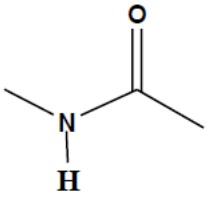
ethanoic methanoic anhydride
(common name: acetic formic anhydride)

Primary amide:


Ethanamide

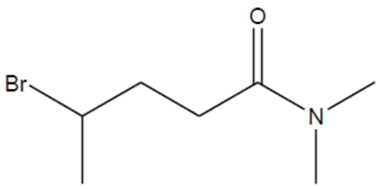

cyclohexanecarboxamide

Secondary amide:



***N*-methylethanamide**

Tertiary amide:

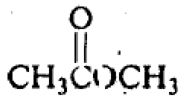


4-bromo-N,N-dimethylpentanamide

II.13. Esthers

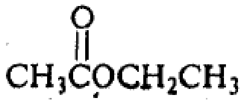
General formula $\mathbf{C_nH_{2n}O_2}$

The name of **the ester** derives from that of the alkane of the same carbon skeleton by replacing the final **e** by the ending **-oate**, and its position only at the end of the chain



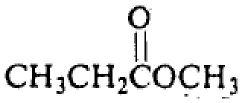
$CH_3\overset{\overset{O}{||}}{C}OCH_3$

methyl ethanoate



$CH_3\overset{\overset{O}{||}}{C}OCH_2CH_3$

ethyl ethanoate



$CH_3CH_2\overset{\overset{O}{||}}{C}OCH_3$

methylpropanoate

Esters are chemical species that often have a pleasant smell (rose, jasmine, lavender, etc.). They are sometimes the source of natural fruity flavors and are very frequently synthesized for use as food flavorings.

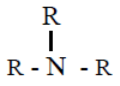
II.14. Amines

There are two systems of naming amines. One method names them as alkylamines and the other calls them as alkanamines. The alkanamine naming system was introduced by Chemical Abstracts and is easier to use as compared to the earlier IUPAC system of alkylamine names. The latest revision of IUPAC rules accepts both systems and examples below are named in both ways.

A distinction is made between primary amines, secondary amines and tertiary amines.

$R-NH-R$

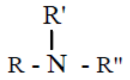
Symmetric secondary amines



$$\begin{array}{c} R \\ | \\ R-N-R \end{array}$$

Symmetric tertiary amines

$R-NH-R'$

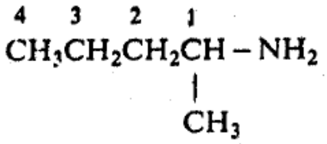


$$\begin{array}{c} R' \\ | \\ R-N-R'' \end{array}$$

Bonding, Functional Group Classification and Nomenclature

CH_3NH_2

methylamine
or methanamine



$$\overset{4}{CH_3}\overset{3}{CH_2}\overset{2}{CH_2}\underset{\underset{CH_3}{|}}{\overset{1}{CH}}-NH_2$$

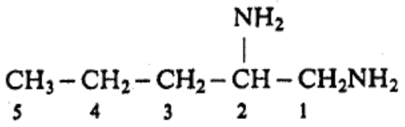
1-methylbutylamine
or 2-pentanamine

(Note that the numbering starts at the carbon and not at the nitrogen of the amine part).

Primary diamines are named by using the suffix diamine after the name of the hydrocarbon.

$$H_2N-\overset{1}{CH_2}-\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{4}{CH_2}-NH_2$$

1,4-butanediamine



$$\underset{5}{CH_3}-\underset{4}{CH_2}-\underset{3}{CH_2}-\underset{2}{\overset{\overset{NH_2}{|}}{CH}}-\underset{1}{CH_2}NH_2$$

1,2-pentanediamine

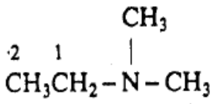
For the secondary and the tertiary amines, the longest alkyl group present is considered as the parent chain. The remaining alkyl groups are named as substituents attached to the nitrogen and a prefix N- is used with the name of the alkyl group.

$H_3C-NH-CH_3$

N-methylmethanamine
(common name : dimethylamine)

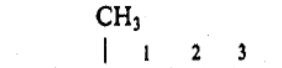
$$CH_3NH-\overset{1}{CH_2}\overset{2}{CH_3}$$

N-methylethanamine
(common name : ethylmethylamine)



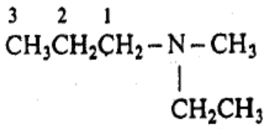
$$\overset{2}{CH_3}\overset{1}{CH_2}-\overset{\overset{CH_3}{|}}{N}-CH_3$$

N,N-dimethylethanamine
(common name : ethyldimethylamine)



$$CH_3CH_2CH_2-\overset{\overset{CH_3}{|}}{N}-\overset{1}{CH_2}\overset{2}{CH_2}\overset{3}{CH_3}$$

N-methyl-*N*-propylpropanamine
(common name : methyldipropylamine)



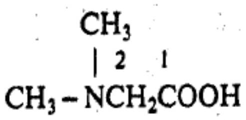
$$\overset{3}{CH_3}\overset{2}{CH_2}\overset{1}{CH_2}-\underset{\underset{CH_2CH_3}{|}}{N}-CH_3$$

N-ethyl-*N*-methylpropanamine
(common name : ethylmethylpropylamine)

When used as a substituent, the – NH2 group is named as amino and is prefixed with a number indicating the carbon atom to which it is attached.

$$H_2N-\overset{2}{CH_2}-\overset{1}{CH_2}OH$$

2-aminoethanol



$$CH_3-\overset{\overset{CH_3}{|}}{N}\overset{2}{CH_2}\overset{1}{COOH}$$

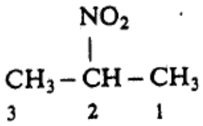
N,N-dimethylaminoethanoic acid

Nitro compounds: The nitro compounds are named as nitroderivatives of the corresponding hydrocarbons.

Examples:

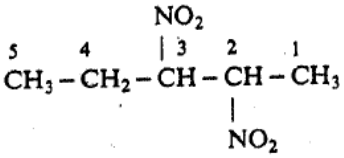
CH_3NO_2

nitromethane



$$\overset{3}{C}H_3-\overset{NO_2}{\overset{|}{\underset{2}{C}H}}-\overset{1}{C}H_3$$

2-nitropropane



$$\overset{5}{C}H_3-\overset{4}{C}H_2-\overset{NO_2}{\overset{|}{\overset{3}{C}H}}-\underset{NO_2}{\underset{|}{\overset{2}{C}H}}-\overset{1}{C}H_3$$

2,3-dinitropentane

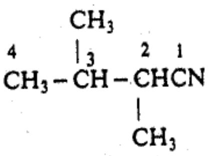
II.15. Nitriles

Nitriles are named in the IUPAC system by using the suffix – nitrile to the name of the hydrocarbon corresponding to the longest carbon chain. Note that here the carbon of the nitrile group is included in the numbering of carbon chain and is numbered as position 1. Some examples are given below:

$\overset{2}{C}H_3\overset{1}{C}N$

ethanenitrile

(common name : acetonitrile)



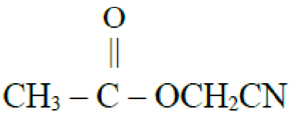
$$\overset{4}{C}H_3-\overset{CH_3}{\overset{|}{\overset{3}{C}H}}-\underset{CH_3}{\underset{|}{\overset{2}{C}H}}\overset{1}{C}N$$

2,3-dimethylbutanenitrile

$N\overset{4}{C}\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}N$

butanedinitrile

When named as a substituent, the – CH group is called a cyano group. For example, the compound.



$$CH_3-\overset{O}{\overset{\|}{C}}-OCH_2CN$$

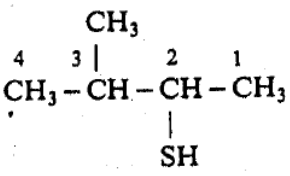
is named as cyanomethyl ethanoate.

II.16. Thiols

In naming thiols, an ending *thiol* is used as a suffix to the name of the corresponding hydrocarbon; for example,

CH_3CH_2SH

ethanethiol

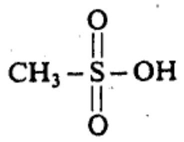


$$\overset{4}{C}H_3-\overset{CH_3}{\overset{|}{\overset{3}{C}H}}-\underset{SH}{\underset{|}{\overset{2}{C}H}}-\overset{1}{C}H_3$$

3-methyl-2-butanethiol

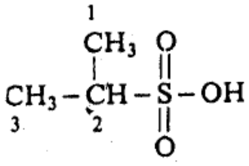
II.17. Sulphonic acids

The names of sulphonic acids use the suffix sulphonic acid with the name of the corresponding hydrocarbon.



$$CH_3-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$$

methanesulphonic acid



$$\underset{3}{CH_3}-\underset{2}{\overset{\overset{1}{CH_3}}{\overset{|}{C}}H}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$$

2-propanesulphonic acid

II.18. Some Examples with Multiple Functional Groups

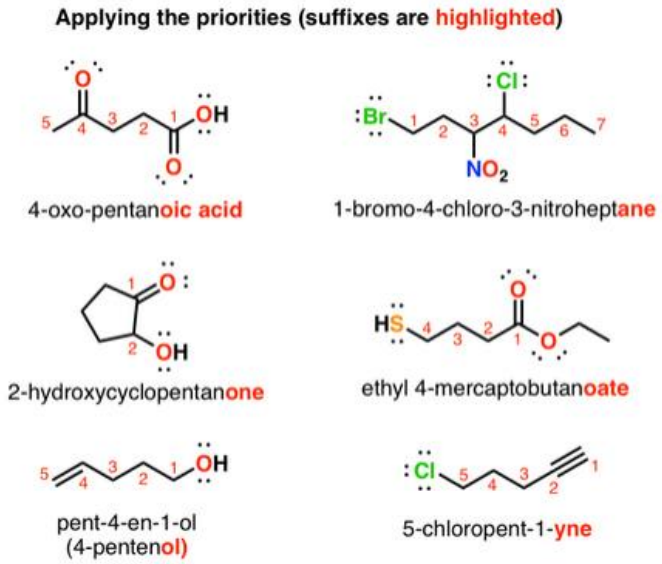
Till now, you have studied about the nomenclature of monofunctional compounds, i.e. the compounds which contain only one functional group. In polyfuctional compounds were more than one functional groups are present, one group is identified as the principal functional group and this principal functional group is used as a suffix in the name of the compound. The priorities for seletion of principal functional group are given below in the order of decreasing precedence. The order is carboxylic acid, sulphonic acid, ester, acid anhydride, acyl halide, amide, nitrile, aldehyde, ketone, alcohol, thiol, amine, alkyne, alkene, ethers, halides, nitro.

The order of priority for various functional groups is decided by considering the following points:

- **(i)** Functional groups that have an IUPAC suffix and terminate a carbon chain, have a highest priority, e.g. carboxylic acids and their derivatives.
- **(ii)** Next are the groups that have a suffix and can be located at any position in the molecule, e.g. hydroxyl and amino groups.

(iii) Groups having no suffix and which are named as substituents, are given the lowest priority, Example being the halogens.

Here are some examples of applying the order of functional group priorities to solve nomenclature problems. The highest ranked functional group becomes the suffix – it's highlighted in red.



Applying the priorities (suffixes are highlighted)

4-oxo-pentanoic acid

1-bromo-4-chloro-3-nitroheptane

2-hydroxycyclopentanone

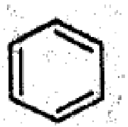
ethyl 4-mercaptobutanoate

pent-4-en-1-ol
(4-pentenol)

5-chloropent-1-yne

(a) Compounds Containing One Aromatic Ring

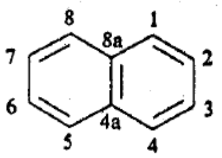
This class includes benzene and its derivatives. The derivatives of benzene include the compounds which can have any of the functional groups discussed before attached to the benzene ring.



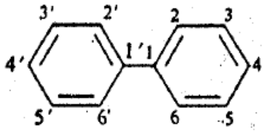
benzene

(b) Compounds Containing Two Aromatic Rings

Examples being naphthalene and biphenyl.



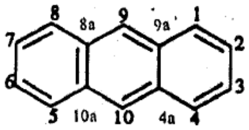
naphthalene



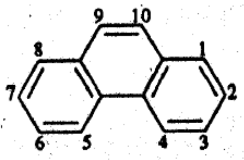
biphenyl

(c) Compounds Having More Than Two Aromatic Rings

Examples are:



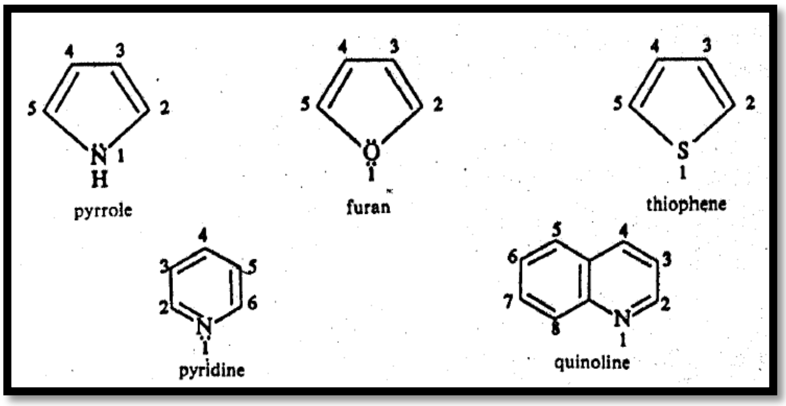
anthracene



phenanthrene

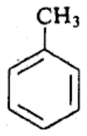
(d) Heterocyclic Compounds

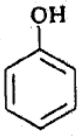
Aromatic compounds containing heteroatoms such as O, N or S in the aromatic ring are called heterocyclic compounds. Some heterocyclic compounds are shown below:

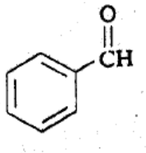


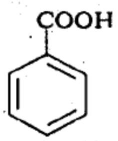
(a) Benzene and its Derivatives

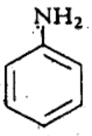
A number of monosubstituted benzene derivatives are known by their special names. These names are in common use for long and hence are approved by IUPAC. Some examples of these compounds are given below along with their common and IUPAC names (in brackets).

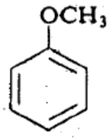

toluene
(methylbenzene)


phenol
(benzenol)

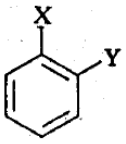

benzaldehyde
(benzenecarbaldehyde)

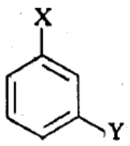

benzoic acid
(benzenecarboxylic acid)

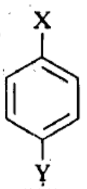

aniline
(benzenamine)


anisole
(methoxybenzene)

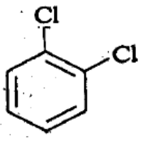
For disubstituted benzene derivatives, the following three arrangements of the substituents are possible.

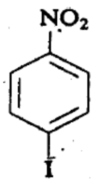

ortho-


meta-

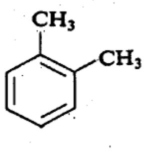

para-

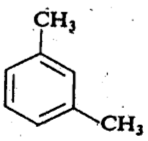
These arrangements are named using the Greek prefixes *ortho-*, *meta* and *para* which are abbreviated as *o-*, *m-* and *p-*. The substituents are then named in the alphabetical order. This is illustrated in the examples below:

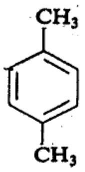

ortho-dichlorobenzene
or *o*-dichlorobenzene


p-iodonitrobenzene

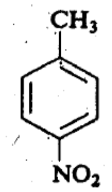
Dimethyl derivatives of benzene are known as xylenes. The three xylenes are;


o-xylene
(1,2-dimethylbenzene)

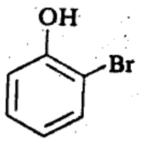

m-xylene
(1,3-dimethylbenzene)


p-xylene
(1,4-dimethylbenzene)

When one substituent is such that it corresponds to the monosubstituted benzene that has a special name, then this substituent is called the principal functionality and the compound is named as a derivative of that parent functionality. For example,

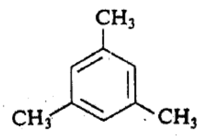


p-nitrotoluene

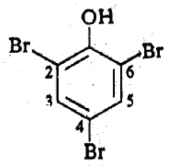


o-bromophenol

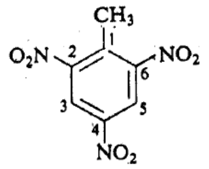
The polysubstituted benzenes are named by identifying the principal functions and then numbering is done such as to keep the principal function as number. The other substituents are then given the lowest possible numbers. This is illustrated in the following examples.



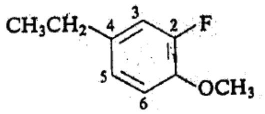
1,3,5-trimethylbenzene
(common name : mesitylene)



2,4,6-tribromophenol



2,4,6-trinitrotoluene (TNT)



4-ethyl-2-fluoroanisole

III. Introduction to Structural Chemistry

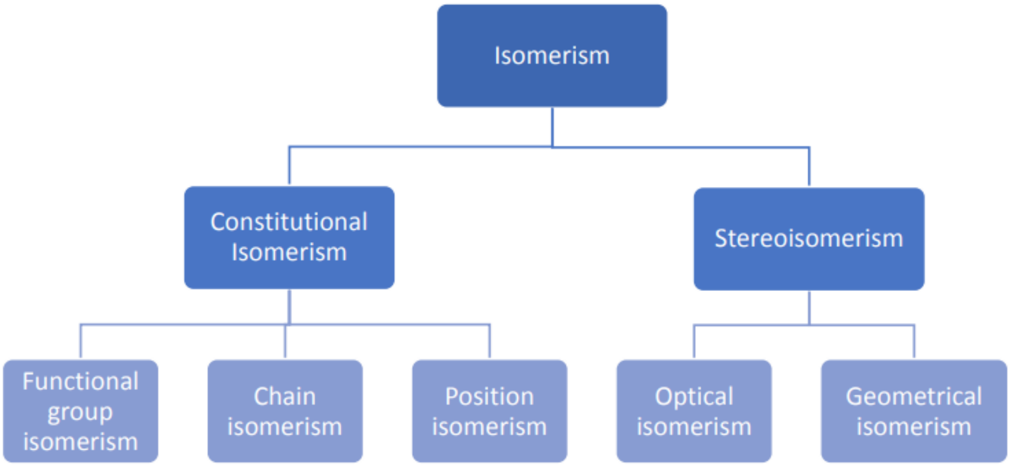
III.1. Notions of stereo-isomerism

Isomers are the compounds with the same qualitative and quantitative composition of elements; therefore, their relative molecular weights and general formulas are identical, but their structures such as sequence of bonding and or arrangement of the atoms or groups in the space are different.

This variation of the structures i.e., different structural formulae or three-dimensional arrangement of atoms can lead to possess different physical and chemical properties and hence these compounds behave as different compounds with same molecular formular.

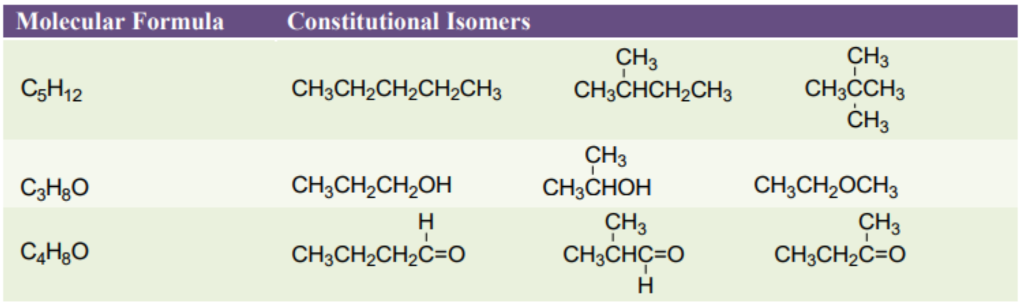
The isomers can be subdivided into two main categories that are constitutional isomers and stereoisomers. Constitutional isomers can be different in different ways of connectivity and stereoisomers are also can have geometrical isomers and optical isomers (enantioisomerism). Other category of isomers named as conformational isomers which are formed due to rotation of single bonds. As those are not always separable and show some differences, it is not discussed under the normal isomerism.

The following flow chart show the different isomers categories



Isomers that differ from the order in which the constituent atoms are connected to each other are called constitutional isomers. Some examples for constitutional isomers are given in the table 1.

Table - 1



Molecular Formula	Constitutional Isomers		
C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	$CH_3\overset{CH_3}{\overset{\vert}{C}}HCH_2CH_3$	$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_3$
C_3H_8O	$CH_3CH_2CH_2OH$	$CH_3\overset{CH_3}{\overset{\vert}{C}}HOH$	$CH_3CH_2OCH_3$
C_4H_8O	$CH_3CH_2CH_2\overset{H}{\overset{\vert}{C}}{=}O$	$CH_3\overset{CH_3}{\overset{\vert}{C}}H\underset{H}{C}{=}O$	$CH_3CH_2\overset{CH_3}{\overset{\vert}{C}}{=}O$

Constitutional isomers (structural isomers) can be different in their chain structures, functional groups due to different connectivity of atoms within the molecule. Different structural isomers are assigned different IUPAC names. Therefore, constitutional isomers can be subcategorized into Chain isomers, position isomers and functional group isomers.

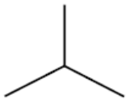
III.1.1. Chain isomerism or Skeletal

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 chain isomerism.

The sequence of atoms on the carbon skeleton is different: have the same molecular formula, may be different and are more or less branched to give isomers with different physical properties.

Ex : C_4H_{10} represents two compounds

Butane, B.P = -0.5°C

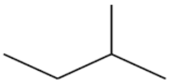


Isobutane B., P. = -10°C

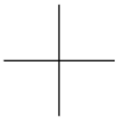
It should be mentioned that the isomer which has the most branched structure will have the lowest boiling point.

Ex : C_5H_{12} represents three compounds

Pentane, B.P = 35°C



Isopentane B.P = 25°C



Neopentane, B.P = 9°C

Also, Skeletal isomerism lies between rings and aliphatic (acyclic) alkenes.

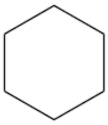
Example: C_6H_{12},

DoU = 1 (a double bond or a ring).

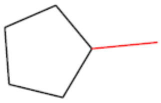
Degrees of Unsaturation (DoU)

$$\mathbf{DoU} = \frac{2C + 2 - N - X - H}{2}$$

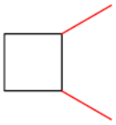
- **C**: is the number of carbons
- **N**: is the number of nitrogens
- **X** : is the number of halogens (F, Cl, Br, I)
- **H** : is the number of hydrogens



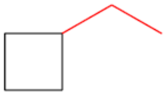
cyclohexane



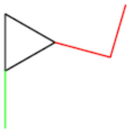
methyl cyclopentane



1,2-dimethylcyclobutane

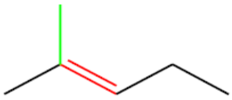


1-ethylcyclobutane



1-ethyl-2-methyl cyclopropane

hex-2-ene

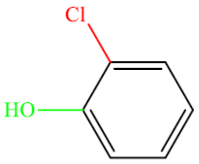


2-methylpent-2-ene

III. 1. 2 Positional isomerism

Compounds having same molecular formula but the position of functional group, multiple bond or branches along the same chain length of carbon atoms varies.

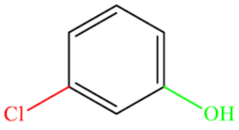
Ex 1 : C_6H_5ClOH, I=4.



B. P = 195°C ,P.F = 9.3°C

Ortho chlorophenol

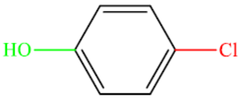
2-chlorophenol



B.P = 214°C, P.F = 33°C

meta chlorophenol

2-chlorophenol



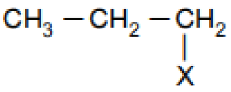
B.P = 219°C P.F = 43.5°C

para chlorophenol

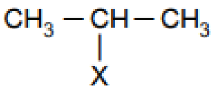
3-chlorophenol

Ex 2 : C_3H_7X

E.g. (i) Molecular formula; C_3H_7X(X=halogen, NH_2, OH or OR)



$$CH_3-CH_2-\underset{\underset{X}{|}}{CH_2}$$

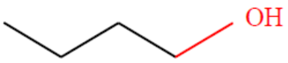


$$CH_3-\underset{\underset{X}{|}}{CH}-CH_3$$

III.1.3. Functional Group Isomerism

When isomers have the same molecular formula but different functional groups, these compounds are called functional group isomers. The following pairs of families show this isomerism.

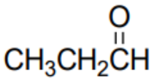
Ex : $C_4H_{10}O$



butanol

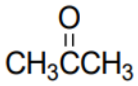
1-methoxypropane

Ex : C_3H_6O



$$CH_3CH_2\overset{\overset{O}{||}}{C}H$$

propanal



$$CH_3\overset{\overset{O}{||}}{C}CH_3$$

propanone

III.2. Stereoisomerism

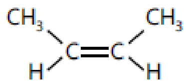
III.2.1. Geometry isomerism

A C=C double bond consist of a σ-bond and a π-bond. Due to the π bond the two carbon atoms cannot freely rotate about the σ-bond. Both alkene carbon atoms and the four atoms attached to them are all in one plane. For geometrical isomers to exist, the two groups attached to each carbon atom of the double bond should not be identical. In such an instance it is possible to have two compounds which differ from each other in the spatial arrangements of the groups joined to the two carbon atoms. These two compounds cannot be superimposed on each other and cannot interconvert by rotation around carbon-carbon bond axis (due to the π-bond). Such compounds are known as geometric isomers.

III.2.1.1. Types of geometrical isomerism: There are 3 types of geometrical isomerism on the basis of groups attached to double bond or the site of restricted rotation. They are mentioned below:

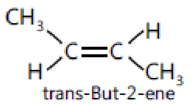
III.2.1.1.1. Cis–Trans Isomers

This kind of isomerism is used when there is at least a common group on both sides of the double bond or the site of restricted rotation (especially cycloalkane)



cis-But-2-ene

(I)

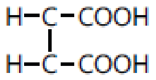


trans-But-2-ene

(II)

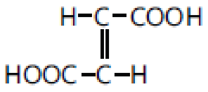
The isomer (I) in which similar groups or atoms lie on the same side of the double bond is called cis–isomer, whereas the isomer (II) in which the similar atoms or groups lie on the opposite side of the double bond is called the trans–isomer.

(I)



$$\begin{array}{l} H-C-COOH \\ \quad\ \| \\ H-C-COOH \end{array}$$

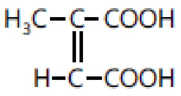
Maleric acid (cis)



$$\begin{array}{r} H-C-COOH \\ \| \qquad\ \\ HOOC-C-H \qquad \end{array}$$

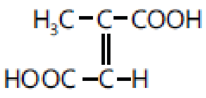
Fumatic acid (trans)

(II)



$$\begin{array}{l} H_3C-C-COOH \\ \qquad\ \| \\ \quad\ H-C-COOH \end{array}$$

Crotonic acid (cis-isomer)



$$\begin{array}{r} H_3C-C-COOH \\ \| \qquad\ \\ HOOC-C-H \qquad \end{array}$$

Mesaconic acid (tran-isomer)

III.2.1.1.1. Properties of cis–trans isomer

(i) Stability: Cis < Trans

Cis forms is less stable then trans because of the mutual repulsion between the same group.

(ii) Dipole moment: Asymmetrical trans molecule has zero dipole moment, even if trans molecule is not symmetrical than its dipole moment is less than that of the cis isomer.

$$\mu(\text{Sym trans})=0$$

$$(\text{unsym trans})\ \mu < \text{cis isomer}$$

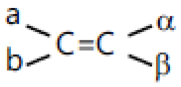
(iii) Polarity: Cis > Trans

(iv) Solubility: Soluble in a polar solvent. Cis > Trans

(v) Boiling point: Cis >Trans (due to high polarity).

(vi) Melting point: Cis < Trans.

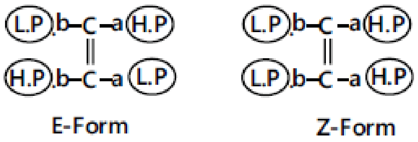
III.2.1.1.2. E–Z Isomerism



A better system E–Z, is applicable for those type of compounds which cannot be express by cis trans nomenclature.

E → **Entgegen** (opposite) **Z** → **Zusamann** (same)

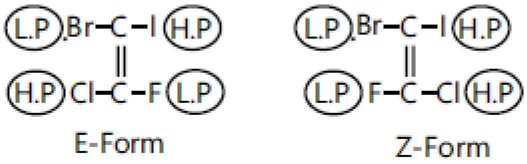
E–form: When two same priority groups present on the opposite side of the double bonded is known **E–form** and when the same priority group present on same side of the double bond is called Z–form.



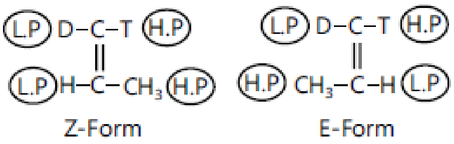
L.P=Low Priority group or atom
H.P.= High Priority group or atom

Priority rule: Chann, ingold & prelong proposed a sequence rule:

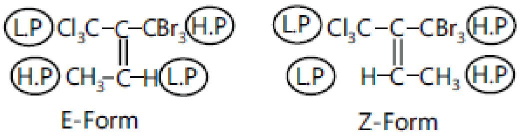
Rule 1: When an atom or groups of atoms which are directly attached to the stereo genic center have a higher atomic number, they will have higher priority. For example

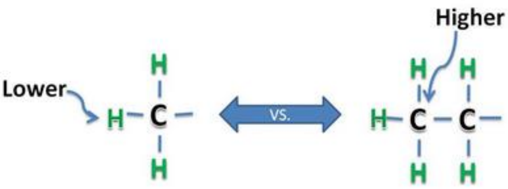


Rule 2: When the atomic number will be same, then higher atomic weight or group of atom have higher priority.

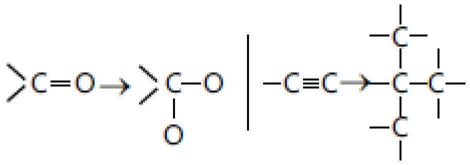


Rule 3: When both atomic number and atomic weight are the same, then priority will be decided by the next joining atom.



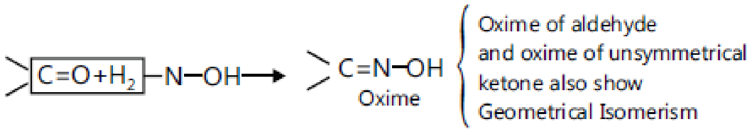


Rule 4: If multiple bonded group attach to the double bonded carbon, then they are considered in the following manner.



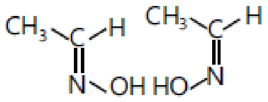
III.2.1.1.3. Syn–Anti Isomerism

Use of the terms "***syn***" and "***anti***" to describe the geometry about double bonds is no longer encouraged, but you'll still come across it, particularly in older articles. ***Syn*** and ***anti*** are identical to **Z**(zusammen) and **E**(entgegen) and were often used to describe the geometry about **carbon-nitrogen** double bonds. In such cases, the lone **pair of electrons** is given the **lowest priority** and the sequence rule applied as usual. Again, the key point is that the lone pair has a lower priority than any atom.



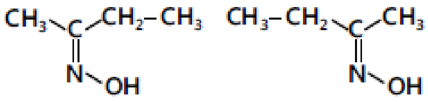
Oxime of aldehyde and oxime of unsymmetrical ketone also show Geometrical Isomerism

Aldoximes



Syn form Anti form

When the –OH group and H atom is on the same side of the double of C and N, then it is the ***syn*** form otherwise ***anti*** form

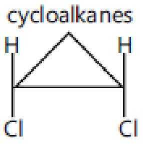


Syn form **Anti form**

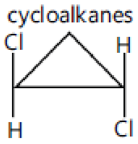
In unsymmetrical Ketoxime, if –OH and the alphabetically alkyl present on the same side of double bond, then it is ***syn*** form and other isomer is ***anti*** form.

III.2.1.1.4. Geometrical Isomerism in Cyclic Compounds

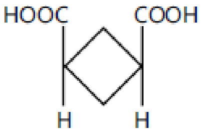
In ring structures, groups are unable to rotate about any of the ring carbon– carbon bonds. Therefore, ***cis / trans*** nomenclature is frequently used for naming cyclic compounds and describes the relative position of two substituents with respect to the ring. If a selected pair of groups are on the same side of a reference plane common to both isomers (the ring of a cyclic compound), the groups are said to be *cis.* If the groups are on opposite sides of the common reference plane, they are said to be *trans.*



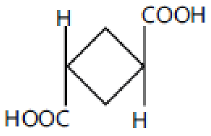
Cis form



Trans form



Cis form



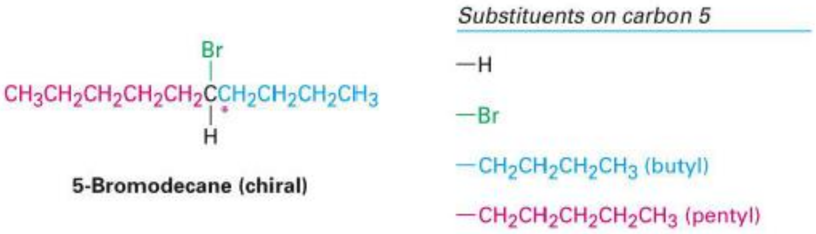
Trans form

III.2.2. Optical Isomerism

Only chiral molecule shows optical isomerism.

III.2.2.1. Chiral molecule: A carbon atom must have four different atoms or groups bonded to it in order to be chiral. If two or more of the groups or atoms on a tetrahedral **C** are identical, the **C** cannot be chiral and it is described as achiral. The chiral molecule shows **enatiomerism / optical isomerism**.

See molecule shown below :



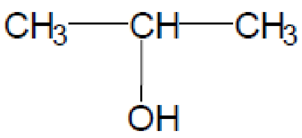
$CH_3CH_2CH_2CH_2CH_2C(Br)(H)CH_2CH_2CH_2CH_3$

5-Bromodecane (chiral)

III.2.2.2. Chiral atom/ asymmetric atom: The carbon atom that connected to four different groups or atom is the chiral atom/ chiral carbon. The chiral atom is also named as **chiral center** of **asymmetric centre**.

III.2.2.3. Optical active molecules: Chiral molecules are optically active and achiral molecules are optically inactive.

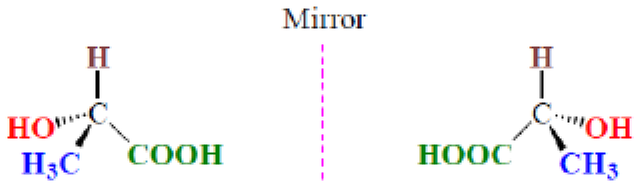
For example: 2-propanol is optically inactive



$CH_3-CH(OH)-CH_3$

III.2.2.4. Non-Superimposable Mirror Images

Chiral molecules and its mirror image are not superimposable each other. See the example given below for lactic acid, which is a chiral molecule.

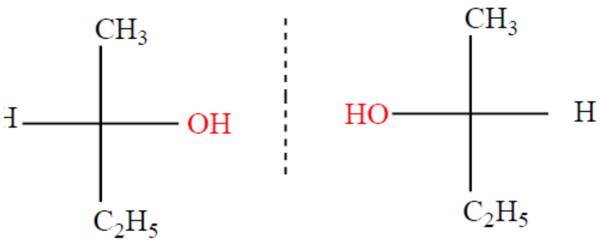


(+)-Lactic acid, $[\alpha]_D = +3.82$ (−)-Lactic acid, $[\alpha]_D = -3.82$

III.2.3. Enantiomers

The chiral molecule and its non-superimposable mirror image are enantiomers. The enantiomers are noted as **(+) / (-)** or **R/S** configurations. These enantiomers are optical isomers and they show different physical properties mainly they can rotate plane polarized light to opposite directions. They may show different chemical reactivities, especially they act different way in a chiral environment.

For example, one enantiomer of a chiral molecule can be the active drug and the other enantiomer can be fatal or mutant.



Enantiomers

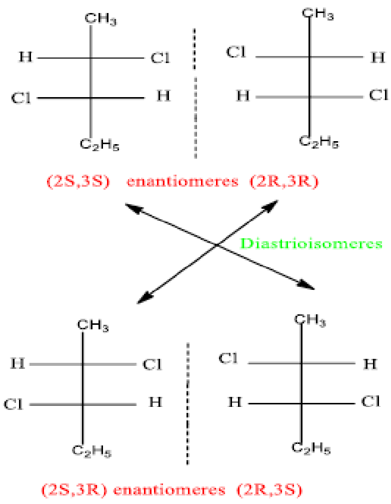
III.2.4. Diastereomers

Those compounds which are neither mirror images nor are superimposable on each other, are called as diastereoisomers.

Ex: Cis–trans isomers are configurational isomers but they are not mirror images and are thus, they are said to be diastereomers.

Diastereoisomerism may be due either to :

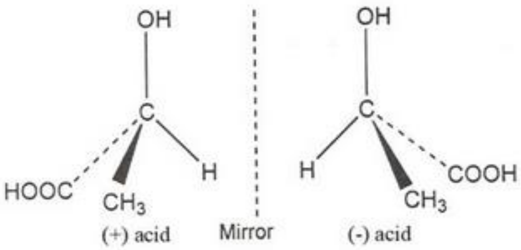
- Presence of a double bond.
- Existence of several asymmetric carbons.



III.2.5. Racemic mixture

The mixture of enantiomers which contain **50:50 ratio** of both enantiomers is racemic mixture or racemate. Racemic mixtures are optically inactive as they cancel off the optical rotation of opposite directions.

Ex :



Enantiomers of lactic acid. Equimolar mixture (+) and (-) forms (racemic mixture)

III.3. Absolute and Relative Configuration

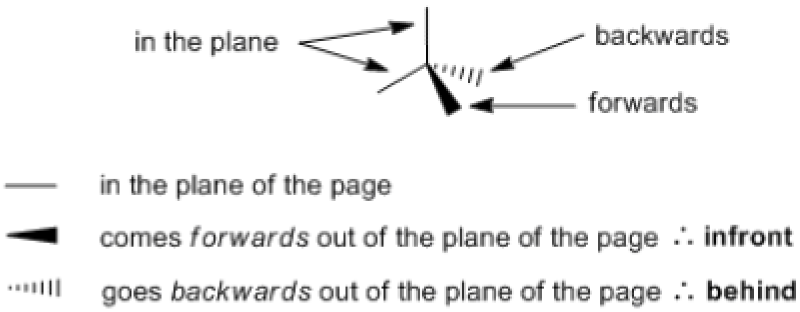
Absolute configuration is the precise three-dimensional **arrangement** of atoms in space Relative configuration compares the three-dimensional arrangement of atoms in space of one compound with those of another compound.

III.3.1. chiral molecule

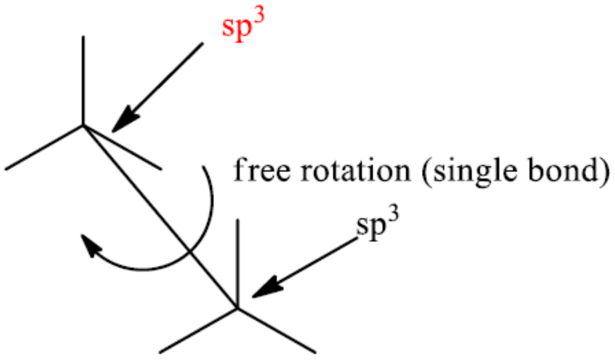
Chiral molecules are shown in different ways

- **Wedge-dash diagrams**
- **Sawhorse formula**
- **Fischer projection**

Wedge-dash diagrams

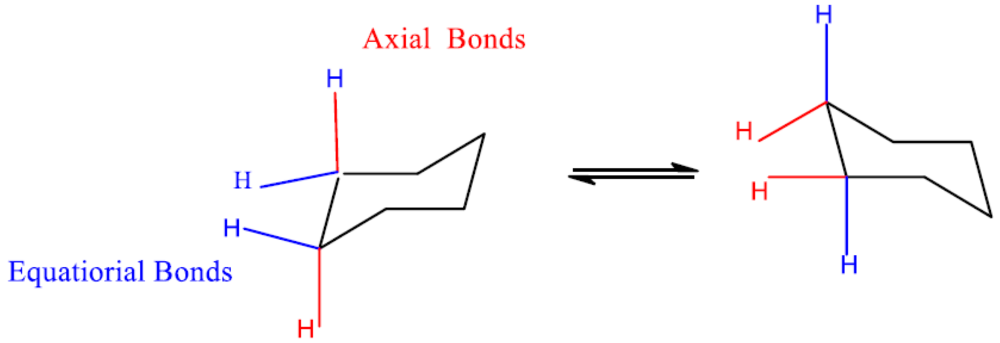


- **Sawhorse formula (cavalier perspective)**



The perspective representation is mainly used for cyclic molecules.

Ex: **Cyclohexane C_6H_{12}**



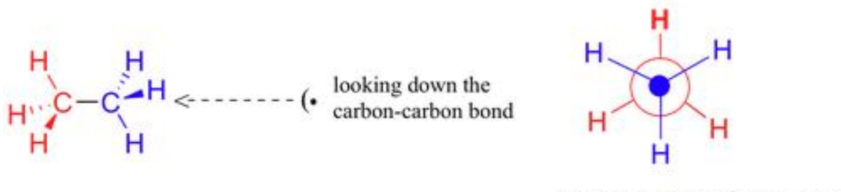
III.3.2. Projective representation or Cram convention

It consists in representing a connection by convention:

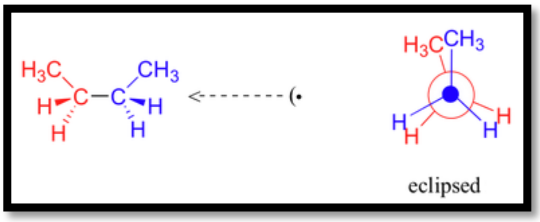
III.3.2.1. Newman projection:

In Newman's representation, the molecule is viewed along the axis of a C-C single bond between two neighboring carbon atoms. The bonds resulting from the two atoms are projected on a plane perpendicular to the axis of the studied bond:

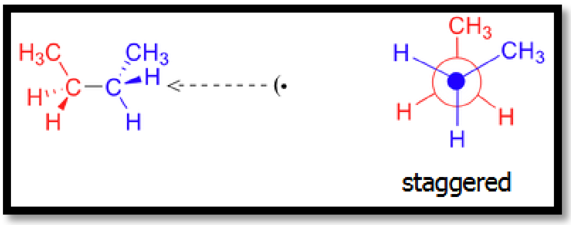
Representation of Ethane



'staggered' conformation
(Newman projection)



eclipsed



staggered

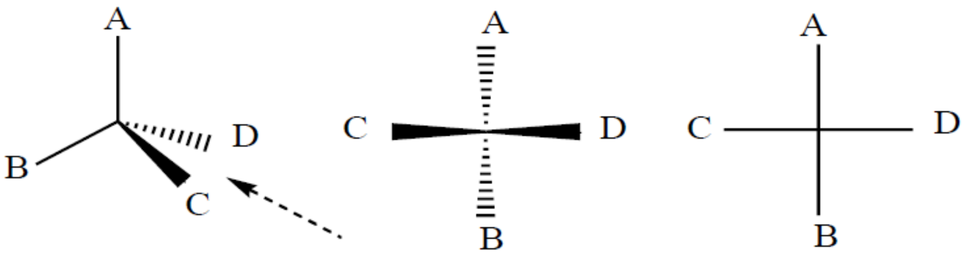
III.3.2.2. Fisher projection

In Fischer projection, bonds are represented by solid vertical and horizontal lines, according to the following conventions:

The vertical lines represent the links behind the plane of the figure.

- The horizontal lines represent the connections in front of the plane of the figure.

- The longest carbon chain is placed vertically and numbered from top to bottom.
- The link with the lowest index (most often associated with the most oxidized carbon) is placed at the top.



III.3.3. Notation of enantiomers by the Cahn-Ingold-Prelog (CIP) notation system

1. Use the Cahn-Ingold-Prelog priority rules to assign priority (one through four) to the four groups on the “chiral” atom.

2. Orient the molecule so that the lowest priority atom is in the back (away from you). Look at the remaining three groups of priority 1-3. If the remaining three groups are arranged so that the priorities 1→2→3 are in a *clockwise* fashion, then assign the chiral center as **R** (“**rectus**” or **right**). If the remaining three groups are arranged 1→2→3 in a *counterclockwise* manner, then assign the chiral center a **S** (“**sinister**” or **left**).

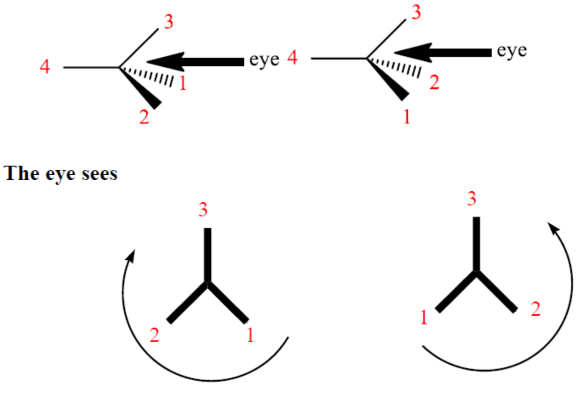
1. The four substituents are ranked in order of priority using the rules of Cahn, Ingold and Prelog; the priority substituent carries the number 1, the last in the order of priority number 4.

2. We look at the molecule in the axis of the C* bond − substituent n°4, the asymmetrical carbon being in the foreground and the substituent n°4 being directed towards the back.

The three substituents then present themselves:

➢ Either in the dextrorse direction (we go from 1 to 2 and to 3 as if we were turning a steering wheel to the right): the carbon then bears the descriptor R (from the Latin rectus “right”).

➢ Either in the sinistrorse direction (we go from 1 to 2 and to 3 as if we were turning a steering wheel to the left): the carbon is then assigned the descriptor S (from the Latin sinister “left”).

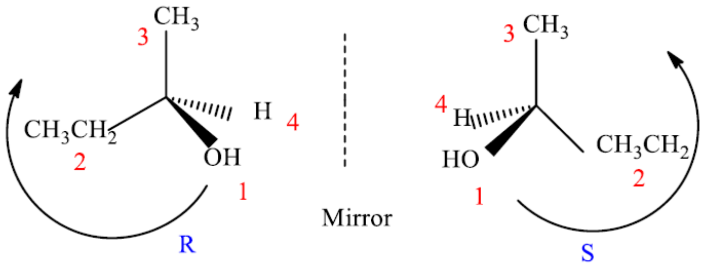


Configuration R

configuration S

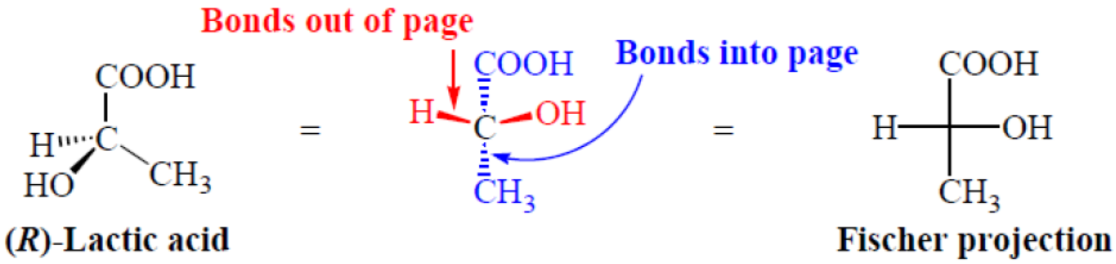
Of course, the mirror image of an atom with descriptor R is an atom with descriptor S and vice versa. It is said that there are two absolute configurations around an asymmetric atom.

$CH_3CH(OH)\ CH_2\ CH_3$



III.4. R and S notation using Fisher Projection Formula

As given above, optical isomers can be represented using Fisher formula. The process is called as projection of the spatial structure to a plane. Carbon atom of the centre of chirality is seldom drawn, but imagine into the point of intersection of the bonds. The vertical bonds would have to be drawn by dotted lines according to this arrangement, while the horizontal bonds would have to be drawn by bold lines, but each bond is drawn by identical width.



The projected formula and the Fischer's notation rule of projecting:

a) the group on the highest oxidation level is found on the top

b) the longest chain is down

c) both previous groups are behind the plane of the vertical plane

d) the other two groups are located horizontally, in front of the plane of the vertical plane

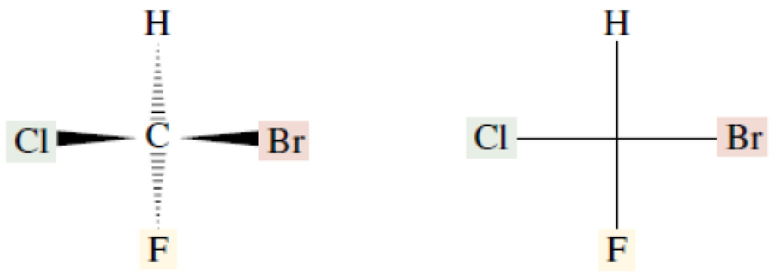
III.4.1. How to assign R & S configuration in Fisher Projection Formular

1) Assign priorities to the four substituents using CIP rules

2) The group of the lowest priority has to be at the top.

3) Determine the direction of rotation in going from priority 1 to 2 to 3, and assign R or S configuration.

4) If the group with the lowest priority (4) is not at the top, switch two groups to make it on the top and switch again for any two groups without switching the lowest priority (4).



(*S*)-Bromochlorofluoromethane

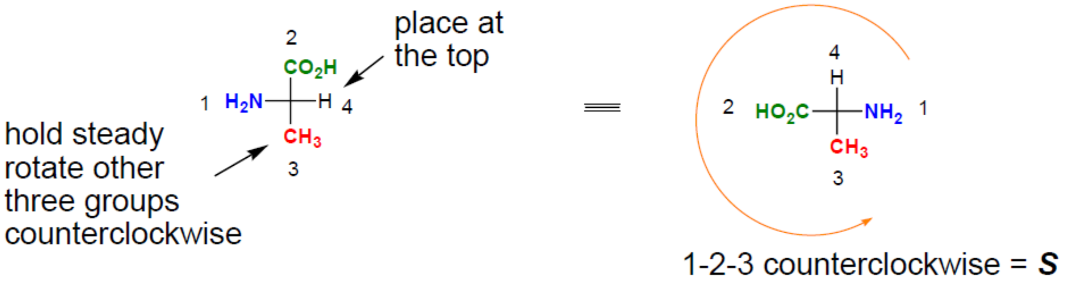
If the lowest priority group is not placed at the top, switch two groups to make it on the top and switch again for any two groups without switching the lowest priority. The reason;

Applying replacement of groups by even number, we get the original configuration, but with different arrangement. The projected formula can be rotated by 180 in the sheet of paper, but not by 90 or 270, since the latter rotations would result in centre of chirality of the opposite configuration, according to the rules of projection.

Rotating 180 degrees is similar to switching two groups twice;

See the example below;

At first H and -COOH groups are switched, this resulted lowest priority group placed at the top. Then, again -COOH and -NH_2 are switched without touching H at the top.

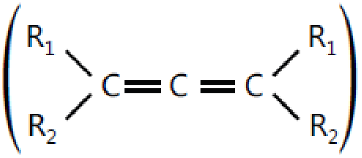


III.4.2. Chirality in Compounds with No Optical Centers

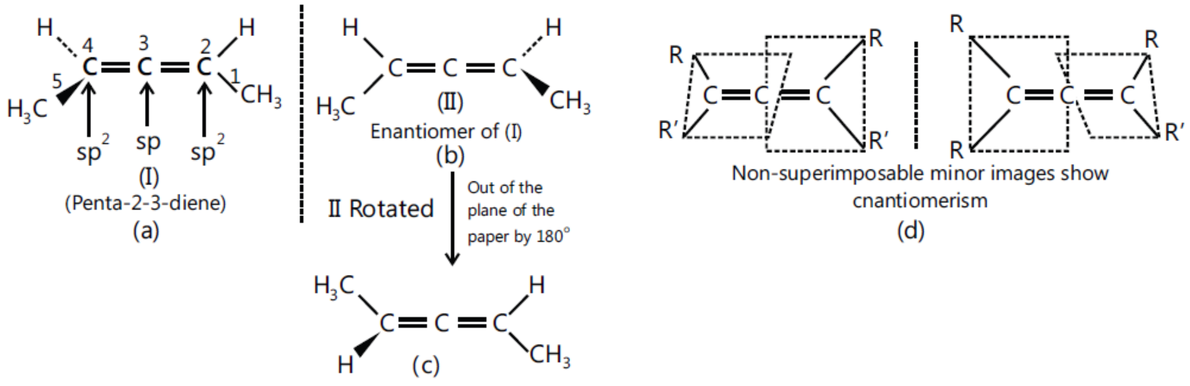
Stereochemistry of C Compounds Not Containing an Asymmetric C Atom (Allenes)

The presence of an asymmetric C atom is not essential for optical activity. The essential requirement is the asymmetry of a molecule as a whole

Allenes of the type are



Ex: penta–2,3–diene (I) has no chiral C atoms, yet it is a chiral molecule and has two enantiomers.



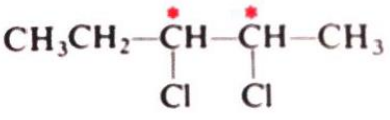
III.4.3. Molecule with more than chiral centers

When compounds is having more than one chiral centres , the number of stereoisomers possible can be calculated as below;

Maximum number of stereoisomers = 2n

where *n* = number of chiral centers

For example: The compound shown below has two chiral centers (stereogenic centers).

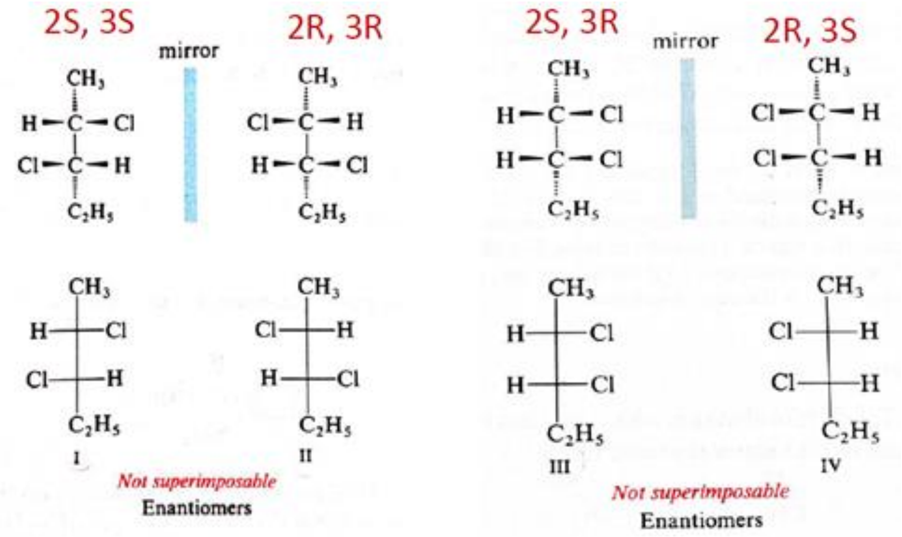


$$CH_3CH_2-\underset{Cl}{\overset{*}{C}H}-\underset{Cl}{\overset{*}{C}H}-CH_3$$

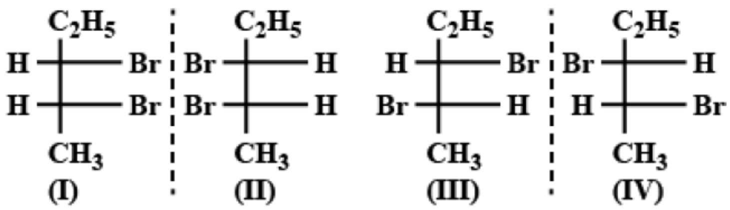
2,3-Dichloropentane

How many stereoisomers are possible?

There are four stereoisomers are possible for the above molecules. Chiral centres of these four isomers can be assigned to R / S configuration using CIP rule.



In the following example, this is more explained;

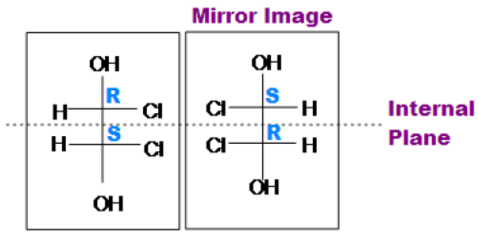


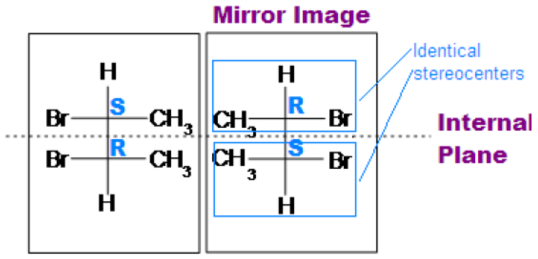
I and II
III and IV — **Enantiomers**

I and III
I and IV
II and III
II and IV — **Diastereomers**

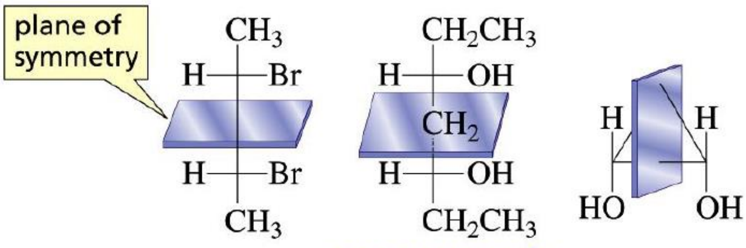
III.4.4. Meso Compounds

In general, a meso compound should contain two or more identical substituted stereocenters. Also, it has an internal symmetry plane that divides the compound in half. These two halves reflect each other by the internal mirror. The stereochemistry of stereocenters should "cancel out". What it means here is that when there is an internal plane that splits the compound into two symmetrical sides, the stereochemistry of both left and right side should be opposite to each other, and therefore, result in optically inactive.





Some examples



meso compounds

IV. Major reactions in organic chemistry

The study of reaction mechanisms represents an effort to rationalize organic chemistry which makes it possible to predict the results of a chemical reaction in advance.

We now know the geometry of isolated molecules as well as their electronic organization. The problem that arises for us is to know how molecules placed in the presence of each other can react to generate new molecules.

Thus, if we mix the molecules of two compounds A and B, we can ask ourselves:

-if A and B can react on each other?

- if they react under certain conditions, which compounds C and D are generated?

-A and B give C et D, what is the "path" should be followed by the chemical system, or in other words, according to what "mechanism" does the reaction take place?

- Are there intermediate compounds likely to form during the transformation?

The answers to all asked questions will allow us to describe the "mechanism" of the reaction, that is to say, all the steps taken by the chemical systems to go from the initial state to the final state.

The study of the mechanism accounts for all the electronic, geometric, energetic and kinetic modifications of the evolving system.

Overall, a chemical reaction can be considered under three essential aspects:

➢ The electronic aspect: rupture and formation of bonds.

a) Ionic (heterolytic rupture)

These reactions are catalyzed by acids or bases.

$$E{-}Nu \longrightarrow E^{+} + Nu^{-}$$

b) Radicular (homolytic rupture)

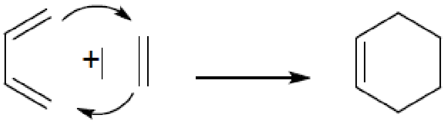
These types of reaction are favored by heating or irradiation.

$$A{-}A \xrightarrow{\Delta \text{ ou } h\upsilon} 2A^{\bullet}$$

c) Molecular (pericyclic)

In this type of reaction there will be a reorganization of the molecular orbitals.

Ex: Diels-alder cycloaddition



➢ The geometric or steric aspect: change in the configurations of the molecules.

➢ The energetic and kinetic aspect: variation in the energy of molecules and rate of transformation of the chemical system.

Knowledge of the course of reactions at the molecular scale makes it possible to explain and predict them.

If we consider a reaction as a whole, that is to say only the starting and finishing compounds, we can classify the reactions into four groups:

The different types of chemical reaction:

- ✓ **Substitution reaction**
- ✓ **Addition reaction**
- ✓ **Elimination reaction**
- ✓ **Rearrangement (transposition) reaction**

IV.1. Electronic aspects of chemical reactions

An "electronic effect" results from the asymmetrical distribution of charges in a molecule or an ion. There are essentially two electronic effects:

- The donor (+I) or attractor (-I) inducing effect
- The mesomeric donor (+M) or attractor (-M) effect

IV.1.1. inductive effect

This is the consequence of the differences in electronegativity between the atoms of a molecule:

$$^{+\delta}{}_{A} \longrightarrow {}_{B}{}^{-\delta}$$

B is more electronegative than A: molecule AB is a dipole.

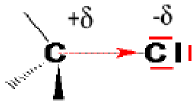
A is donor inducer (+I)

B is attractor inductor (-I)

The inductive effect is transmitted by the σ bonds. It pays off quickly when you move away from the donor or attractor group.

a) Attractor -I inducing effect

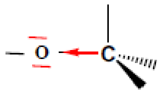
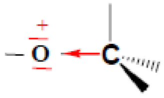
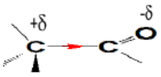
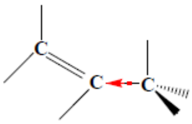
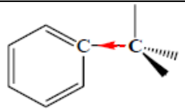
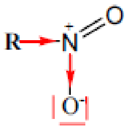
In an organic molecule any atom more electronegative than carbon is – I



Chloride (Cl) has **3** doublets **n**

Therefore increasing **electronegativity** order is I < **Br** < **Cl** < **F**.

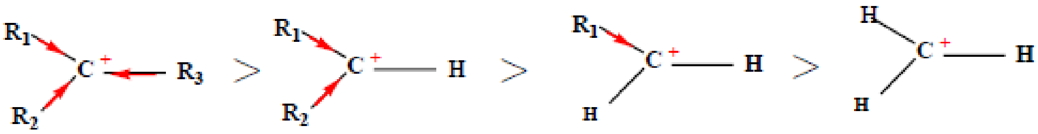
Examples:

					
Ether	**Xonium**	**Carbonyle derivative**	**ethylenic**	**Aromatic**	**Nitro**

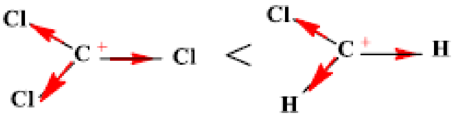
b) Effect stabilization (+I)

The inductive donor effect of the alkyl group compensates for the positive charge of the carbocation and stabilizes it

Decreasing stability

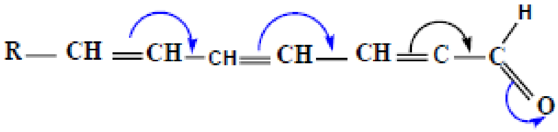


On the other hand, the inductive attractor effect destabilizes the carbocation by increasing its positive charge.

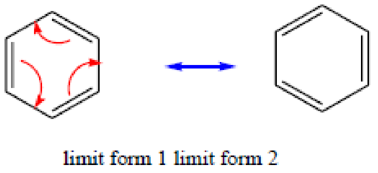


II. 1.2. The mesomeric effect

The mesomeric effect results from the delocalization of **π** electrons. It propagates without weakening along a chain of conjugated carbons

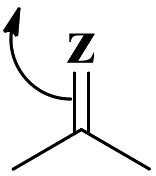


Example of Benzene C_6H_6:



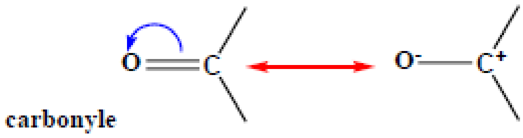
a) The Mesomeric -M Attractor Effect:

It can be summarized by the diagram:



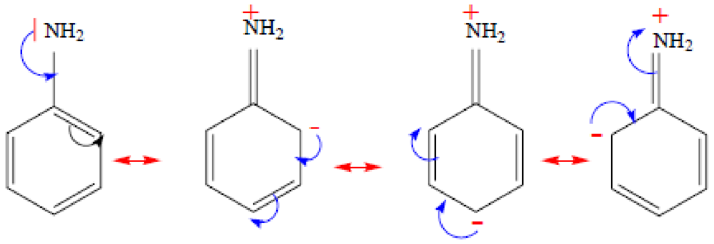
Z= O, S, O

Example

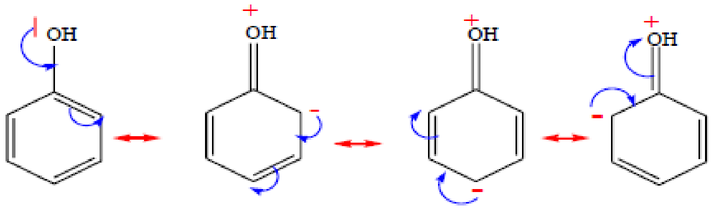


b) The +M effect in aromatic series

Common +M groups include alkoxy ($-OCH_3$), amino ($-NH_2$), and hydroxyl (-OH) groups. These substituents can donate electrons due to their lone pairs.

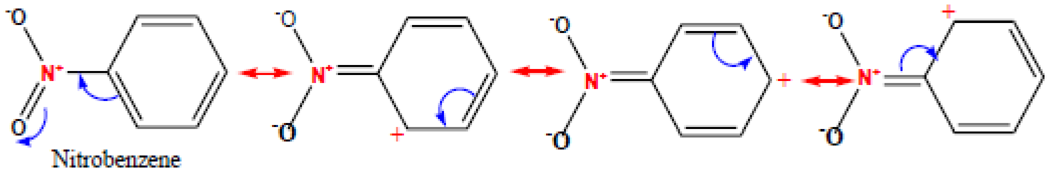


Phenol



c) The -M effect in the aromatic series

Common -M groups include nitro ($-NO_2$), cyano (-CN), carbonyls (like -C=O), and halogens (to a lesser extent).



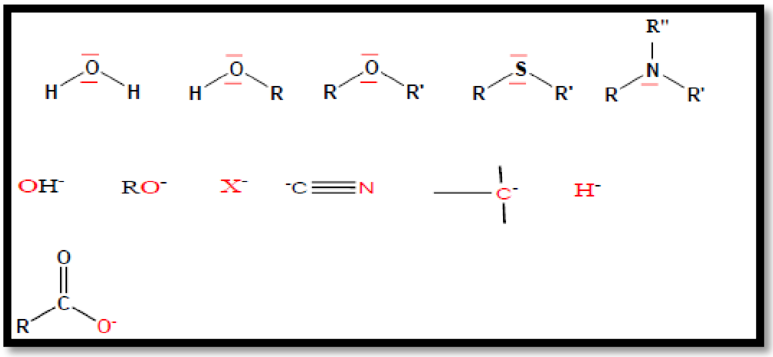
VI.2. The reaction in organic chemistry

Three types of reactions in our case:

IV. 2.1. Nucleophilic and electrophilic reagents

IV. 2.1.1. Nucleophiles: A nucleophile has one or more n-doublets or is an anion.

Nucleophiles are species that donate an electron pair to an electrophile to form a chemical bond. They are characterized by having a negative charge or a lone pair of electrons, which allows them to seek out positively charged or electron-deficient species.

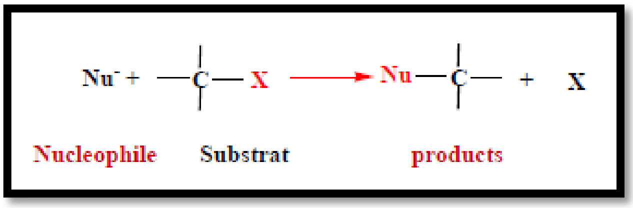


IV. 2.1.2. Electrophile: An electrophile has an electron void. It is a cation or a neutral molecule.

Electrophiles are species that accept an electron pair from a nucleophile. They are often positively charged or neutral molecules with electron-deficient atoms, making them attractive to nucleophiles.

Examples:

- **Carbocations (R_3C^+):** Highly reactive electrophiles that can be attacked by nucleophiles in various reactions.
- **Alkyl Halides (R-X):** In electrophilic substitution reactions, alkyl halides can act as electrophiles when attacked by nucleophiles.

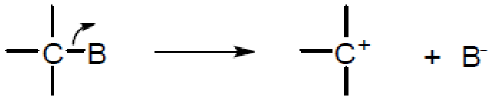


IV. 2.2.Reactive intermediates

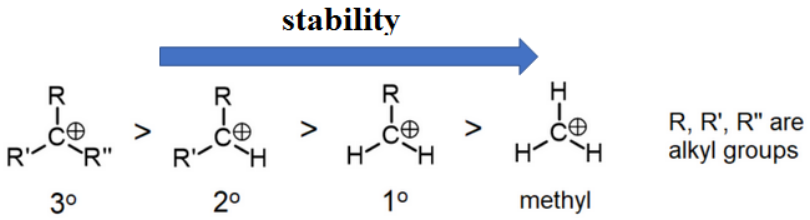
IV. 2.2.1. Carbocation

A carbocation is an ion with a positively-charged carbon atom. Among the simplest examples are methenium CH_3^+, methanium $C_2H_5^+$, and ethanium $C_2H_7^+$.

The formation of the carbocation is due to the presence of an element more electronegative than carbon. The breaking of the bond is not symmetrical and therefore this element takes the lone pair with it.

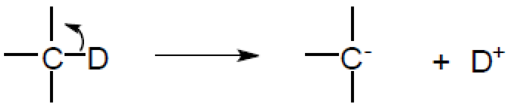


- The formation of the carbocation is favored by a polar protic solvent.
- The carbocation is sp2 hybridized.
- The carbocation is all the more stable as the carbon is linked to donor groups.
- Conjugation stabilizes the carbocation by mesomeric effect.
- Electro-attracting groups destabilize the carbocation.



IV. 2.2.2. Carbanions

Carbanions can be formed by heterolytic rupture of a C-Z bond, which the carbon is more electronegative.



- This rupture is favored by a **polar aprotic** solvent.

- The carbanion is **sp3** hybridized.

- Inversely to carbocations, carbanions are more stable when the carbon is **linked** to **electron-withdrawing** groups.

- Groups with an **inductive donor** effect **destabilize** the carbanion.

- **Conjugation** stabilizes carbanions by **mesomeric** effect.

IV. 2.2.3. Radicals

Radicals are formed by the homolytic rupture of a bond that is not very polarized by the effect of temperature or irradiation. The rupture occurs symmetrically and each atom takes its electron.

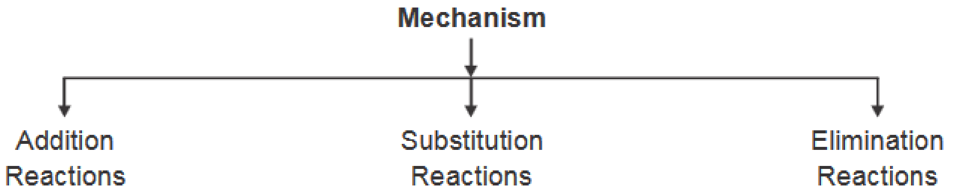
$$A{-}A \xrightarrow{\Delta \text{ ou } h\upsilon} 2A^{\cdot}$$

- A radical is usually sp2 hybridized.
- The stability of the radical is similar to the carbocation.

VI.3. Organic chemistry mechanism

A detailed and stepwise description of pathway by which reactant is converted into product is called reaction mechanism.

Types of Reaction Mechanism



VI.3.1. Addition Reaction

Addition reactions are the characteristics property of the multiple bonds. (e.g. alkenes and alkynes, nitriles, imines (Schiff base)).

The addition reaction can be divided into **three** types

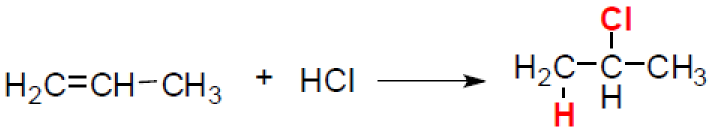
1. Free Radical additions

2. Nucleophilic additions

3. Electrophilic additions.

VI.3.1.1. Free Radical Addition: In general, the addition of halogen acid to unsymmetrical alkenes gives **Markownikoff's addition product.**

Markownikoff's Addition: When an unsymmetrical reagent added to an unsymmetrical multiple bonds (**alkene or alkyne**) the negative part of reagent attached to that carbon atom which has lesser no. of H atom.



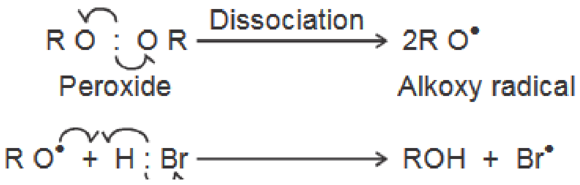
$$H_2C{=}CH{-}CH_3 + HCl \longrightarrow H_2\underset{H}{C}{-}\overset{Cl}{\underset{H}{C}}{-}CH_3$$

However, this is not always the case. Addition of **HBr** to unsymmetrical alkenes in presence of peroxide gives a product which is different from the Markownikoff's product this is known as **Antimarkownikoff's addition**. This is also known as peroxide effect or Kharasch effect.

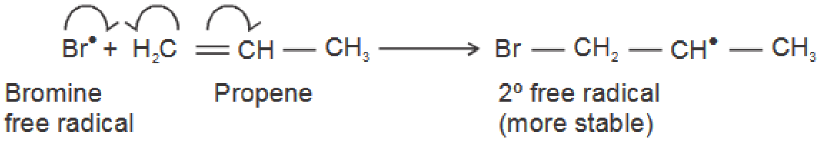
$$\underset{\text{Propene}}{CH_3-CH=CH_2} + HBr \xrightarrow[\text{(Antimarkowinkoff's addition)}]{\text{Peroxide}} \underset{\text{(n-propyl bromide)}}{CH_3-CH_2-CH_2-Br}$$

Following steps are involved in the free radical mechanism.

(1) **Chain Initiation Step**: Peroxide dissociates into two free radicals called alkoxy radicals.



2) **Chain Propagation Step**: Bromine radical adds to a double bond, forming a new free radical with the odd electron on the carbon atom.



Since **secondary free** radical is more **stable** than the **primary** free radical, only the secondary free radical is formed. The alkyl free radical (secondary free radical) reacts with an **HBr** molecule to generate bromine radical.

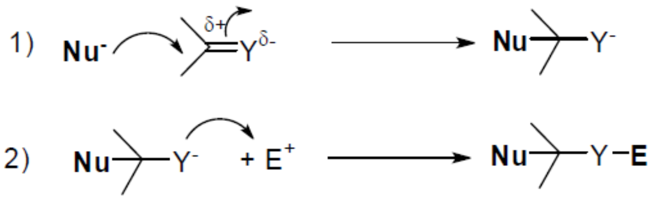
$$Br-CH_2-CH^\bullet-CH_3 + HBr \longrightarrow Br-CH_2-CH_2-CH_3 + Br^\bullet$$

(3) Chain Termination Step: Termination occurs by any or all of the reactions which use up species involved in the propagation steps.

$$Br^\bullet + Br^\bullet \longrightarrow Br_2$$

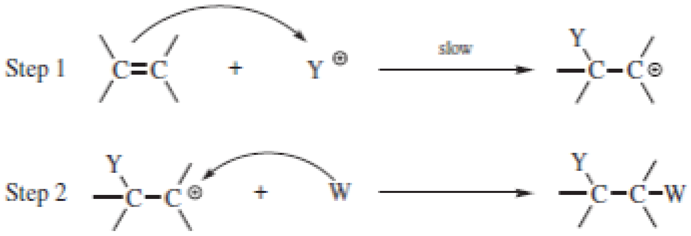
VI.3.1.2. Nucleophilic Addition: Such reaction are usually encountered in compound containing Polar functional groups e.g., carbonyl, $-C \equiv N$, C = S etc.

The most important examples are encountered in compounds containing carbonyl group.



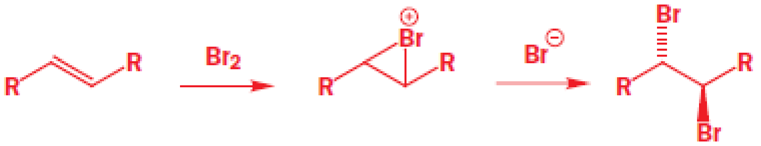
VI.3.1.3. Electrophilic Addition Reactions

The first step is addition of electrophile by formation of σ bond through donation of π electrons to the electrophile and carbocation is formed. The next step is reaction of the positively charged intermediate (carbocation) with a species carrying lone pair or negative charge i.e nucleophiles. This step is the same as the second step of the SN1 mechanism.



Examples of electrophilic addition reactions:

(a) **Addition of bromine to alkenes**: The addition reaction of bromine to alkenes proceeds via a cyclic bromonium ion intermediate. This intermediate is similar to those encountered in the neighbouring-group mechanism of nucleophilic substitution. This reaction is used as a colour test to detect the presence of multiple bonds. The brown colour of bromine disappears when it is added to a compound with double or triple bonds.



(b) Addition of unsymmetrical reagents to unsymmetrical alkenes (Markownikoff rule): For example in the reaction of propene with HBr, H+ acts as an electrophile which is added to the carbon bearing double bond followed by attack of bromide ion (Br-).

$$CH_3\text{-}CH{=}CH_2 \xrightarrow{HBr} \underset{\text{major}}{CH_3\overset{Br}{C}HCH_3} \quad CH_3CH_2CH_2{-}Br$$

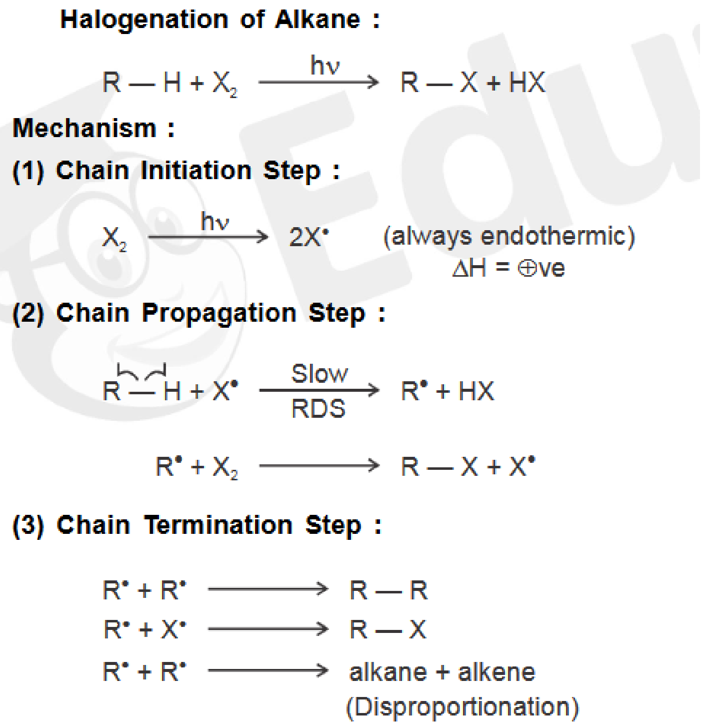
VI.3.2. Substitution Reaction: The replacement of one group by another is called substitution reaction. $A - B + X \longrightarrow A - X + B$

There are three main types of these reactions

Free Radical Substitution, Electrophilic Substitution, Nucleophilic Substitution

VI.3.2.1. Free Radical Substitution

Example



Halogenation of Alkane :

$$R - H + X_2 \xrightarrow{h\nu} R - X + HX$$

Mechanism :

(1) Chain Initiation Step :

$$X_2 \xrightarrow{h\nu} 2X^\bullet \quad \text{(always endothermic)} \quad \Delta H = \oplus ve$$

(2) Chain Propagation Step :

$$R - H + X^\bullet \xrightarrow[\text{RDS}]{\text{Slow}} R^\bullet + HX$$

$$R^\bullet + X_2 \longrightarrow R - X + X^\bullet$$

(3) Chain Termination Step :

$$R^\bullet + R^\bullet \longrightarrow R - R$$

$$R^\bullet + X^\bullet \longrightarrow R - X$$

$$R^\bullet + R^\bullet \longrightarrow \text{alkane + alkene (Disproportionation)}$$

VI.3.2.2. Electrophilic Substitution Reaction

Aromatic Electrophilic Substitute Reactions.

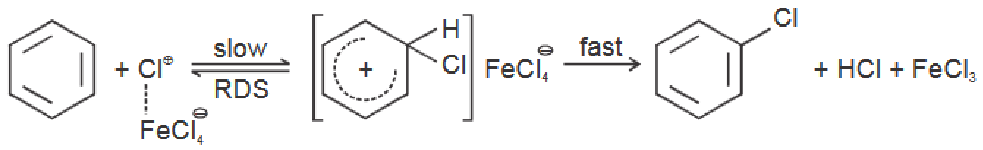
Electrophilic substitutes are characteristics reactions of aromatic compounds.

Aromatic compounds can be halogenated with halogen in the presence of a catalyst often called as a halogen carrier, for ex. $FeCl_3$, $FeBr_3$, $AlCl_3$ or $AlBr_3$ etc.

For example

(i) $Cl - Cl + FeCl_3 \longrightarrow Cl^{\oplus} \text{-----} FeCl_4^{\ominus}$

(ii)



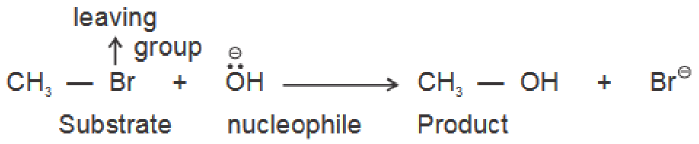
Some Typical Aromatic Electrophilic Substitution Reactions: Halogenation, Nitration, Sulphonation, Friedel-Crafts-Reactions (R-X).

VI.3.2.3. Nucleophilic Substitution Reaction : Replacement (Displacement) of an atom or group by a nucleophile is known as Nucleophilic substitution reaction.

The group that is replaced (leaving group) carries its bonding electron.

$$R - X + Nu^{\ominus} \longrightarrow R - Nu + X^{\ominus}$$

Example:



$$CH_3 - Br + \overset{\ominus}{\ddot{O}H} \longrightarrow CH_3 - OH + Br^{\ominus}$$

Substitution reactions at saturated carbon can be mechanistically categorized as unimolecular **(SN1)** and **(SN2)** Bimolecular.

(1) **SN1 (Substitution Nucleophilic Unimolecular)** : A nucleophilic substitution reaction at a saturated carbon involving only one species in the transition state of the rate determining step is said to follow mechanism.

Such a reaction takes place in two steps:

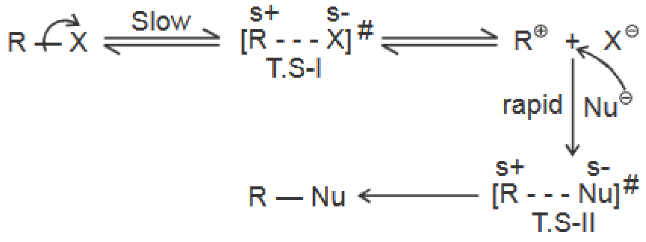
Step 1 : Formation of carbocation

$$R - X \xrightleftharpoons{\text{Slow}} R^{\oplus} + X^{\ominus}$$

Step 2 : Capture the carbocation by the nucleophile

$$R^{\oplus} + \overset{\ominus}{\ddot{N}u} \xrightarrow{\text{fast}} R - Nu$$

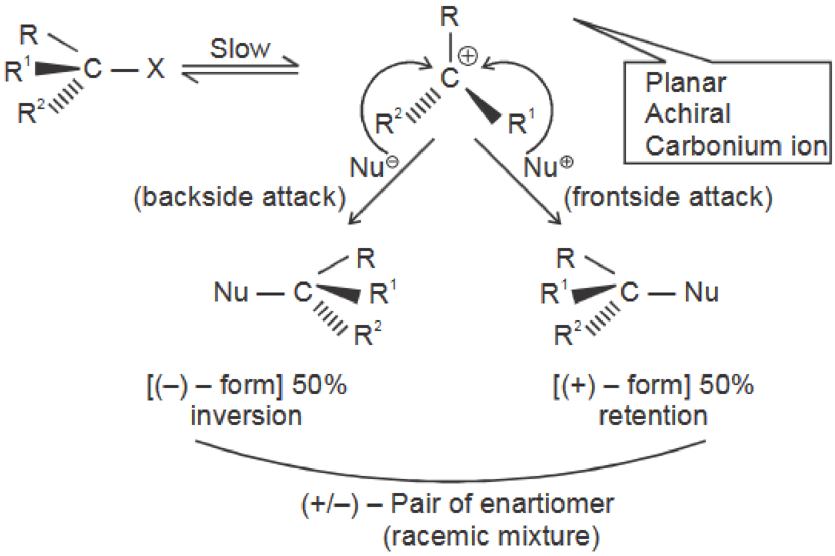
The overall reaction may be represented as :



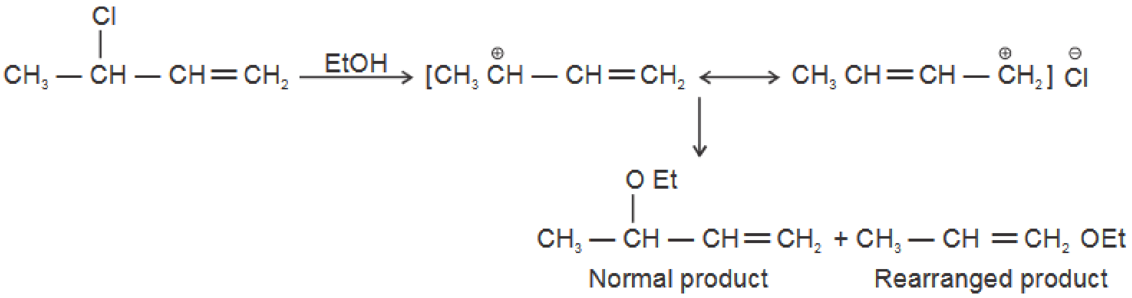
The **SN1** reaction shows first-order kinetics as rate of the reaction depends only on the concentration of the substrate (RX) and does not depend on the concentration of the nucleophile reacting with it. The rate expression is therefore: Rate = k [RX]; Where **k** is the rate constant.

Stereochemistry of the SN1 Reaction : The SN1 reaction proceed with partial racemisation and some inversion.

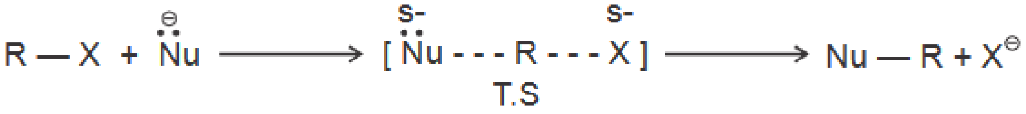
An **SN1** reaction involve the formation of a carbocation in the slow and rate-determining step if there is a free carbocation, it would be **planar** and **achiral**: the incoming nucleophile **(Nu^-)** subsequently should attack the species with equal ease from either of the plane leading to **50 : 50** mixture of **two enantiomers.**



Rearrangement in SN1 Reaction: Since mechanism involves carbocation intermediate therefore, unexpected products are also formed. for example, hydrolysis of 2-bromo-3-methyl butane yields 2- methyl-2-butanol



2) SN2 (Substitution Nucleophilic Bimolecular): The concerted (**one step**) mechanism with no intermediate for the displacement of a leaving group by a nucleophile in aliphatic and alicyclic compounds involving both nucleophile and substrate in the transition state is termed as substitution nucleophilic bimolecular and symbolically designated as **SN2.**



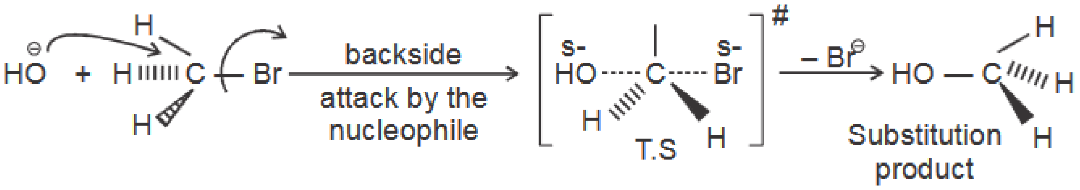
$$R-X + \overset{\ominus}{\ddot{N}u} \longrightarrow [\overset{s-}{\ddot{N}u}---\underset{T.S}{R}---\overset{s-}{X}] \longrightarrow Nu-R + X^{\ominus}$$

Kinetically evidence shows that the rate of this reaction is proportional to both the concentration of substrate and nucleophile. Thus the reactions follow second-order kinetics and are described by the rate expression: Rate = **k** [RX] [Nu]; Where **k** is rate constant.

Stereochemistry of SN2 Reaction: SN2 mechanism take place with stereoelectronic controls involving a backside attack by the nucleophile on the bond between the C-atom and the leaving group in a concentrated process without intermediate.

Let us take the example of alkaline hydrolysis of methyl bromide to give methanol

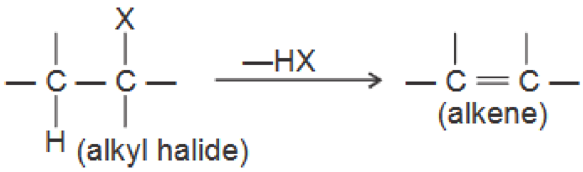
$$CH_3Br + \overset{\ominus}{O}H \longrightarrow CH_3OH + Br^{\ominus}$$



Thus, the mechanism leads to **inversion** of **configuration** at the chiral center under attack. This inversion of configuration is called the **walden inversion**.

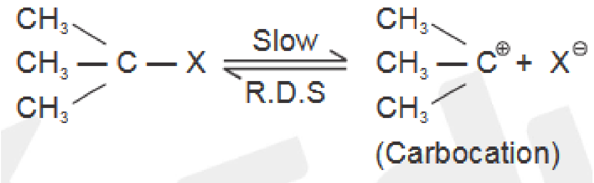
VI.3.3. Elimination Reaction

The elimination reactions are reverse of addition reactions. In elimination reaction **two groups** are **removed** from a molecule, neither being **replaced** by another group. In these reactions a atom or group from α-carbon atom and a proton from the β-carbon are eliminated.

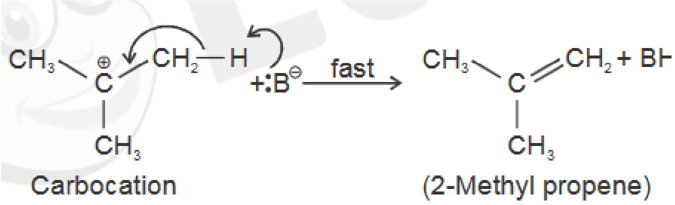


VI.3.3.1. E1 (Unimolecular Elimination Reactions): Like **SN1** reaction the **E1** (elimination, unimolecular) mechanism is a **two-step** process:

Step 1: The first step is the rate-determining step involving heterolysis of the substrate to form a carbenium ion intermediate that rapidly loses a β-proton in the second step.



Step 2: The second step involves the fast abstraction of a proton from the adjacent β-carbon atom giving rise to the formation of the alkene.



Rate = **k**[substrate]

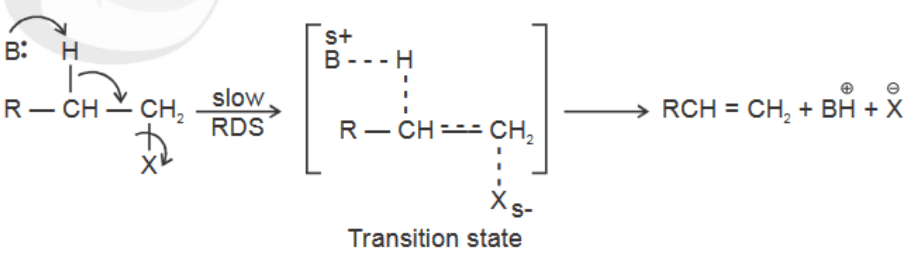
E1 reactions maintain regio-and stereo selectivity.

(1) Regioselectivity: **E1** elimination affords predominantly the thermodynamically more stable alkenes (i.e. more substituted alkenes; **Saytzeff elimination**).

(**2) Stereoselectivity**: **E1** elimination gives predominantly the **E-alkene** rather than the **z-isomer** because of steric reason.

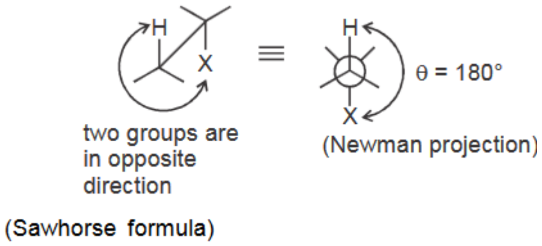
VI.3.3.2. E2 (Elimination, Bimolecular) Reaction: The **E2** (elimination, bimolecular) mechanism is a concerted (**one-step**) process involving the simultaneous **removal** of **two groups**, one of which is usually a proton that is pulled off by an added base. Thus in case of an alkyl halide undergoing E2 reaction, a new C = C (**π**) bond beings to form at the same time as the C-H and C-X (**two σ**) bonds being to break.

The mechanism of this reaction is represented as follows:

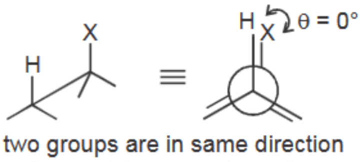


E2 bimolecular and kinetically second order. Rate = **k**[Substrate][Base]

Stereochemistry of E2 Path: There are two ways in which the C-H and C-X bonds can be in the same plane. They can be parallel to one another either in the same side of the molecular (syn-periplanar) or on the opposite sides of the molecule (anti-periplanar).

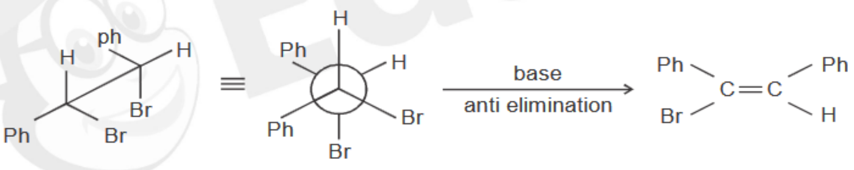


Anti periplanar conformation

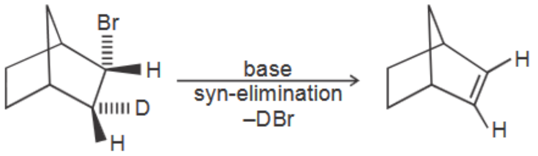


Syn-periplanar conformation

Anti-elimination :



Syn elimination -



VI.3.4. Rearrangements (Transpositions)

A rearrangement (transposition or migration) is the **movement** of an atom or a group of atoms **Z** linked to atom **A** towards another atom **B** within the same molecule (**Z-A-B** becomes **A-B-Z**), referred to as an "**intramolecular mechanism**." However, some rearrangements involve an intermolecular mechanism.

The main mechanisms of rearrangement encountered are:

- **Nucleophilic or Anionotropic Rearrangements**: These are very common. The migrating group is nucleophilic, such as $\mathbf{R^-}$ or $\mathbf{H^-}$, as it takees its bonding pair during the migration.
- **Electrophilic or Cationotropic Rearrangements**: These are quite rare. The migrating group is electrophilic, such as R^+ or H^+, as it does not carry its bonding pair.

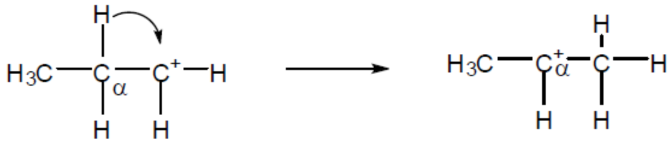
- **Radical Rearrangements**: These are rare. The migrating group is a radical (R• or H•), as it carries only a single bonding electron.

There are other specific rearrangements that will not be covered in this course because they require extensive knowledge of organic chemistry.

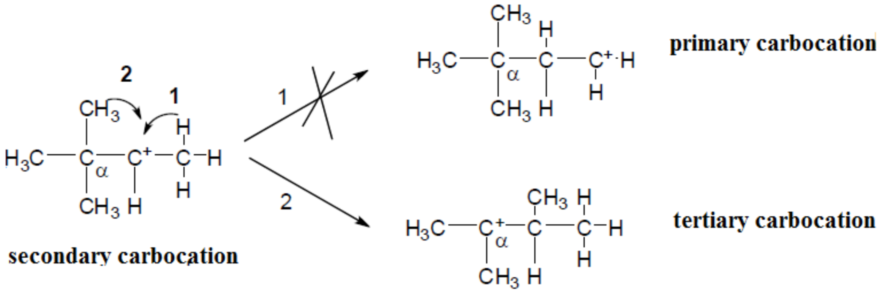
a) Rearrangement of a Carbocation

In the different mechanisms studied above, many reactions proceed through a carbocation. This carbocation sometimes undergoes rearrangements. The rearrangements of carbocations are due to the migrations (transpositions) of hydrogen atoms or carbon groups located in the **α** positions of the positively charged carbon atom. These migrations can only yield carbocations that are more stable than the original ones and never the opposite.

Example 1: Rearrangement of the primary n-propyl carbocation to the secondary isopropyl carbocation.

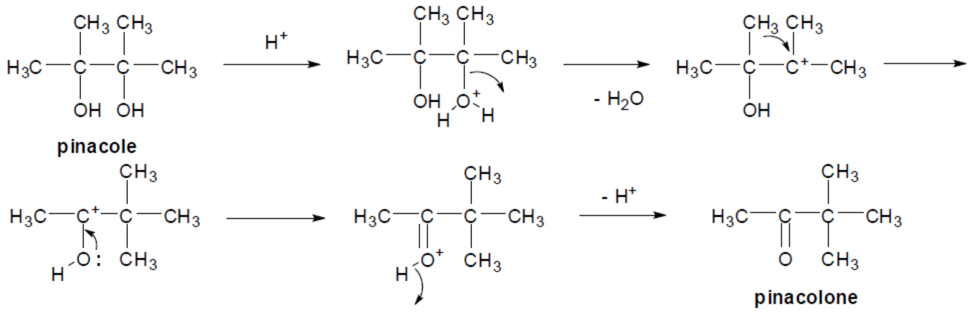


Example 2: rearrangement of 3,3-dimethyl-but-2-yle cation

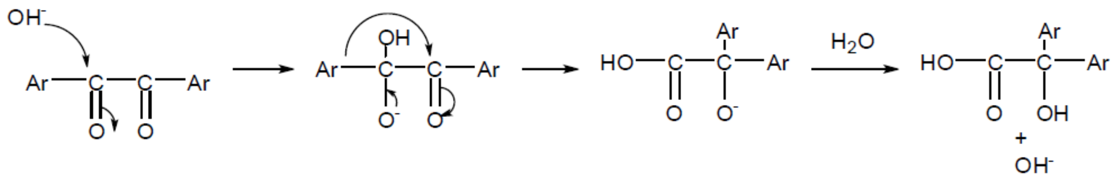


b) Pinacol Rearrangement

In acidic condition, **1,2-diols** undergo intramolecular dehydration followed by rearrangement to affords the corresponding **ketones**. Among these well-known diols is pinacol, which undergoes the pinacol rearrangement in acidic conditions to form pinacolone.



c) Benzylic Transposition: α-Dicarbonyl compound undergo benzylic transposition in basic media, leading to α-hydroxy acids.



d) Baeyer-Villiger Rearrangement or Oxidation

Ketones are transformed into the corresponding esters through rearrangement in the presence of **peracid**. This oxidation reaction is known as the Baeyer-Villiger reaction.