Chapter I: Basics of organic chemistry

I. Introduction

- Organic chemistry studies **carbon and its compounds**.
- Carbon forms a huge variety of molecules essential in **medicine, agriculture, and daily life**.

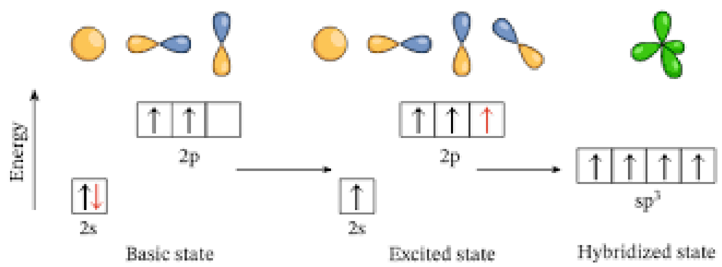
I.1. Historically:

  - Ancient use of natural organic substances (dyes, medicines, poisons).
  - 18th–19th century: isolation of pure compounds, elemental analysis, and rejection of the “vital force” theory after **Wöhler synthesized urea (1828)**.
  - Development of **valence theory (1858)** and rapid advances in synthesis, mechanisms, and structural theories.

- Today: organic chemistry also explains **biological molecules (proteins, DNA)**.

I.2. The Carbon Atom

- **Definition**: Carbon forms covalent bonds with H, O, N, and other nonmetals; bonds with itself to make chains or rings.
- **Nucleus**: Contains protons (+) and neutrons (0); electrons (−) orbit outside.
- **Structure**:
  - Atomic number: 6, symbol: C
  - Ground-state configuration: $1s^2\ 2s^2\ 2p^2$
- **Orbitals**:
  - 1s orbital (2 e^-)
  - 2p orbitals (6 e^- max; carbon has 2)



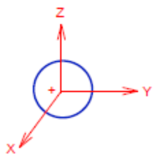
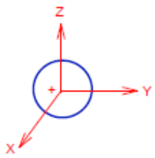
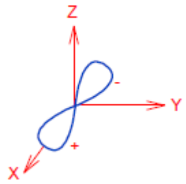
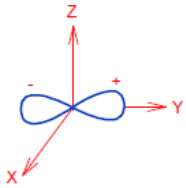
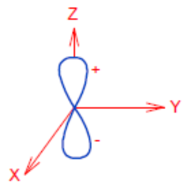
I.3. Properties of Carbon

- **Ionization energies**: 1st = 11.26 eV, 2nd = 24.38 eV, etc.
- **Electronegativity**: 2.55
- Good **electrical (61×10^3 $S\cdot m^{-1}$)** and **thermal conductivity (129 $W\cdot m^{-1}\cdot K^{-1}$)**.
- **Isotopes**:
  - **C-12** (99.9%): standard for atomic masses.

- **C-13** (1.1%): used in NMR, metabolic studies.
- **C-14** (trace): radioactive, used in **radiocarbon dating**.

I.4. Electronic Structure & Hybridization

- **Hybridization**: mixing of orbitals to form new hybrid orbitals for bonding.
- **Fundamental state**: $1s^2\ 2s^2\ 2p^2$ → valence = 2
- **Excited state**: $1s^2\ 2s^1\ 2px^1\ 2py^1\ 2pz^1$ → valence = 4
- **Quantum numbers**:
  - n (principal) → shell **n** (n = 1, 2, 3…)
  - *l* (azimuthal) → orbital shape (s, p, d, f) ***l*** (l = 0, 1, 2, ..., n−1)
  - m (magnetic) → spatial orientation ***m*** ($-l \le m \le +l$)
  - s (spin) → electron spin (+½, −½)

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	

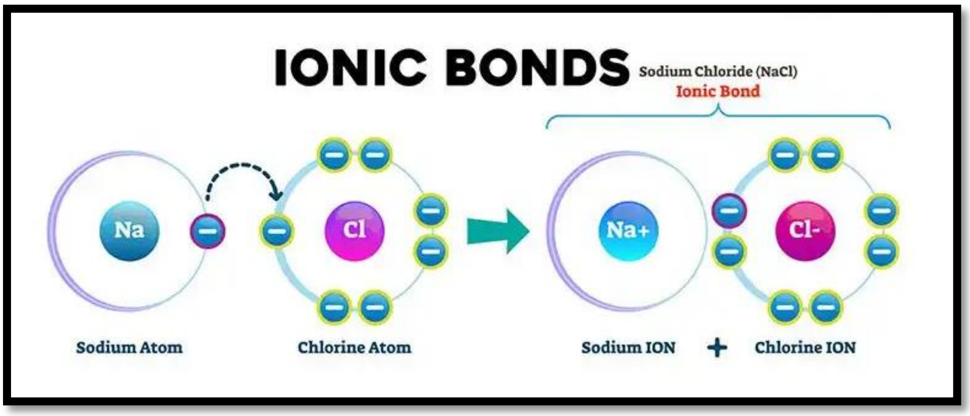
I.5. Chemical Bond

- A bond forms when atoms share or transfer electrons, lowering the system's total energy.
- Carbon, the basis of organic chemistry, mainly forms **covalent bonds**.
- The **valence shell** (outermost shell) is always involved in bonding.

I.5.1. Types of Bonds

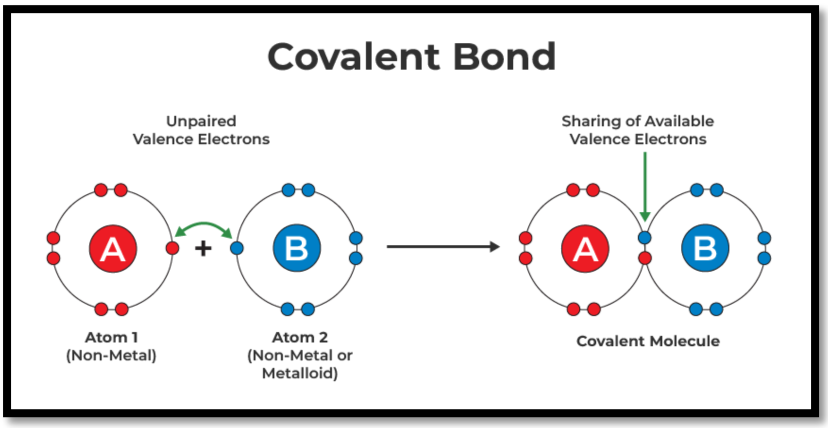
I.5.1.1. Ionic Bond

- **Formation:** Transfer of electrons (metal → nonmetal).
- **Example:** NaCl.
- **Properties:** High melting/boiling points, conduct electricity in molten/aqueous state.



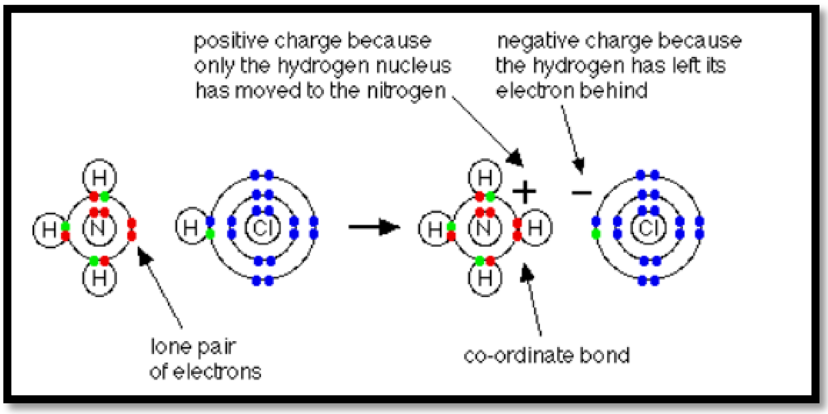
I.5.1.2. Covalent Bond

- **Formation:** Sharing of electrons (usually between nonmetals).
- **Types:**
  - Single (H_2)
  - Double (O_2)
  - Triple (N_2)



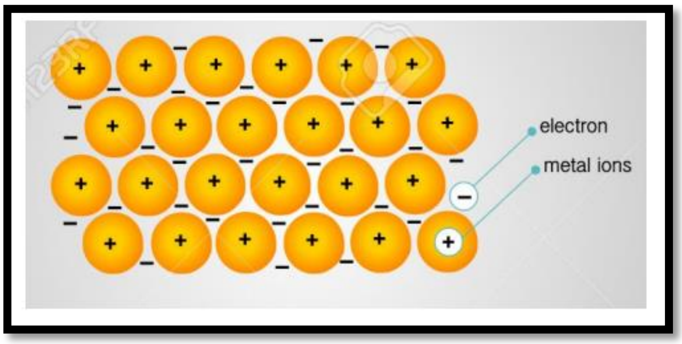
I.5.1.3. Coordinate covalent bond (dative): both electrons from the same atom.

Properties: Variable melting/boiling points, usually poor conductors.



I.5.1.4. Metallic Bond

- **Formation:** "Sea of delocalized electrons" around positive metal ions.
- **Example:** Copper (Cu).
- **Properties:** High conductivity, malleable, ductile, high melting/boiling points.

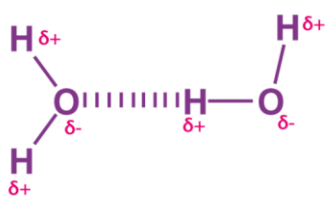


I.5.1.5. Polar vs. Nonpolar Covalent Bonds

- **Nonpolar:** Equal sharing (H_2, O_2).
- **Polar:** Unequal sharing due to electronegativity difference (H_2O).

I.5.1.6. Hydrogen Bond

- **Weaker** than ionic/covalent bonds.
- **Example:** H in water attracted to O of neighboring molecule.
- **Significance:** Explains many unique properties of water.

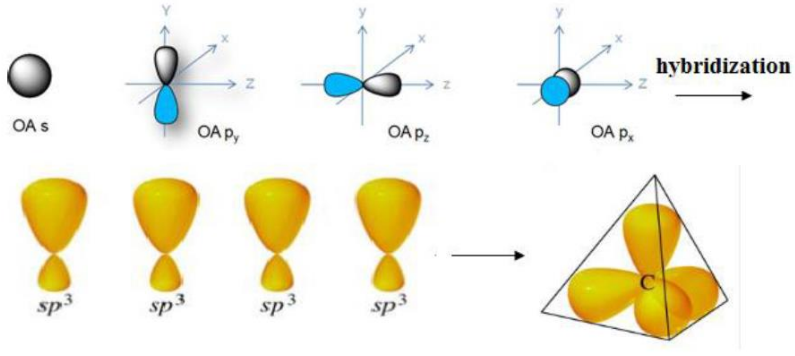


I.5.2. Hybridization of Carbon

Hybridization = mixing of atomic orbitals (s and p) to form new hybrid orbitals that determine **molecular geometry, bond angles, and reactivity**.

I.5.2.1. sp^3 Hybridization (Tetrahedral)

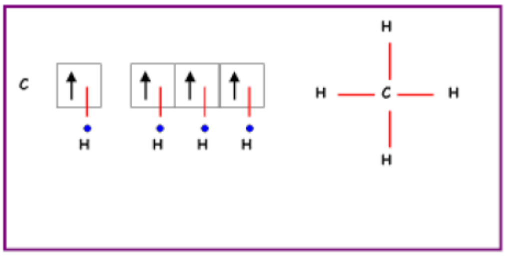
- Combination: 1s + 3p → 4 sp^3 orbitals
- Geometry: **Tetrahedral**
- Bond angle: **109.5°**
- All bonds identical.



4 sp3 hybrid orbitals

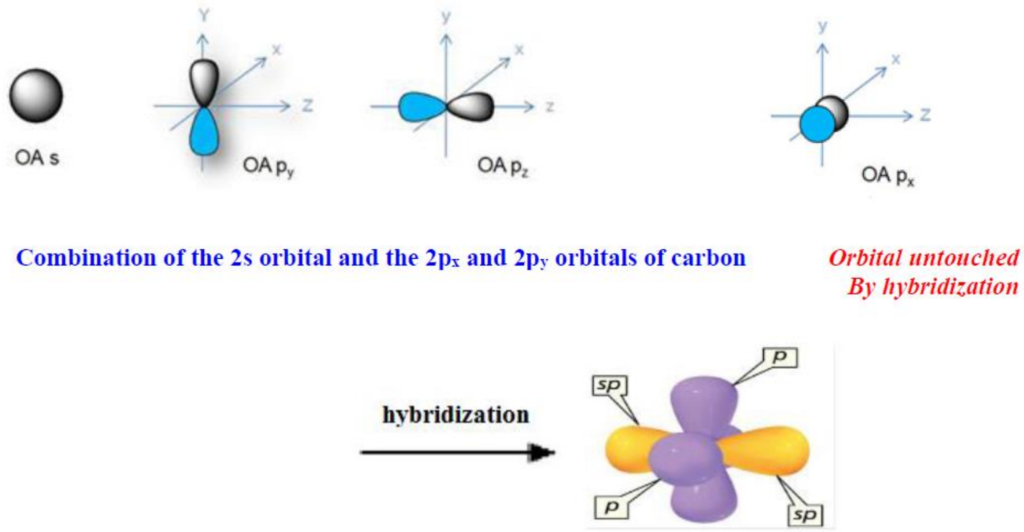
Spatial layout

- Example: $\mathbf{CH_4}$ (methane)



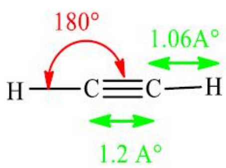
I.5.2.2. sp^2 Hybridization (Trigonal Planar)

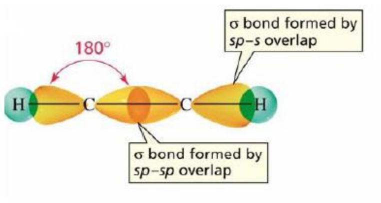
- Combination: 1s + 2p → 3 sp^2 orbitals + 1 unhybridized p orbital
- Geometry: **Trigonal planar**
- Bond angle: ~**120°**
- Example: $\mathbf{C_2H_4}$ (ethylene, double bond).



I.5.2.3. sp Hybridization (Linear)

- Combination: 1s + 1p → 2 sp orbitals + 2 unhybridized p orbitals (py, pz)
- Geometry: **Linear**
- Bond angle: **180°**
- Example: $\mathbf{C_2H_2}$ (acetylene, triple bond).





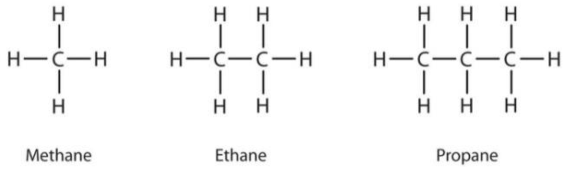
The triple bond between the 2 C
1 σ bond + 2 π bonds

I.6. Structural Formulas

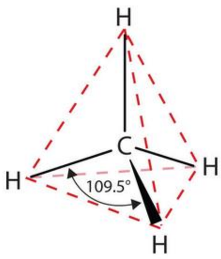
I.6.1. Complete Structural Formula

1. Complete Structural Formula (Lewis Structure)

- Shows **all bonds** between atoms using dashes:
  - Single bond → —
  - Double bond → ═
  - Triple bond → ≡
- Example: Methane (C_2H_6), ethane (C_2H_4), propane (C_3H_8).



- VSEPR theory explains 3D shapes (e.g., methane = tetrahedral).



I.6.2. Condensed Structural Formula

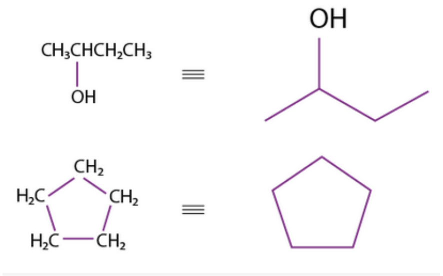
In condensed structural formulas, the bonds to each carbon are omitted, but each distinct structural unit (group) is written with subscript numbers designating multiple substituents, including the hydrogens.

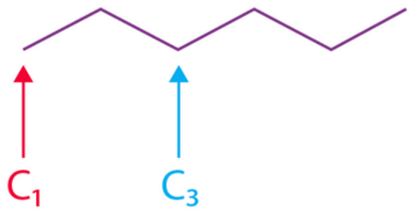
For example, the complete structural formula for ethane, ethene and ethyne is shown as below:

$H_2C = CH_2$	$CH_3\,CH_3$	$HC = CH$
Ethene	Ethane	Ethyne

I.6.3. Bond Line Structural Formula

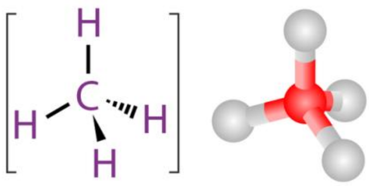
A bond line structural formula is another way of structural representation of organic compounds. Here, every bond is represented as a line in a zigzag manner. If not specified, every terminal is assumed to be a methyl ($-CH_3$) group.





I.6.4. 3D Representation (Wedge-Dash Notation)

- Used to show molecules in **three dimensions**:
  - Solid wedge (▲): bond **coming out** of the plane (toward viewer).
  - Dashed wedge (▿): bond **going back** into the plane (away from viewer).
  - Line (—): bond **in the plane** of the paper.
- Example: methane (CH_4) drawn in wedge-dash form.



I.7. Functional Group Classification

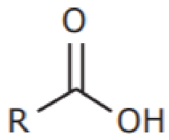
Functional Group Classification

- Inorganic chemistry is organized by the **periodic table**; in organic chemistry, the vast number of compounds is managed by **grouping them into families**.
- **Functional groups**: specific atoms or groups of atoms in molecules that determine characteristic chemical properties.
- These properties are largely **independent of the rest of the molecule**, making classification and study easier.
- The advantage: compounds' **properties and reactivity can be predicted** from their structures.

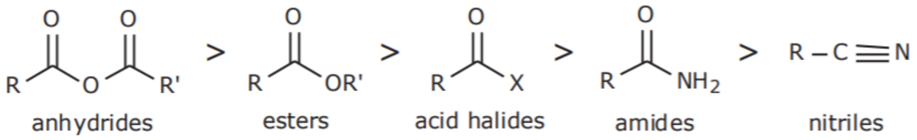
- In **IUPAC nomenclature**, compounds are classified based on the **main functional group**, chosen according to a **priority system**.
- Priority depends on the **oxidation state of the central carbon**: the higher the oxidation state, the higher the priority (e.g., **carboxylic acids** > **alcohols**).

I.7.1. Functional Groups

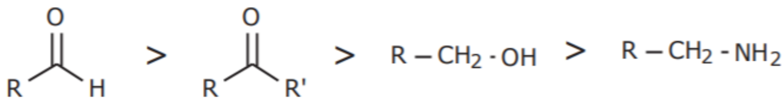
1. Carboxylic Acids **(highest priority among carbon-containing functional groups).**



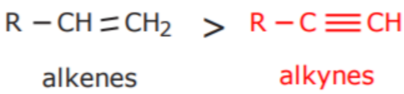
2. Carboxylic Acids derivatives



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

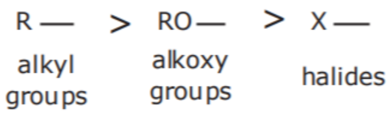


4. **Alkenes and Alkynes**

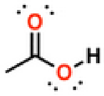
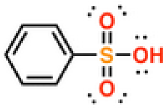
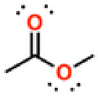
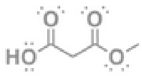
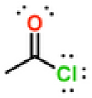
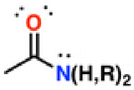
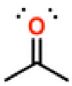


Note: substances containing double and triple bonds are called ***alkenynes.*** (notice that the name ends in *yne*). Chain numbering starts from the end closest to either group, unless they're both equidistant from the chain ends, in which case the *double bond* takes priority and is given the lower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

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



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.		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. ($C \equiv C$) **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

- Early names of organic compounds were based on **origin** (e.g., citric acid from citrus fruits) or **properties** (e.g., aromatic compounds named for fragrance).
- With the discovery of more compound, especially hydrocarbons, **isomerism** became important:
  - **Isomers**: same molecular formula, different bonding/structure.
  - Example: C_4H_{10} → **n-butane** (straight chain) & **isobutane** (branched chain).
- Functional groups greatly **increase the number of possible compound**.
- Random naming was impractical → need for a **systematic nomenclature**.
- **1892 (Geneva):** first systematic rules proposed.
- **1931:** International Union of Chemists (I.U.C.) gave its report → I.U.C. system.
- Later refined by **IUPAC (International Union of Pure and Applied Chemistry)**, which sets the current widely accepted rules.

- Nomenclature of organic compounds is based on **alkanes**.
- **Unbranched alkanes** = *normal (n-) alkanes*.
- **Homologous series**: compounds differing by **–CH_2– unit**.

II.1. Alkane

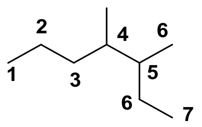
Table: IUPAC Names of straight chain alkanes having general formula C_nH_{2n+2}

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

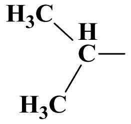
*** Prior to 1979 version of IUPAC rules, icosane was spelled as eicosane.**

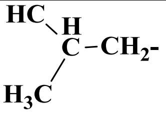
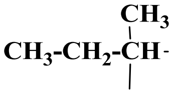
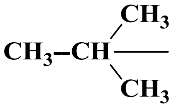
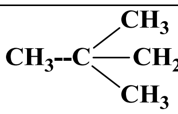
The branched chain alkanes are named by using the following steps:

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.

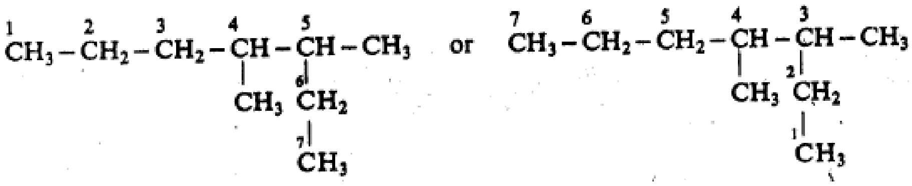


2. Identify the substituent alkyl groups attached to the parent chain. Some common alkyl groups are listed in Table below. You can locate that both the substituents in the example cited above are methyl groups.

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

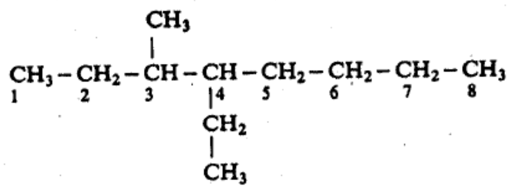
$CH_3CH_2CH_2CH_2$-	*n*-butyl	butyl
	*Iso*-butyl	2-methylpropyl
	*Sec*-butyl	1-methylpropyl
	*tert*-butyl	1,1-dimethylethyl
	*neo*-pentyl	2,2-dimethylpropyl

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:



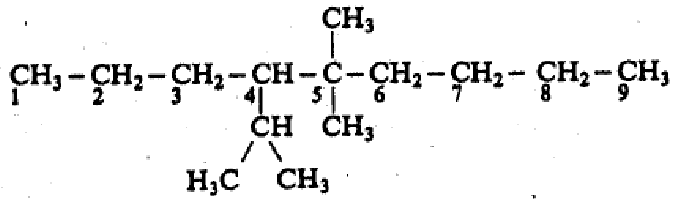
4. Perfixes *di*, *tri*, *tetra*, *penta* etc, are used when the substituents occur more than once. Since in the above compound the methyl substituent is occurring twice, the name is prefixed with *di* for the above compound.
5. The name of the compound is written by writing the location and name of 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:



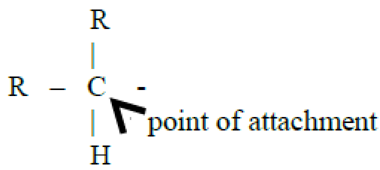
4-ethyl-3-methyloctane

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.

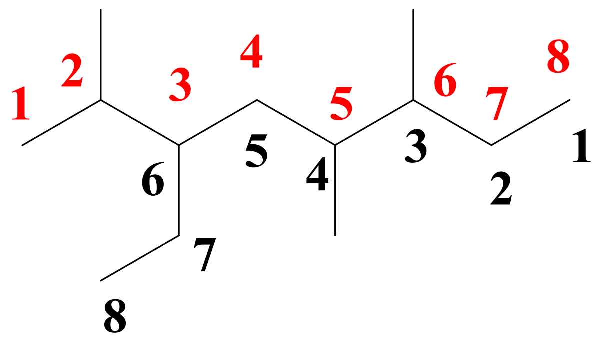
8. The alkyl substituents can be further classified as primary, secondary or tertiary. An alkyl group is called a primary alkyl group if the carbon atom at the point of attachment is bonded to only one other carbon. For example, R – CH_2 – is a primary alkyl group. Similarly, a secondary alkyl group 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:



secondary alkyl group

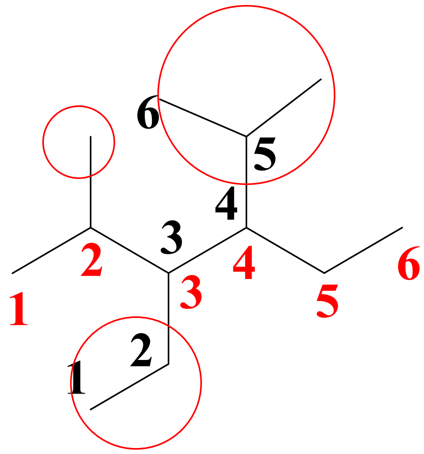
9. When more than one carbon chains of equal length are available, the numbering is done considering the following points:

(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

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

$$\overset{1}{CH_3} - \overset{2}{CH} = \overset{3}{CH} - \overset{4}{CH_2} - \overset{5}{CH_3}$$
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.

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

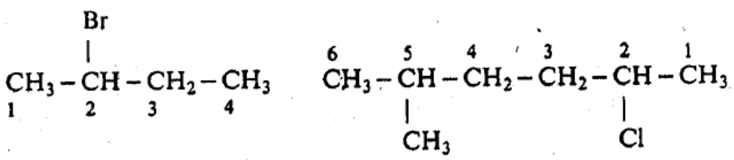
The correct name is pent – l-ene-4-yne

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:

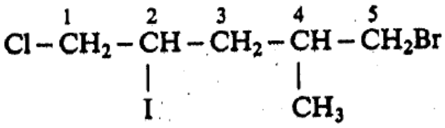
n-butyl chloride isobutyl bromide

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:



2-bromobutane 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,



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.

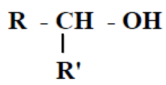
- Name the substituents, and give their numbers as for an alkane or alkene.

- We distinguish:

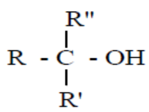
Primary alcohol

R – CH_2OH

Secondary alcohols



Tertiary alcohols

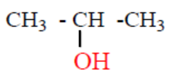


Example

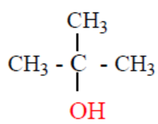
Ethanol

CH_3 - CH_2 - OH

Propan-2-ol



2-methylpropan-2-ol



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:

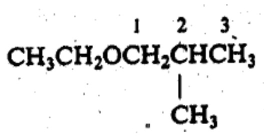
CH_3OCH_3
dimethyl ether

$CH_3OCH_2CH_3$
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,

$$CH_3O\overset{1}{C}H_2\ \overset{2}{C}H_3$$

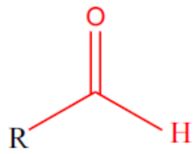
is named as **1-methoxyethane** and not as **ethoxymethane.** Similarly, the compound,



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

II.7. Aldehydes

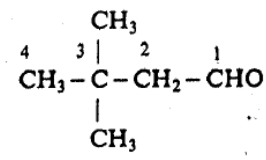
Aldehydes are carbonyl compounds. They have the characteristic group:



aldehydes

Note: Functional carbon is trigonal.

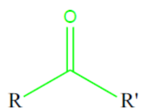
In the IUPAC system of nomenclature, they are named as **alkanals**. The simplest aldehyde is **methanal.** Since the aldehyde group – **CHO**) is always at the end of the chain, it is always numbered as C– 1 in the chain, but this number is not specified in the name, i.e. the compound.



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

II.8. Ketones

ketones are carbonyl compounds. They have the characteristic group:

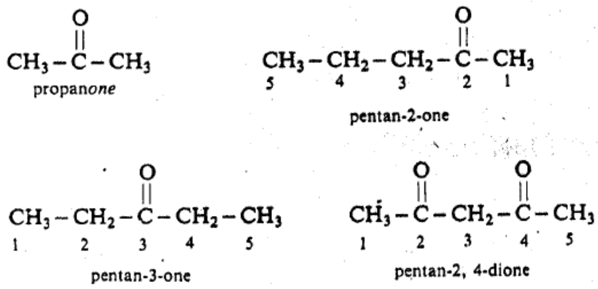


Ketone

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

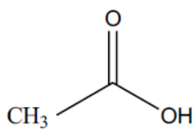


II.9. Carboxylic acids

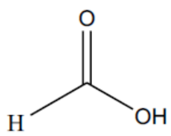
Carboxylic acids have in common the characteristic group: **R – COOH**

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

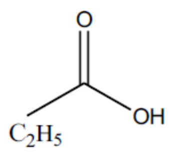
the IUPAC names are derived by replacing ***e*** ending of the alkane by ***oic acid.*** As for aldehydes, the carboxyl carbon is numbered **1**. However, in case of the dicarboxylic acids, the final ***e*** of the hydrocarbon is not dropped.



Ethanoic acid
Acetic acid



Methanic acid
Formic acid



Propanoic acid

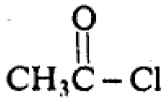
Ex: dicarboxylic acids

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

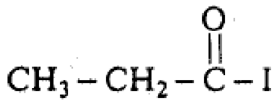
2,3-dihydroxybutanedioic acid (Tartaric acid)

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 $R\text{–}\overset{\overset{O}{||}}{C}-$ acyl group. The acyl group is named by using *yl* as the ending instead of ending *ic*in the carboxylic acid. Some examples are:

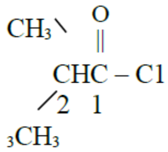


(acet~~ic~~ + yl → acetyl)
acetyl chloride



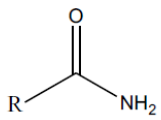
propanoyl iodide

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

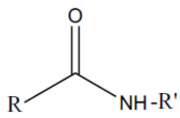


II.11. Amides

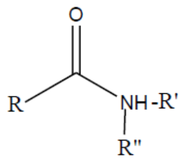
The common names for acid amides are derived by replacing the suffix ***ic*** or ***oic*** of the carboxylic acid by the suffix amide. A distinction is made between primary amides, secondary amides and tertiary amides.



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

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

II.12. Acid anhydrides

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

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

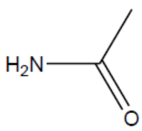
The anhydride which is obtained from ethanic acid (common name: acetic acid) is commonly known as acetic anhydride. The IUPAC name for this anhydride is ethanoic anhydride.

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

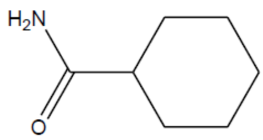
$$H-\overset{\overset{\large O}{\|}}{C}-O-\overset{\overset{\large O}{\|}}{C}-CH_3$$

ethanoic methanoic anhydride
(common name: acetic formic anhydride)

Primary amide:

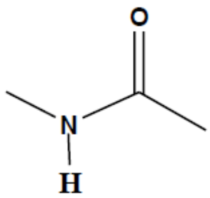


Ethanamide



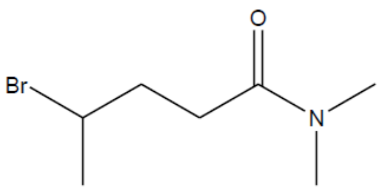
cyclohexanecarboxamide

Secondary amide:



***N*-methylethanamide**

Tertiary amide:

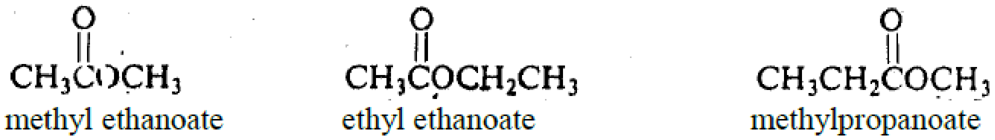


4-bromo-N,N-dimethylpentanamide

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



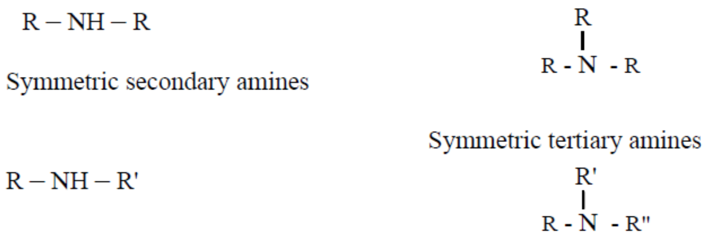
Esters are chemical species that often have a pleasant smell (rose, jasmine, lavender, etc.). They are sometimes the source of natural fruity flavors and are very frequently synthesized for use as food flavorings.

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.

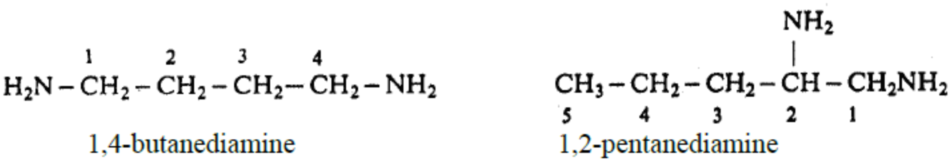
A distinction is made between primary amines, secondary amines and tertiary amines.



Bonding, Functional Group Classification and Nomenclature

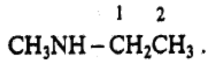
(Note that the numbering starts at the carbon and not at the nitrogen of the amine part).

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

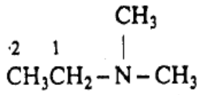


For the secondary and the tertiary amines, the longest alkyl group present is considered as the parent chain. The remaining alkyl groups are named as substituents attached to the nitrogen and a prefix N- is used with the name of the alkyl group.

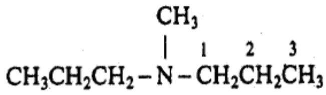
N-methylmethanamine
(common name : dimethylamine)



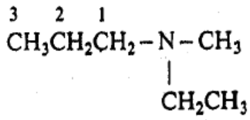
N-methylethanamine
(common name : ethylmethylamine)



N,N-dimethylethanamine
(common name : ethyldimethylamine)

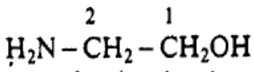


N-methyl-*N*-propylpropanamine
(common name : methyldipropylamine)

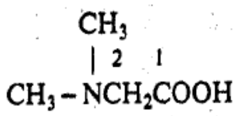


N-ethyl-*N*-methylpropanamine
(common name : ethylmethylpropylamine)

When used as a substituent, the – NH_2 group is named as amino and is prefixed with a number indicating the carbon atom to which it is attached.



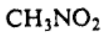
2-aminoethanol



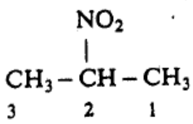
N,N-dimethylaminoethanoic acid

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

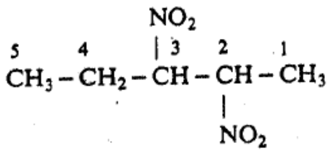
Examples:



nitromethane



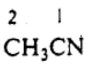
2-nitropropane



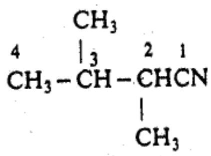
2,3-dinitropentane

II.15. Nitriles

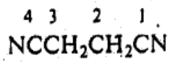
Nitriles are named in the IUPAC system by using the suffix – nitrile to the name of the hydrocarbon corresponding to the longest carbon chain. Note that here the carbon of the nitrile group is included in the numbering of carbon chain and is numbered as position 1. Some examples are given below:



ethanenitrile
(common name : acetonitrile)



2,3-dimethylbutanenitrile



butanedinitrile

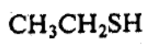
When named as a substituent, the – CH group is called a cyano group. For example, the compound.

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

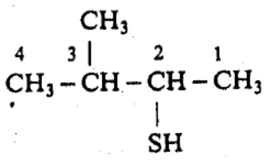
is named as cyanomethyl ethanoate.

II.16. Thiols

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



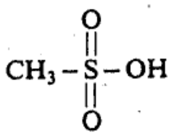
ethanethiol



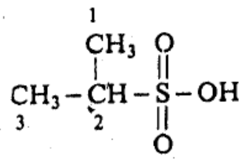
3-methyl-2-butanethiol

II.17. Sulphonic acids

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



methanesulphonic acid



2-propanesulphonic acid

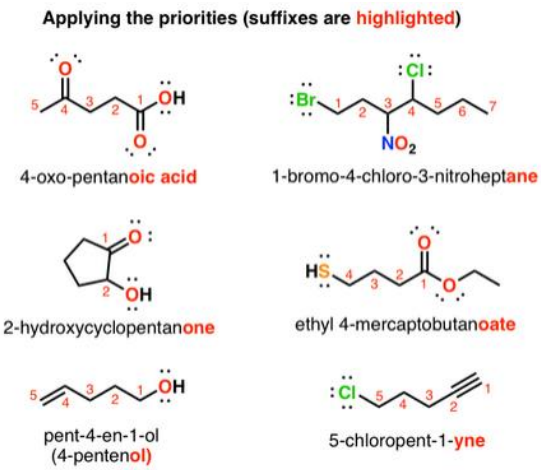
II.18. Some Examples with Multiple Functional Groups

- **Monofunctional compounds**: contain one functional group.
- **Polyfunctional compounds**: contain more than one functional group → one is chosen as the **principal group** (named as suffix).
- **Priority order** (decreasing):

Carboxylic acid > **Sulphonic acid** > **Ester** > **Acid anhydride** > **Acyl halide** > **Amide** > **Nitrile** > **Aldehyde** > **Ketone** > **Alcohol** > **Thiol** > **Amine** > **Alkyne** > **Alkene** > **Ether** > **Halide** > **Nitro**.

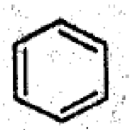
- Rules for priority:
    1. Groups with an **IUPAC suffix that terminate a chain** (e.g., carboxylic acids) = **highest priority**.
    2. Groups with a suffix but can occur **anywhere in chain** (e.g., –OH, $-NH_2$) = **next**.
    3. Groups with **no suffix** (treated as substituents, e.g., halogens) = **lowest priority**.

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.



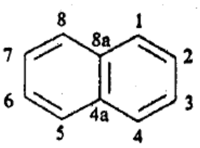
(a) Compounds Containing One Aromatic Ring

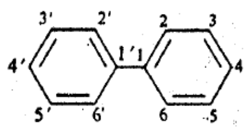
This class includes benzene and its derivatives. The derivatives of benzene include the compounds which can have any of the functional groups discussed before attached to the benzene ring.


benzene

(b) Compounds Containing Two Aromatic Rings

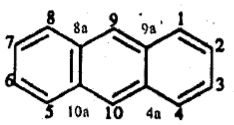
Examples being naphthalene and biphenyl.

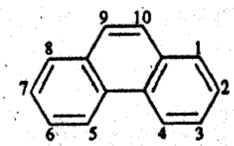

naphthalene


biphenyl

(c) Compounds Having More Than Two Aromatic Rings

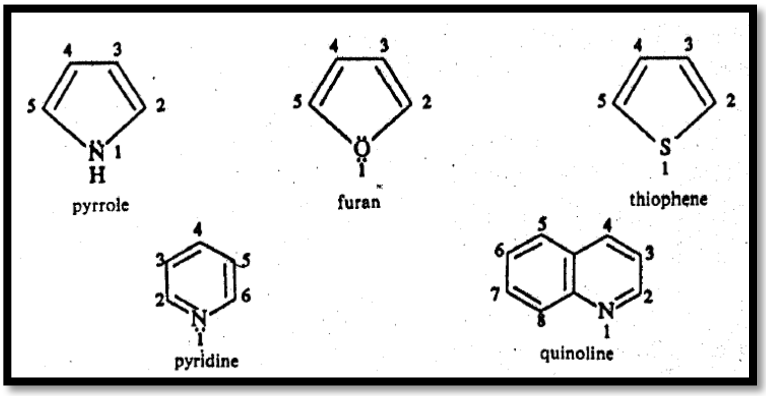
Examples are:


anthracene


phenanthrene

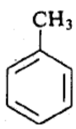
(d) Heterocyclic Compounds

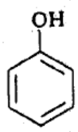
Aromatic compounds containing heteroatoms such as O, N or S in the aromatic ring are called heterocyclic compounds. Some heterocyclic compounds are shown below:

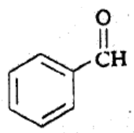


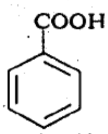
(a) Benzene and its Derivatives

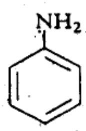
A number of monosubstituted benzene derivatives are known by their special names. These names are in common use for long and hence are approved by IUPAC. Some examples of these compounds are given below along with their common and IUPAC names (in brackets).

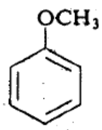

toluene (methylbenzene)


phenol (benzenol)

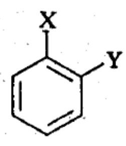

benzaldehyde (benzenecarbaldehyde)

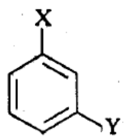

benzoic acid (benzenecarboxylic acid)

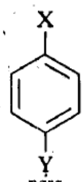

aniline (benzenamine)


anisole (methoxybenzene)

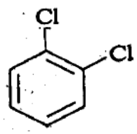
For disubstituted benzene derivatives, the following three arrangements of the substituents are possible.


ortho-

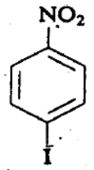

meta-


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:

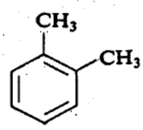


ortho-dichlorobenzene
or *o*-dichlorobenzene

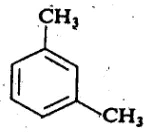


p-iodonitrobenzene

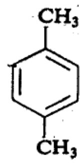
Dimethyl derivatives of benzene are known as xylenes. The three xylenes are;



o-xylene
(1,2-dimethylbenzene)

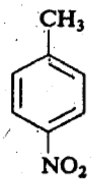


m-xylene
(1,3-dimethylbenzene)

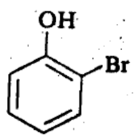


p-xylene
(1,4-dimethylbenzene)

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,

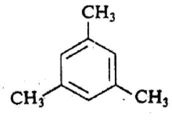


p-nitrotoluene

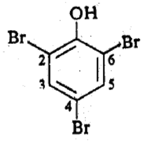


o-bromophenol

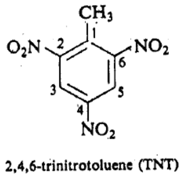
The polysubstituted benzenes are named by identifying the principal functions and then numbering is done such as to keep the principal function as number. The other substituents are then given the lowest possible numbers. This is illustrated in the following examples.



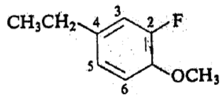
1,3,5-trimethylbenzene
(common name : mesitylene)



2,4,6-tribromophenol



2,4,6-trinitrotoluene (TNT)

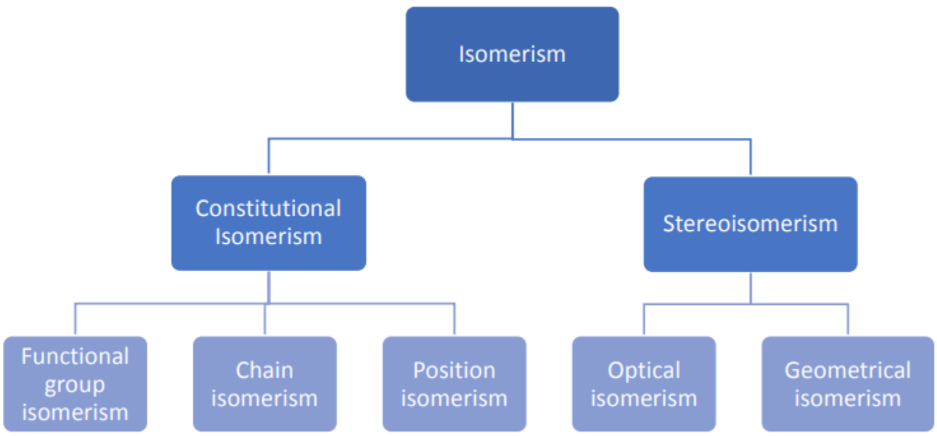


4-ethyl-2-fluoroanisole

III. Introduction to Structural Chemistry

III.1. Notions of stereo-isomerism

- **Isomers**: same molecular formula but different structures → different physical/chemical properties.
- **Two main categories**:
    1. **Constitutional isomers** → differ in **connectivity** of atoms.
    2. **Stereoisomers** → same connectivity but differ in **spatial arrangement**.
        - **Geometrical isomers** (cis/trans).
        - **Optical isomers** (enantiomers).
- **Conformational isomers**: arise from **rotation around single bonds**; usually not considered under classical isomerism since they are not always separable.



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 $CH_3CHCH_2CH_3$	CH_3 CH_3CCH_3 CH_3
C_3H_8O	$CH_3CH_2CH_2OH$	CH_3 CH_3CHOH	$CH_3CH_2OCH_3$
C_4H_8O	H $CH_3CH_2CH_2C{=}O$	CH_3 $CH_3CHC{=}O$ H	CH_3 $CH_3CH_2C{=}O$

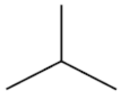
Constitutional isomers (structural isomers) can be different in their chain structures, functional groups due to different connectivity of atoms within the molecule. Different structural isomers are assigned different IUPAC names. Therefore, constitutional isomers can be subcategorized into Chain isomers,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

III.1.1. Chain (Skeletal) Isomerism

- **Definition**: Compounds with the **same molecular formula** but **different carbon skeletons**.
- Difference arises from variations in the **branching of the carbon chain**.
- Results in **different physical properties** of the isomers.

Ex : C_4H_{10} represents two compounds

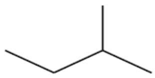

Butane, B.P = -0.5°C

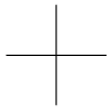

Isobutane B., P. = -10°C

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

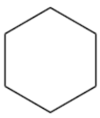

Pentane, B.P = 35°C

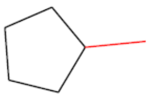

Isopentane B.P = 25°C

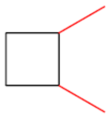

Neopentane, B.P = 9°C

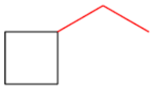
Also, Skeletal isomerism lies between rings and aliphatic (acyclic) alkenes.

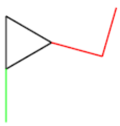
Example: C_6H_{12}, I = 1 (a double bond or a ring).


cyclohexane

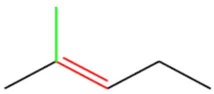

methyl cyclopentane


1,2-dimethylcyclobutane


1-ethylcyclobutane


1-ethyl-2-methyl cyclopropane

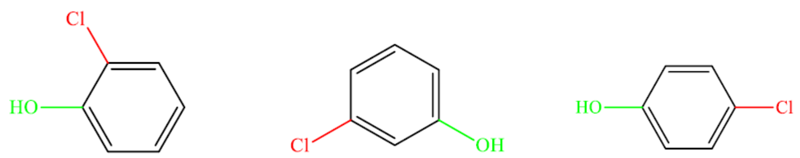

hex-2-ene


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 vary.

Ex 1 : C_6H_5ClOH, I=4.

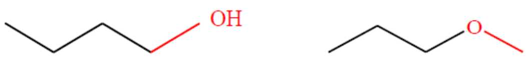


B. P = 195°C ,P.F = 9.3°C	B.P = 214°C, P.F = 33°C	B.P = 219°C P.F = 43.5°C
Ortho chlorophenol	meta chlorophenol	para chlorophenol
2-chlorophenol	2-chlorophenol	3-chlorophenol

Ex 2 : C_3H_7X

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

propanal propanone

III.2. Stereoisomerism

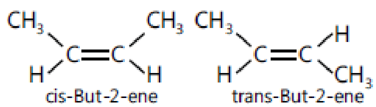
III.2.1. Geometrical Isomerism

- **Cause**: Restricted rotation around **C=C double bond** (σ + π bond).
- **Condition**: Each carbon of C=C must carry **two different groups**.
- **Result**: Different spatial arrangements → **geometrical isomers** (not interconvertible by rotation).

Types:

III.2.1.1. Cis–Trans Isomerism

- **Cis**: similar groups on same side.
- **Trans**: similar groups on opposite sides.

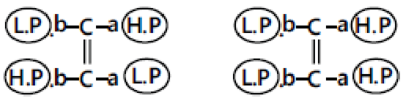


cis-But-2-ene (I) trans-But-2-ene (II)

- **Properties**:
  - Stability: Cis < Trans
  - Dipole moment: Cis > Trans (Sym. trans = 0)
  - Polarity: Cis > Trans
  - Solubility (polar solvents): Cis > Trans
  - Boiling point: Cis > Trans
  - Melting point: Cis < Trans

III.2.1.2. E–Z Isomerism (general system)

- **E (entgegen)** = high-priority groups opposite.
- **Z (zusammen)** = high-priority groups same side.

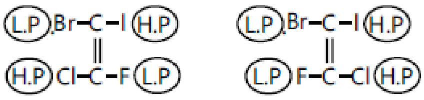


E-Form Z-Form

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

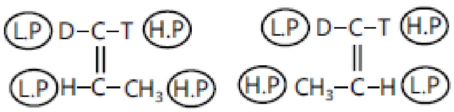
- **Priority rules (Cahn–Ingold–Prelog)**:

1. Higher atomic number → higher priority.



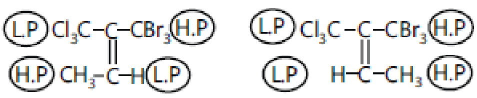
E-Form Z-Form

2. If same → higher atomic mass.

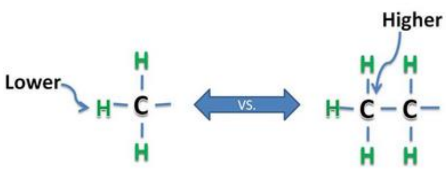


Z-Form E-Form

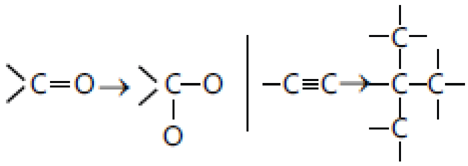
3. If still same → consider next attached atom.



E-Form Z-Form

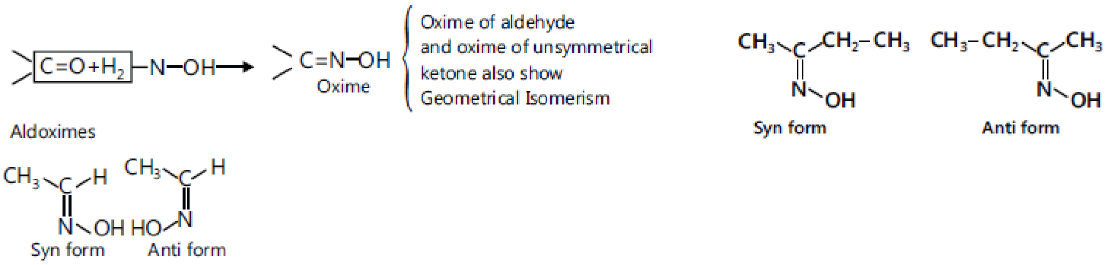


4. Multiple bonds treated as if atoms are duplicated.



III.2.1.3. Syn–Anti Isomerism (older usage, esp. C=N double bonds)

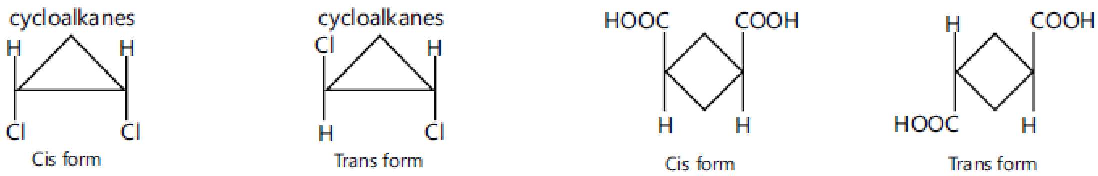
- **Syn**: –OH and H on same side (or OH with alphabetically first alkyl in ketoximes).
- **Anti**: –OH and H (or OH and alkyl) on opposite sides.
- Essentially corresponds to **Z (syn)** and **E (anti)**.



Geometrical & Optical Isomerism

1. Geometrical Isomerism in Cyclic Compounds

- No free rotation in rings.
- **Cis**: substituents on the same side of the ring plane.
- **Trans**: substituents on opposite sides.

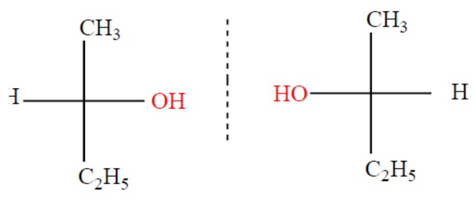


2. Optical Isomerism

- Requires **chirality** (C atom bonded to **4 different groups** = chiral center).
- **Chiral molecules** → optically active.
- **Achiral molecules** → optically inactive.
- **Non-superimposable mirror images** = enantiomers.

Enantiomers:

- Same molecular formula & connectivity.
- Rotate plane-polarized light in **opposite directions** (+ / – or R/S).
- Can differ in chemical/biological activity (e.g., drugs).



Enantiomers

Diastereomers:

- Stereoisomers that are **not mirror images**.
- **Examples**: molecules with multiple chiral centers.

Racemic mixture (racemate):

- 50:50 mixture of two enantiomers.
- **Optically inactive** (rotations cancel).

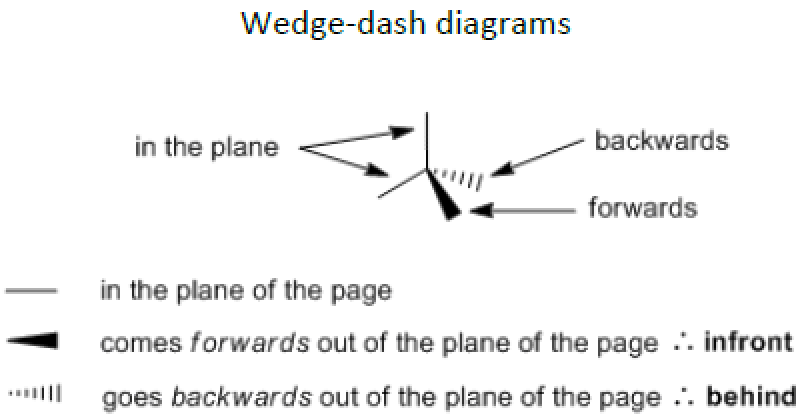
Absolute & Relative Configuration

1. Configuration

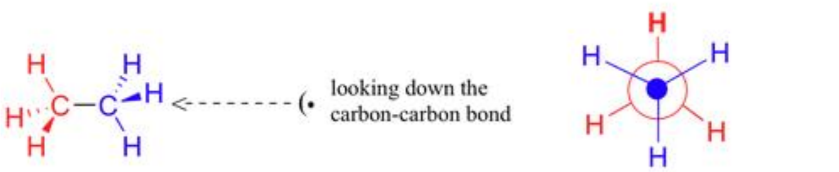
- **Absolute configuration**: exact 3D arrangement of atoms.
- **Relative configuration**: compares arrangement to another known compound.

2. Representations of Chiral Molecules

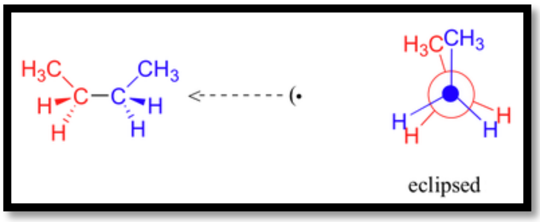
- **Wedge-dash diagrams**
- **Sawhorse formula** (cyclic molecules)

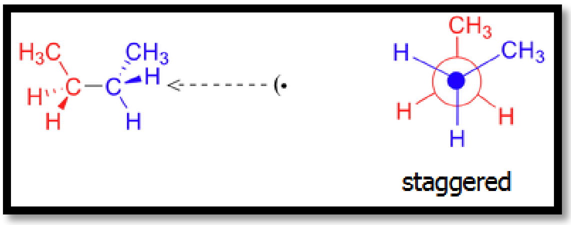


- **Newman projection** (view along C–C bond axis)

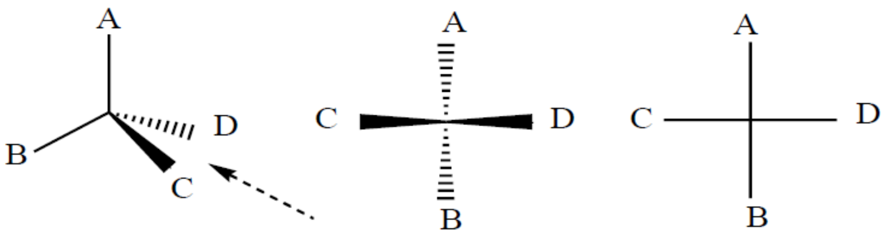


'staggered' conformation
(Newman projection)





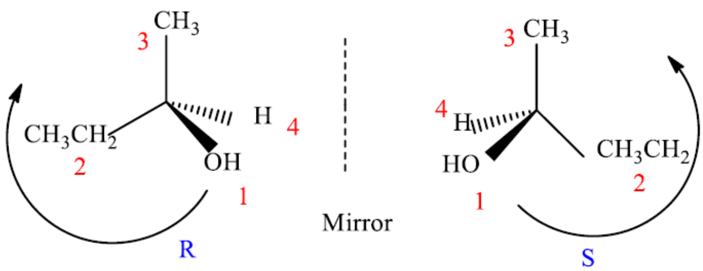
- **Fischer projection**:
  - Vertical = bonds behind plane.
  - Horizontal = bonds in front.
  - Longest chain vertical; most oxidized group at top.



3. Cahn–Ingold–Prelog (CIP) System (R/S Notation)

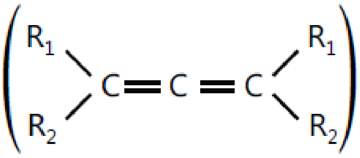
- Assign priorities (atomic number → atomic mass → next atom → treat multiple bonds as repeated atoms).
- Lowest priority group at the back.
- **Clockwise (1→2→3) = R (rectus).**
- **Counterclockwise (1→2→3) = S (sinister).**
- Mirror images: R ↔ S.

$CH_3CH(OH)\,CH_2\,CH_3$



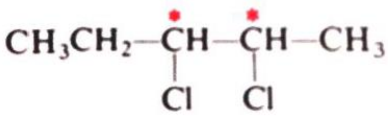
4. Chirality without Chiral Centers

- Possible if the **molecule as a whole is asymmetric** (e.g., allenes like penta-2,3-diene).



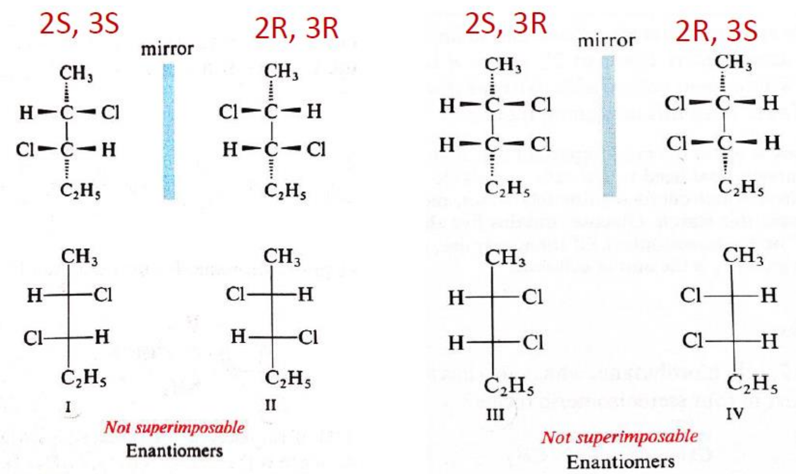
5. Molecules with Multiple Chiral Centers

- Maximum stereoisomers = **2^n** (n = number of chiral centers).



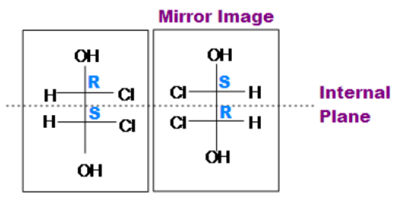
2,3-Dichloropentane

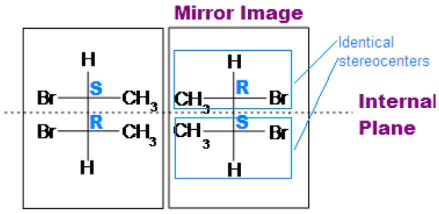
- Example with 2 centers → 4 stereoisomers: (2S,3S), (2R,3R), (2R,3S), (2S,3R).



6. Meso Compounds

- Have ≥2 stereocenters but contain an **internal symmetry plane**.
- Mirror halves cancel stereochemistry → **optically inactive**.





IV. Major reactions in organic chemistry

1. Reaction Mechanism

- Explains **how** and **why** reactions occur.
- Describes the **steps** from reactants → intermediates → products.
- Considers **electronic, geometric, energetic, and kinetic** changes.

2. Key Aspects of a Reaction

- **Electronic aspect** (bond breaking/formation):
  - **Ionic (heterolytic)** → acid/base catalysis.

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

  - **Radical (homolytic)** → favored by heat or light.

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

  - **Molecular (pericyclic)** → orbital reorganization (e.g., Diels–Alder).

- **Geometric aspect** → changes in molecular configuration (stereochemistry).
- **Energetic/Kinetic aspect** → energy variation & reaction rate.

3. Main Types of Organic Reactions

1. **Substitution**
2. **Addition**
3. **Elimination**
4. **Rearrangement (transposition)**

V.1. Electronic Aspects of Chemical Reactions

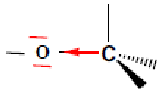
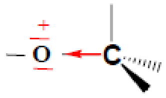
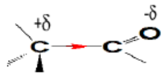
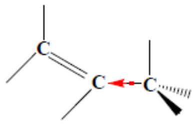
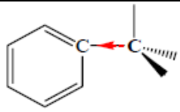
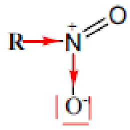
1. Electronic Effects

- Caused by **uneven charge distribution** in molecules.
- Two main types:
  - **Inductive effect**: transmitted through **σ-bonds**.
  - **Mesomeric effect**: due to **π-electron delocalization**.

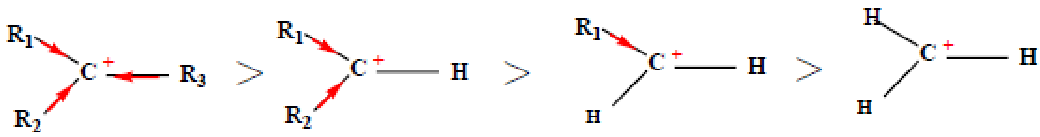
2. Inductive Effect (I-effect)

- Originates from **electronegativity differences**.

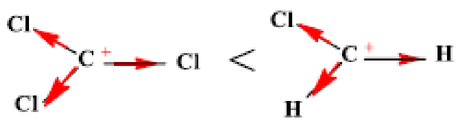
- **-I effect (attractor)** → atoms/groups more electronegative than C (e.g., F, Cl, Br, I, –NO_2).

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

- **+I effect (donor)** → alkyl groups donate electrons, stabilizing carbocations.
- Effect **weakens with distance** along the chain.

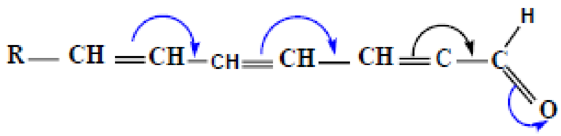


- **Stability**: +I stabilizes carbocations, while –I destabilizes them.

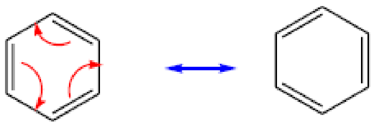


3. Mesomeric Effect (M-effect)

- Results from **delocalization of π electrons** in conjugated systems.

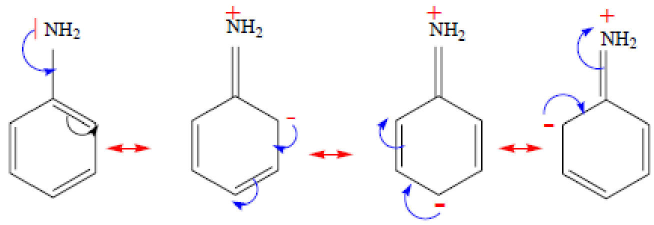


- Propagates without weakening in conjugated chains (e.g., benzene).

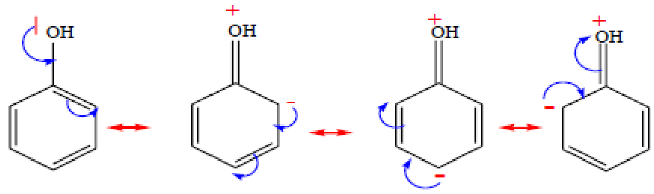


limit form 1 limit form 2

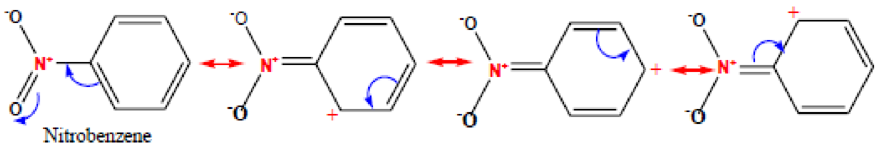
- **+M (electron-donating)**: –OH, –OCH_3, –NH_2 (donate via lone pairs).



Phenol



- **–M (electron-withdrawing)**: –NO_2, –CN, –C=O, halogens.

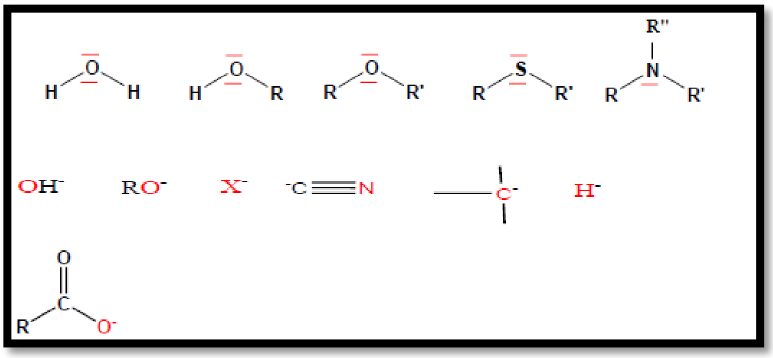


Nitrobenzene

VI.2. Reactions in Organic Chemistry

Types of reagents:

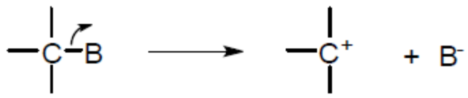
- **Nucleophiles** → electron-pair donors (anions or species with lone pairs). They attack electron-deficient centers.

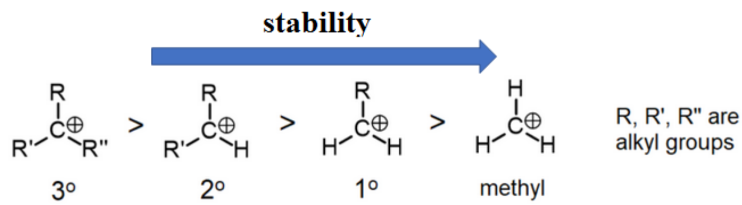


- **Electrophiles** → electron-pair acceptors (cations or electron-deficient molecules).

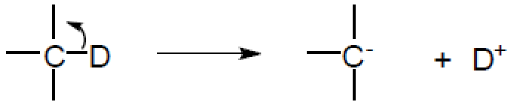
Reactive intermediates:

1. **Carbocations (C^+): (Electrophiles)**
   - sp² hybridized, electron-deficient.
   - Stability ↑ with donor groups, conjugation (mesomeric effect).
   - Destabilized by electron-withdrawing groups.
   - Formation favored in polar protic solvents.





2. **Carbanions (C^-): (Nucleophiles)**
    - sp^3 hybridized, electron-rich.
    - Stability ↑ with electron-withdrawing groups, conjugation.
    - Destabilized by electron-donating groups.
    - Formation favored in polar aprotic solvents.



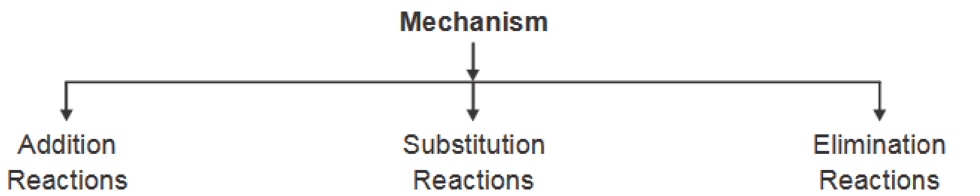
3. **Radicals (C·):**
    - Formed by homolytic bond cleavage (heat/irradiation).
    - Generally sp^2 hybridized.
    - Stability similar to carbocations.

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

VI.3. Organic chemistry mechanism

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

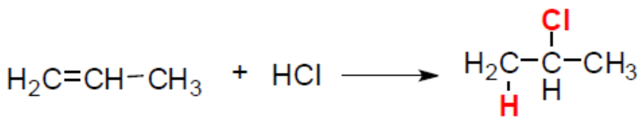
Types of Reaction Mechanism



VI.3. Types of Organic Reactions

1. Addition Reactions (characteristic of multiple bonds)

- **Free Radical Addition**:
    - Follows **Markovnikov's rule** (negative part attaches to C with fewer H).

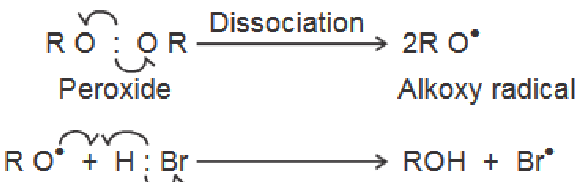


- ○ **Antimarkovnikov addition** occurs with peroxides (Kharasch effect).

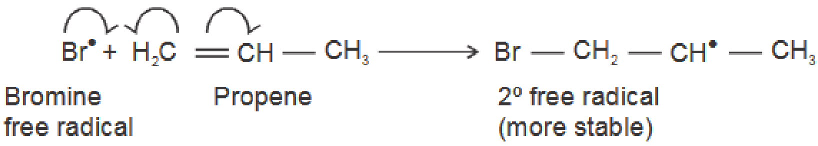
$$\underset{\text{Propene}}{CH_3 - CH = CH_2} + HBr \xrightarrow[\text{(Antimarkowinkoff's addition)}]{\text{Peroxide}} \underset{\text{(n-propyl bromide)}}{CH_3 - CH_2 - CH_2 - Br}$$

- ○ **Mechanism: initiation → propagation → termination.**

- **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.

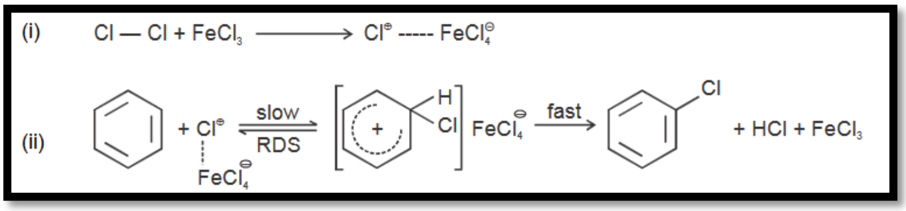
$$Br^{\bullet} + Br^{\bullet} \longrightarrow Br_2$$

- **Nucleophilic Addition**:
  - ○ Seen with **polar groups** (C=O, C≡N, C=S).
  - ○ Nucleophile attacks electron-deficient carbon.
- **Electrophilic Addition**:
  - ○ Step 1: Electrophile adds to π bond → carbocation intermediate.
  - ○ Step 2: Nucleophile attacks carbocation.

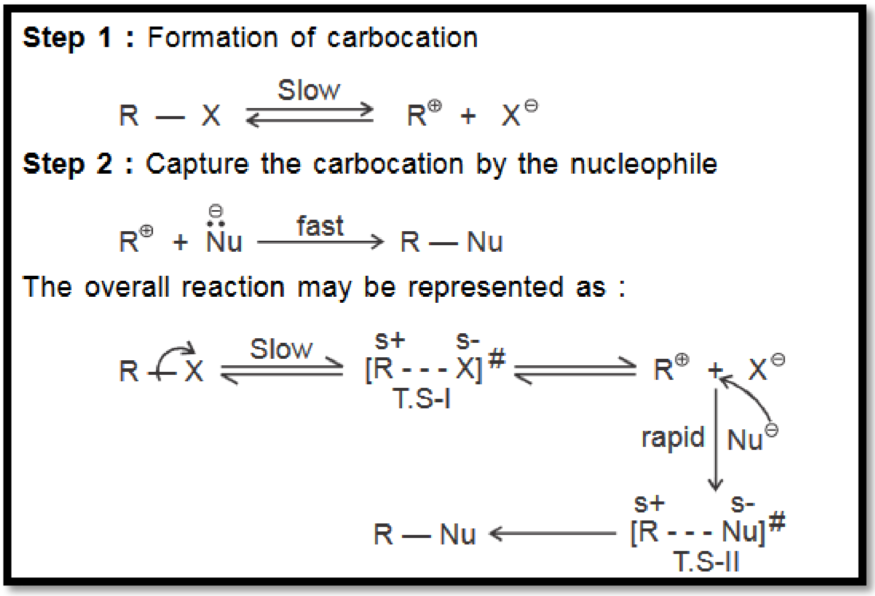
- Examples: addition of Br_2 (color test for alkenes), addition of HX (Markovnikov's rule).

2. Substitution Reactions (replacement of one group by another)

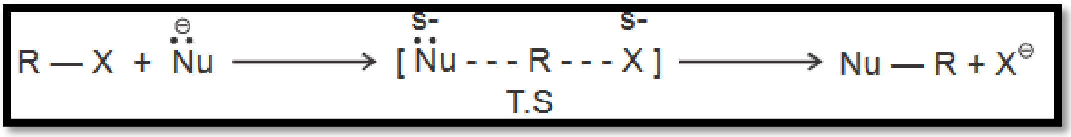
- **Free Radical Substitution**: e.g., halogenation of alkanes.
- **Electrophilic Substitution**: typical of **aromatic compounds** (halogenation, nitration, sulfonation, Friedel–Crafts).



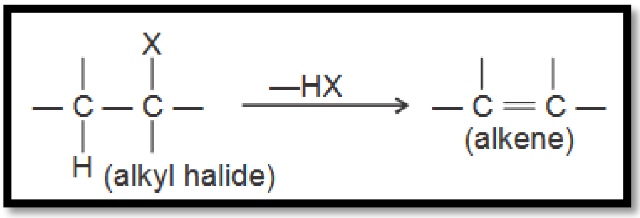
- **Nucleophilic Substitution**:
  - **SN1**: 2-step, carbocation intermediate, 1st order kinetics, partial racemization, possible rearrangements.



  - **SN2**: 1-step, concerted, 2nd order kinetics, backside attack → Walden inversion.

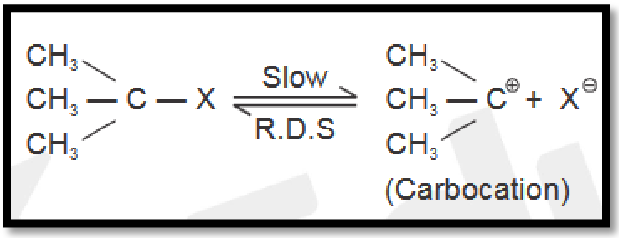


3. Elimination Reactions (reverse of addition)

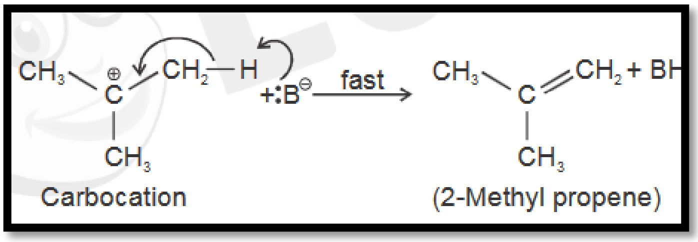


- **E1 (Unimolecular)**:
  - 2-step via carbocation.
  - Regioselectivity: Saytzeff's rule (more substituted alkene).
  - Stereoselectivity: favors E-alkene.

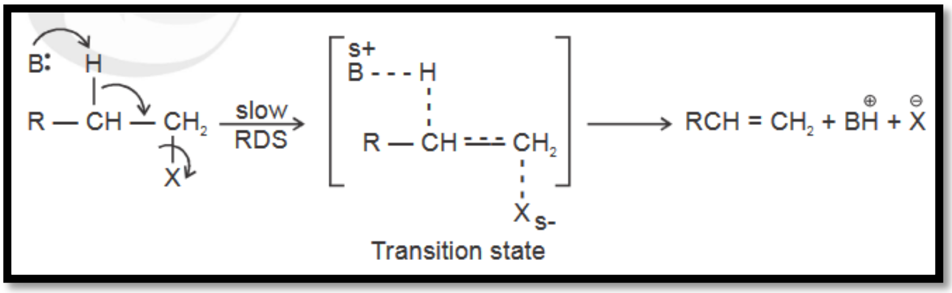
Step 1: The first step is the rate-determining step involving heterolysis of the substrate to form a carbenium ion intermediate that rapidly loses a β-proton in the second step.



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.



- **E2 (Bimolecular)**:
  - 1-step, concerted.
  - Requires anti-periplanar geometry.
  - Rate = k[substrate][base].



4. Rearrangements (Transpositions)

- Migration of atom/group within the same molecule.
- **Types**: nucleophilic, electrophilic, radical.
- **Carbocation rearrangements**: via H^- or R^- shifts → more stable cations.
- **Examples**:
  - n-propyl → isopropyl carbocation.
  - **Pinacol rearrangement** → ketones.
  - **Benzylic transposition** → α-hydroxy acids.
  - **Baeyer–Villiger oxidation** → ketones → esters.