

**Organic chemistry- Some Basic Principles
and Techniques****CLASS-11****SUB-CHEMISTRY**

The hydrides of carbon (hydrocarbons) and their derivatives are called organic compounds. The branch of chemistry which

deals with these compounds is called organic chemistry.

Berzelius (1808) defined organic chemistry as the chemistry of substances found in living matter and gave the vital force theory.

Synthesis of urea. The first organic compound synthesised in laboratory, by Wohler.

Reasons for Large Number of Organic Compounds

(a) **Catenation** It is the tendency of self combination and is maximum in carbon. A carbon atom can combine with other carbon

atoms by single, double or triple bonds. Thus, it forms more compounds than the others.

(b) Tetravalency and small size Carbon

being tetravalent, is capable of bonding with four other C atoms or some other monovalent atoms. Carbon can form compound with oxygen, hydrogen, chlorine, sulphur, nitrogen and phosphorus. These compounds have specific properties depending upon the nature of the element or group attached with the carbon.

Furthermore, these compounds are exceptionally stable because of the small size of carbon.

General Characteristics of Organic Compounds

1. These are the compounds of carbon with H, O, N, S, P, F, Cl, Br and I.
2. These are generally found in living organisms. e.g., carbohydrates, proteins etc.
3. These may be gases, liquids or solids.

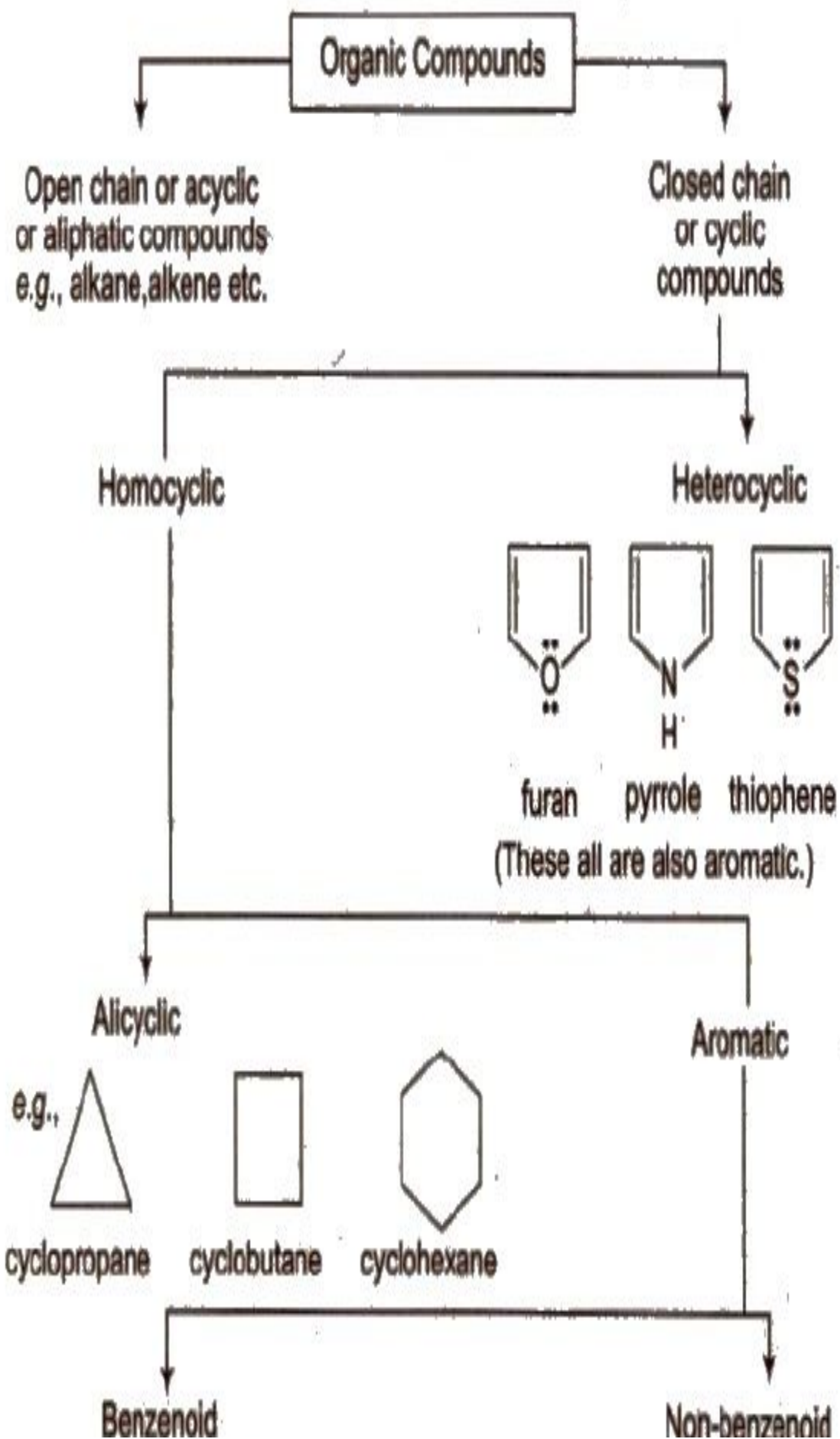
4. Being covalent in nature, these have low boiling point and melting point and soluble in organic solvents.

5. These are generally volatile and inflammable.

6. They do not conduct electricity because of the absence of free ions.

7. They possess distinct colour and odour.

Classification of Organic Compounds



Classification of Carbon Atoms

1. On the Basis of Number of C Attached

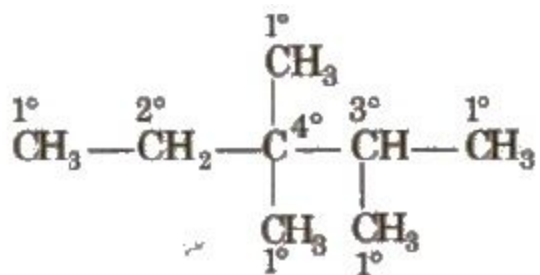
(i) **Primary carbon atom** When carbon atom is attached with one other carbon atom only, it is called primary or 1° carbon atom.

(ii) **Secondary carbon atom** When carbon atom is attached with two other carbon atoms, it is called secondary or 2° carbon atom.

(iii) **Tertiary carbon atom** When carbon atom is attached with three other carbon atoms, it is called tertiary or 3° carbon atom.

(iv) **Quaternary carbon atom** When carbon atom is attached with four other carbon atoms, it is called quaternary or 4° carbon atom.

Reactivity order of carbon atoms is as follows
 $3^\circ > 2^\circ > 1^\circ$.



On the Basis of Position of Functional Group

(i) **α – carbon** Carbon which is directly attached to the functional group.

(ii) **β - carbon** Carbon which is directly attached to the n-carbon.

Functional Group

The atom e.g., -Cl, -Br etc., or group of atoms e.g., -COOH, -CHO, which is responsible for the chemical properties of the molecule, is

called functional group

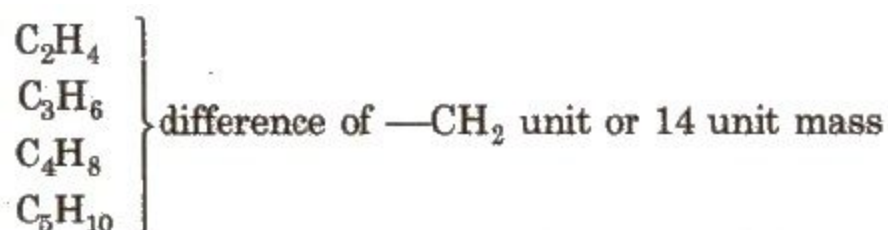
Double and triple bonds are also functional groups.

$R - F \leftarrow$ functional group.

R is called alkyl group, it contains only single bond; alkenyl group if contains double bond and alkynyl group if contains triple bond.

Homologous Series

The series in which the molecular formula of adjacent members differ by a $-\text{CH}_2$ unit, is called homologous series and the individual members are called homologous. e.g., The homologous series of alkene group is



The general characteristics of this series are :

1. All the homologues contain same functional group. That's why their chemical properties are almost similar.

2. All the members of a series have same general formula, e.g.,

Series	General formula
Alkanes	C_nH_{2n+2}
Alkenes	C_nH_{2n}
Alkynes	C_nH_{2n-2}
Alcohol and ether	$C_nH_{2n+2}O$
Aldehyde and ketone	$C_nH_{2n}O$
Acid and ester	$C_nH_{2n}O_2$

3. All the members can be prepared by almost similar methods.

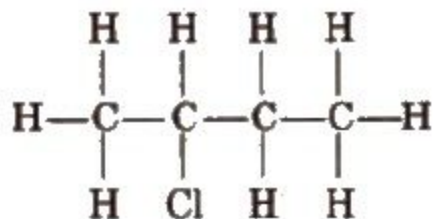
4. With increase in the molecular weight of a series, the physical properties varies gradually.

Representation of Different Formulae

An organic compounds can be represented by the following ways :

1. Complete formula

In it, all the bonds present between any two atoms are shown clearly.



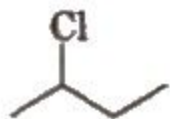
2. Condensed Formula

In it, all the bonds are not shown clearly.

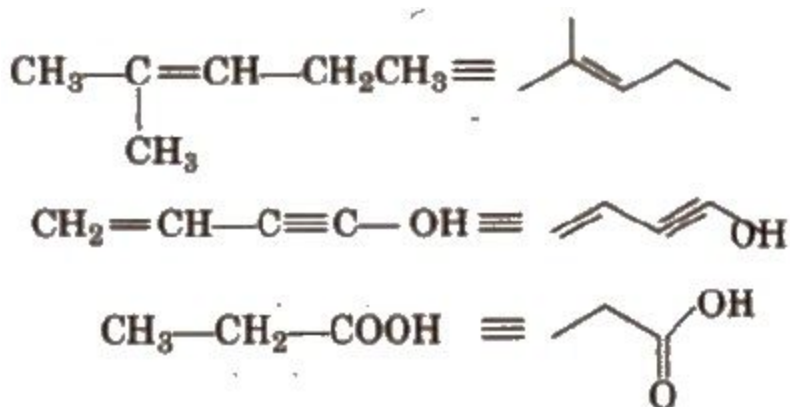


3. Bond Line Formula

In it, every fold and free terminal represents a carbon and lines represent the bonds. e.g.,



In such formulae, it is assumed that required number of H-atoms are present, where ever, they are necessary (to satisfy tetravalency of carbon) e.g.,



Nomenclature of Organic Compounds

Trivial System

It is the oldest system in which names are derived from source or some property. These are mainly derived from Latin or Greek names e.g.,

acetic acid (acetum = vinegar), oxalic acid (oxalic), malic acid (pyrus malus), citric acid (citric), formic acid (obtained from red ant)

IUPAC System

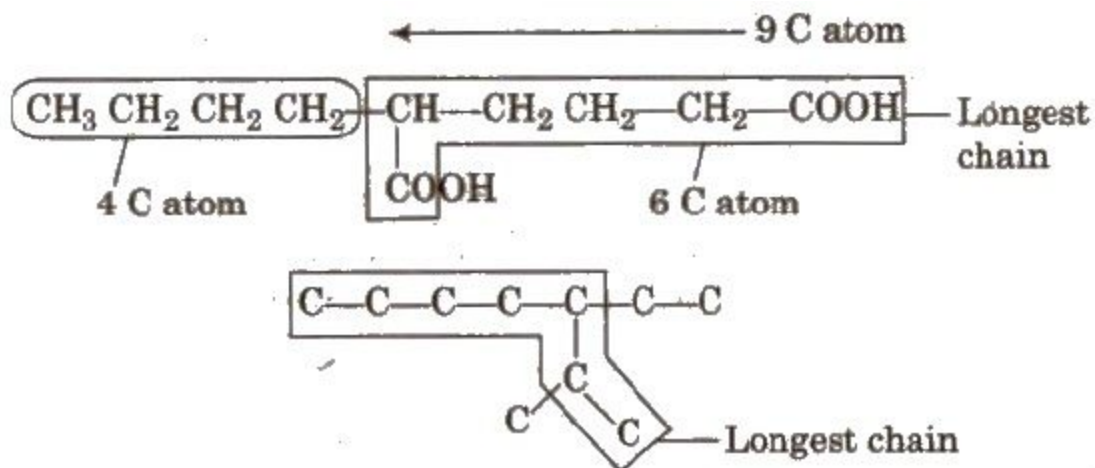
The IUPAC (International Union of Pure and Applied Chemistry) system, given in 1957, is superior and widely used. IUPAC amends these rules from time to time. Here, we are following the 1993 recommendations of IUPAC nomenclature.

Following rules are used to write the IUPAC name of an organic compound.

Rule I

Longest chain rule The chain containing the principal functional group, secondary functional group and multiple bonds as many as possible is the longest possible chain.

In the absence of functional group, secondary group and multiple bonds, the chain containing the maximum number of C-atoms will be the longest possible chain e.g



Choose the word root from the table given below for the longest possible chain.

Word Root for Carbon Chain

Chain length	Word root	Chain length	Word root
C ₁	Meth-	C ₇	Hept
C ₂	Eth-	C ₈	Oct
C ₃	Prop-	C ₉	Non
C ₄	But-	C ₁₀	Dec
C ₅	Pent	C ₁₁	Undec
C ₆	Hex-	C ₁₂	Dodec

Rule 2

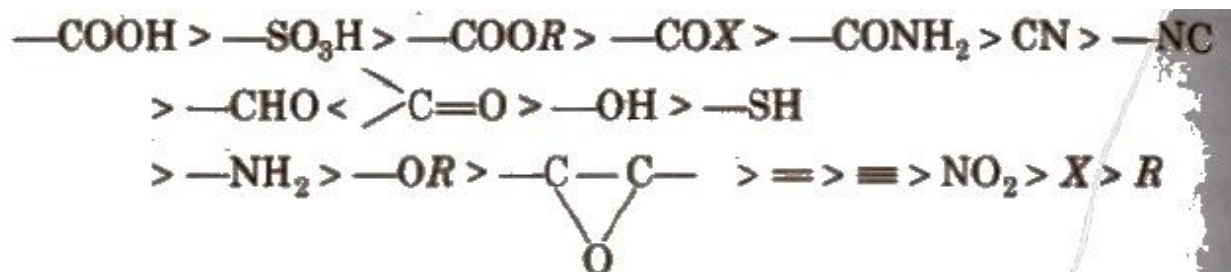
Lowest number rule Numbering is done in such a way so that

1. branching if present gets the lowest number.

2. The sum of numbers of side chain is lowest.

3. The principal functional group gets the lowest number.

Select the principal functional group from the preference series :



Functional group other than the principal functional group are called substituents.

Rule 3.

Naming the prefixes and suffixes Prefix represents the substituent and suffix is used for principal functional group.

Primary prefixes are cycle, bicyclic, di, tri, tetra, penta, hexa, hepta, octa, nona, deca, undeca, dodeca etc.

Secondary prefixes are tabulated below :

Substituent	Prefix	Substituent	Prefix
—F	Fluoro	—N=N—	diazo
—Cl	Chloro	—N=O	nitroso
—Br	Bromo	—NO ₂	nitro

Primary suffix are ene, ane, or yne used for double, single and triple bonds respectively.

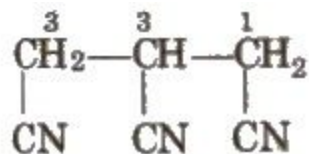
Secondary suffixes are tabulated below :

S. No.	Class	Formula	Prefix	Suffix
1.	Acid halides	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—X} \end{array}$	halocarbonyl	—oyl halide —carbonyl halide
2.	Alcohols	—OH	hydroxy	—ol
3.	Aldehydes	—CHO	formyl	—al —carbaldehyde
4.	Ketones	$\begin{array}{c} > \text{C}=\text{O} \end{array}$	oxo	—one
5.	Amides	—CONH ₂	carbamoyl	—amide
6.	Amine	—NH ₂	amino	—amine
7.	Carboxylic acid	—COOH	carboxy	—carboxylic acid
8.	Ester	—COOR	oxy carbonyl	—alkyl alkanoate
9.	Nitriles	—CN	cyano	—nitrile
10.	Sulphonic acid	—SO ₂ —OH	sulpho	—sulphonic acid

Hence, according to the rules, given above, the IUPAC name of a compound can be written as

or Prefixes + Root word + Suffixes Primary
prefix + secondary prefix + Root word +
primary suffix + secondary suffix

If more than two similar functional groups are present, all the groups are considered as substituent, e.g.,



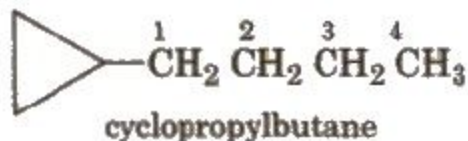
propane-1, 2, 3-cyanide

Naming Alicyclic Compounds

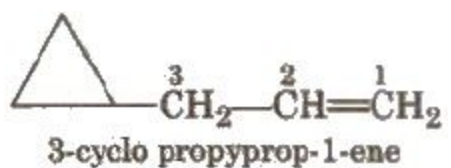
For alicyclic compounds, prefix cyclo is used

e.g.,

If the alkyl chain contains a greater number of C-atoms than the ring, the ring is designated as substituent, e.g.,



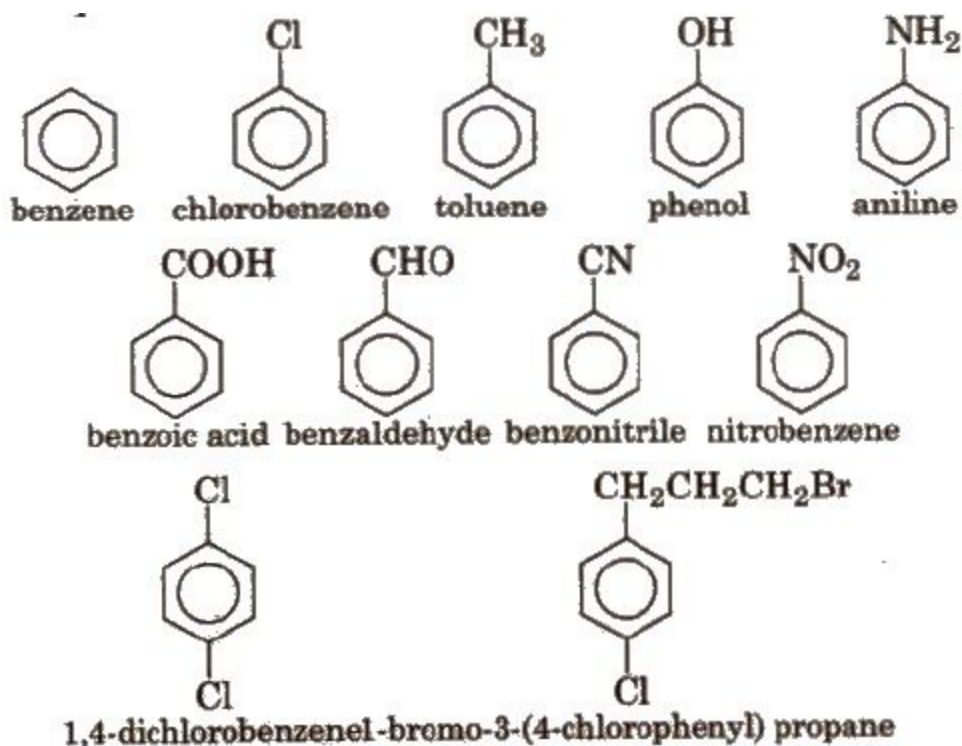
If side chain contains a multiple bond or a functional group, the ring is treated as a substituent e.g



Naming Aromatic Compounds

IUPAC accepted their common trivial names

e.g.,

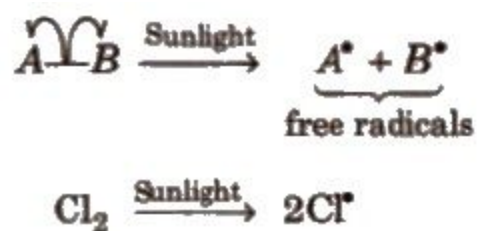


Fission of a Covalent Bond

1. Homolytic Fission

In this, one of the electrons of the shared pair in a covalent bond goes with each of the bonded atoms. The neutral chemical species

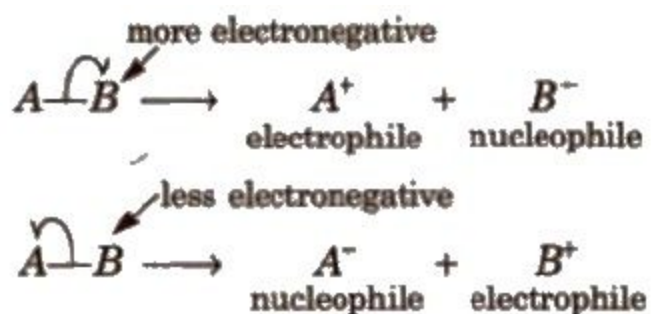
thus formed, is called free radical. Generally, homolytic fission takes place in non-polar, covalent molecules in the presence of sunlight or high temperature.



Free radicals are highly reactive. neutral and electron deficient species

2. Heterolytic Fission

In this, the bond breaks in such a fashion that the shared pair of electrons goes with one of the fragments.



Carbon bearing a positive charge is called carbocation and carbon bearing negative charge is called carbanion.

Heterolytic fission generally takes place in polar covalent molecules but in non-polar

molecules, it takes place in the presence of catalyst like AlCl_3 (anhy.), FeCl_3 (anhy.)etc.

Attacking Reagent

These are of two types :

1. Electrophiles or Electrophilic Reagents

These are electron deficient species i.e., behave as Lewis acids. The following species behave as electrophiles :

(i) All non-metal cations and metal cations which have vacant d- orbitals.

e.g., Cl^+ , NO_2^+ , CH_3CO^+ etc.

(ii) Lewis acids (incomplete octet) e.g., BF_3 , ZnCl_2 (anhydrous), FeCl_3 (anhydrous), AlCl_3 (anhydrous), $:\text{CH}_2$ etc.

(iii) Non-metal (acidic) oxides e.g., CO_2 , SO_2 etc.

2. Nucleophiles or Nucleophilic Reagents

These are electron rich species i.e., behave as Lewis bases.

These attack at electron deficient area.

The following species behave as nucleophiles

:

(i) All anions *e.g.*, Cl^- , NH_2^- , OH^- etc.

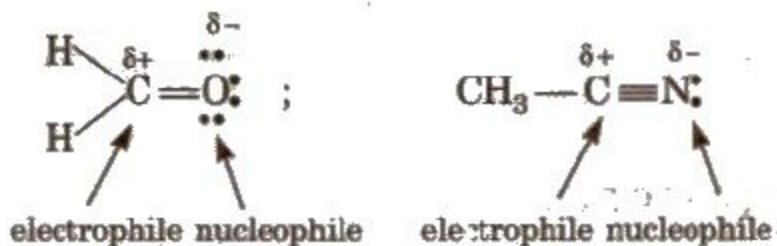
(ii) Lewis bases *e.g.*, :NH_3 , H_2O , $\text{R}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}-\text{R}$, $\text{R}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}\text{H}$ etc.

(iii) Benzene, alkenes etc.

Nucleophilicity order is



In case of same nucleophilic site,
nucleophilicity parallels basicity i.e.. as the
basicity increases, nucleophilicity also
increases.



Reaction Intermediates

These are formed as a intermediate during the course of a reaction.

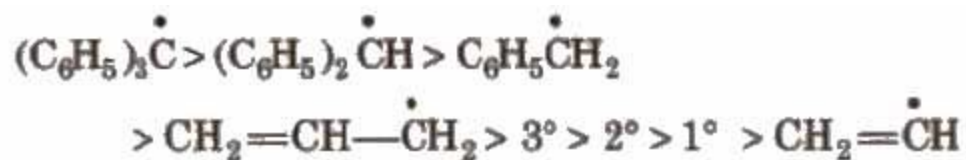
These are short lived and highly reactive.

Free radicals, carbocations, carbanions, carbenes and nitrenes are important reactions intermediates.

1. Free Radicals

These are the product of homolysis and contain an odd electron. These are highly reactive planar species with Sp^2 hybridisation.

Their order of stability is



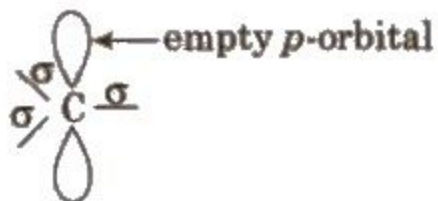
2. Carbocations

These are the product of heterolysis and contain a carbon bearing positive charge.

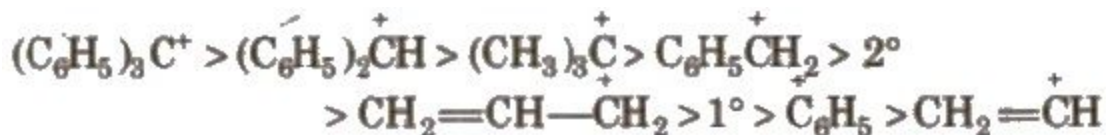
These are electron deficient species.

Carbocations contain six electrons in the valence shell.

These are also planar chemical species i.e., sp^2 hybridised with an empty p-orbital



The stability order of carbocations is

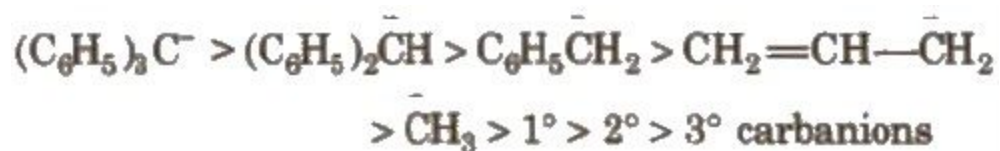


3. Carbanions

These are also the product of heterolysis and contain a carbon bearing negative charge and 8 electrons in its valence shell

These have pyramidal shape with Sp^3 hybridised carbon (having one lone pair)

The order of stability of carbanions is

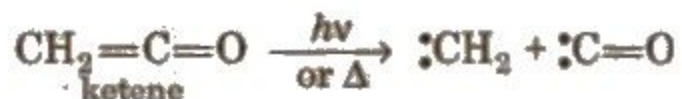


4. Carbenes

These are divalent carbon species having two non-bonding electrons along With two bond pairs.

These are obtained by photolysis or pyrolysis.

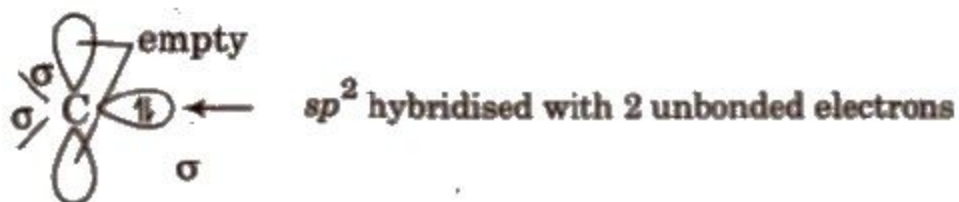
e.g.,



These being electron deficient behave as Lewis acids. These are of two types:

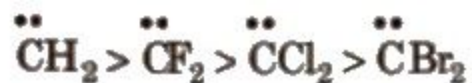
(i) **Singlet carbene** In it, the C-atom is Sp² hybridised. Then Hybridised orbitals contain

no electrons and a hybridised orbital contains two electrons :

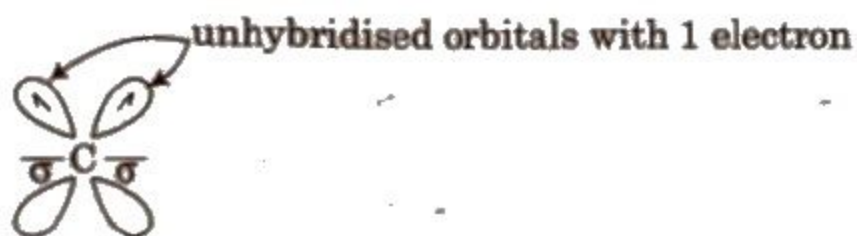


Singlet carbene has bent structure and is less stable than triplet carbene.

The order of stability of singlet carbenes is



(ii) **Triplet carbene** In it, the central C-atom is sp -hybridised. The sp – hybridised orbitals contain 1 electron each .



Triplet carbene has linear geometry.

5. Nitrene

These are neutral monovalent nitrogen species in which N atom has two unshared

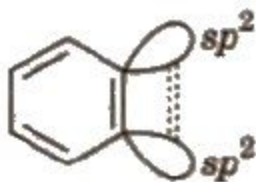
pair of electrons with a monovalent atom or group attached.



These are obtained by thermolysis of azides and as reactive as carbenes.

6. Arynes

It contains a formal carbon-carbon triple bond in aromatic molecule.



The additional bond is formed between two neighbouring C-atoms by sideways overlapping of two Sp² orbitals. The new bond lies along with side of the ring and has little interaction with the 1t electron cloud lying above and below the ring.

The sideways overlapping is weak and thus, makes the benzene more reactive.

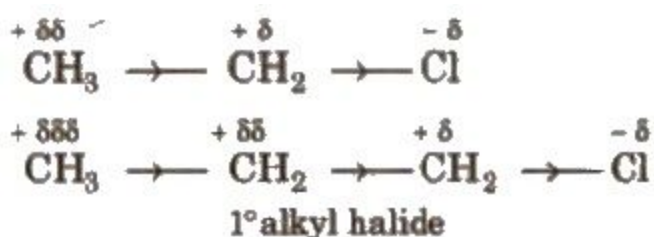
Inductive Effect

It is just like shifting of shared pair of electrons in polar covalent molecules. If shared pair is more shifted towards the more electronegative atom, the less electronegative atom acquires slight positive charge and more electronegative atom acquires partial negative charge, e.g.,



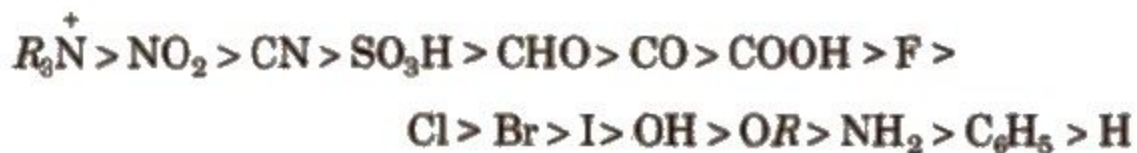
It is a permanent effect and propagates through carbon chain.

Atoms or groups having greater electron affinity than hydrogen. are said to have electron attracting or negative inductive effect (- I) while that having, smaller electron affinity than hydrogen are said to have electron releasing or positive inductive effect (+ I) e.g.,

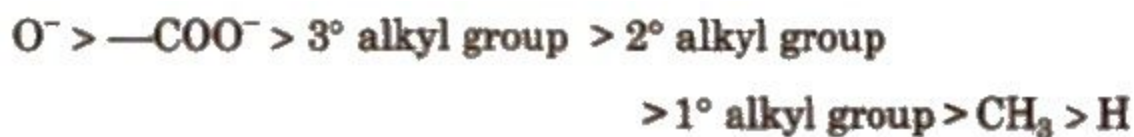


Here, Cl has – I effect and alkyl group has + I effect.

Order of groups producing – I effect is



Order of groups producing + I effect is



Applications of Inductive Effect

1. Presence of groups showing + I effect increases the stability of carbocation while presence of groups showing – I effect decreases their stability.

2. Strength of acid increases with the attachment of group showing $-I$ effect and decreases with the attachment of group showing $+I$ effect.

3. Presence of $+I$ showing groups increases the basic strength of amines.

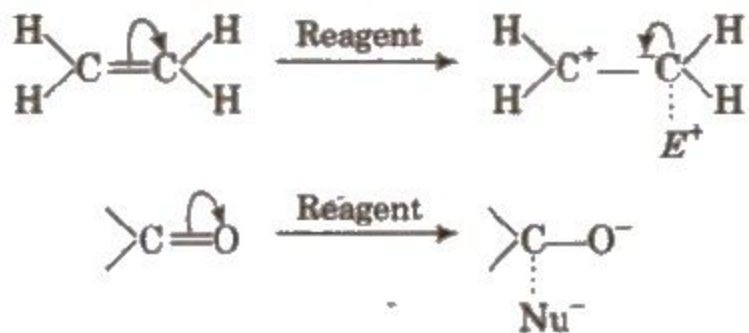
4. Reactivity of carbonyl compound is increased by $-I$ showing groups.

5. Reactivity of alkyl halides towards S_N1 is increased by $+I$ showing groups.

Electromeric Effect

It is defined as the polarity produced in a multiple bonded compound as a reagent approaches it. In the presence of attacking reagent, the two π electrons are completely transferred to any of the one atom. This effect is temporary.

This may be of + E type (when displacement of electron pair is away from the atom or group) or of – E type (when the displacement is towards the atom or group). e.g.,



Hyperconjugation

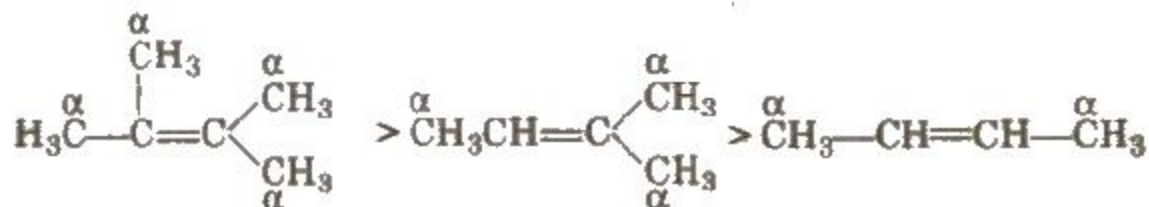
It involves delocalisation of σ electron of a C – H bond of an alkyl group attached directly to an atom of unsaturated system or to an atom with an unshared p-orbital.



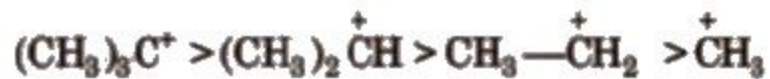
This effect is also called no bond formation or Baker Nathan effect.

Applications of Hyperconjugation

(i) **Stability of alkenes** More the number of α -hydrogen atoms, more stable is the alkene.



(ii) **Stability of carbocation** Greater the number of alkyl groups attached to a positively charged carbon atom, the greater is the stability.



Resonance Effect

When all the properties of a molecule cannot be shown by a single structure and two or more structures are required to show all the properties of that molecule, then the structures are called resonating structures or canonical forms and the molecule is referred as resonance hybrid. This phenomenon is called resonance.

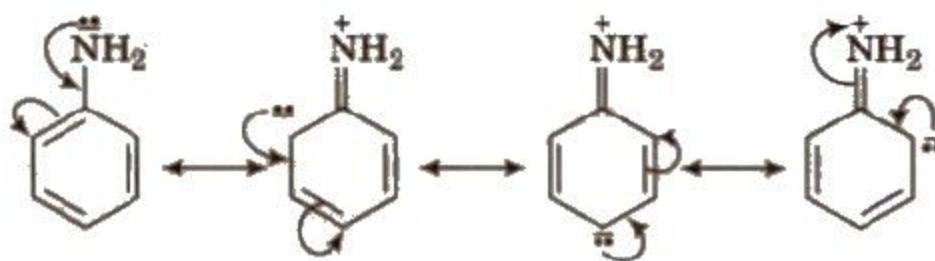
In resonance,

1. The arrangement of atoms must be identical in all the formulae.
2. The energy content of all the canonical forms must be nearly same.
3. Each canonical form must have the same number of unpaired electrons.

It involves delocalisation of π electrons. This effect may be of + R type or – R type.

Positive Resonance Effect (+R)

Electron donating groups with respect to conjugate system show +R effect. Central atom of functional groups should be more electronegative than the surrounding atoms or groups to show +R effect. e.g., halogens, -OH, -OR, -OCOR, -NH₂, -NHCOR etc

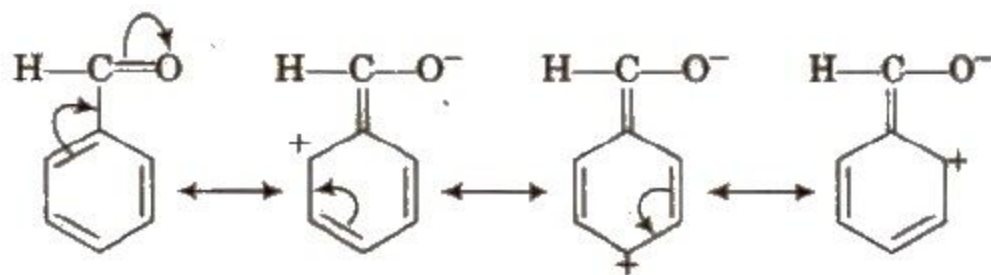


Electron donating groups producing + R effect are ortho and para directing. They activate the benzene ring towards the electrophilic SUBstitution reactions except

halogens. Halogens slightly deactivate the benzene ring towards the electrophilic substitution reaction. More the E.D.G. more is the basic nature.

Negative Resonance Effect (-R)

Electron withdrawing groups with respect to conjugate system show – R effect. Central atom of functional groups should be less electronegative than surrounding atoms or groups to show – R effect. e.g., halogens, – COOH, – COOR, – CHO, – CN, – NO₂ etc.



Electron withdrawing group (E.W.G.)

producing – R effect are meta directing. They deactivate the benzene ring towards the electrophilic substitution reaction. More the E.W.G, more is the acidic nature.

Resonance Energy

Number of π bonds \propto contributing structures
 \propto resonance energy \propto stability.

In benzene, resonance energy is 36 kcal/mol.

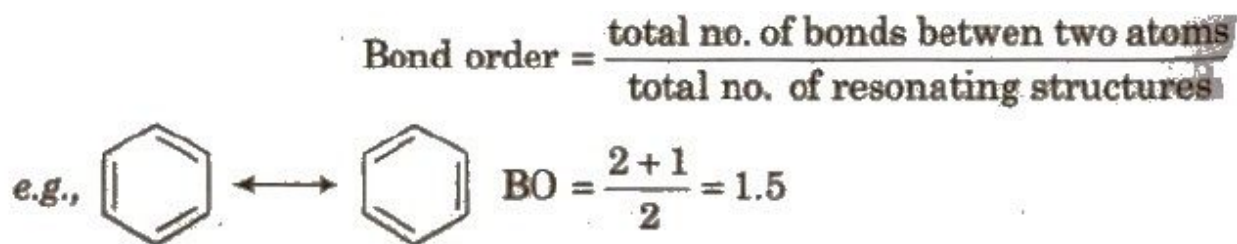
Stability of Canonical Forms

It can be judged by the following rules :

1. Non-polar structure is more stable than the polar structure.
2. Among polar structures, structure with maximum number of covalent bonds is most stable.
3. The structure with maximum charge separation is more stable.

4. Structure with positive charge on more electropositive element and negative charge on more electronegative element is more stable.

Resonance and Bond order



Isomerism

The compound having same molecular formula but differ in properties are known as

isomers and the phenomenon is known as isomerism.

There are two main types of isomerism i.e.,

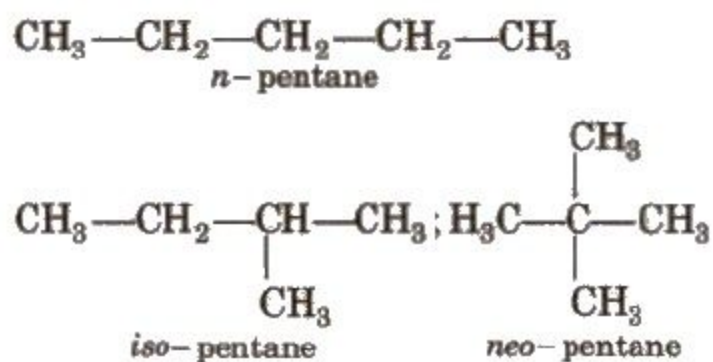
1. Structural Isomerism

In this type of isomerism, compounds have same molecular formula but different structures.

It can further be of following types:

(i) Chain Isomerism

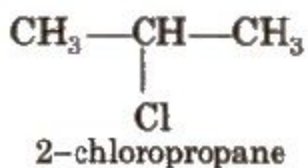
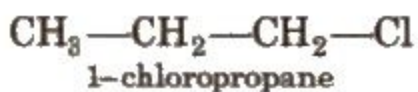
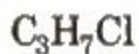
It arises when two or more compounds have similar molecular formula but different carbon skeletons, e.g.,



(ii) Position Isomerism

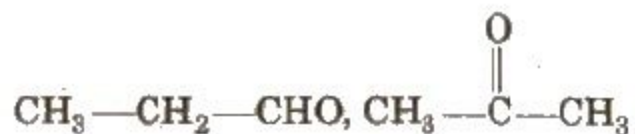
When two or more compounds have same molecular formula but different position of functional groups or substituents, they are

called positional isomers and the phenomenon is called position isomerism

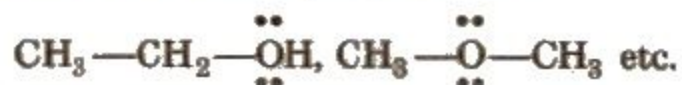


(iii) Functional Isomerism

It arises when two or more compounds have the same molecular formula but different functional group. e.g., $\text{C}_3\text{H}_6\text{O}$ represents an aldehyde and a ketone as

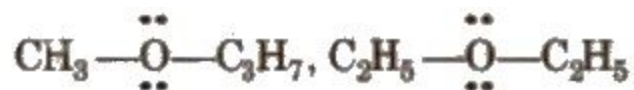


$\text{C}_2\text{H}_6\text{O}$ represents an alcohol and an ether.



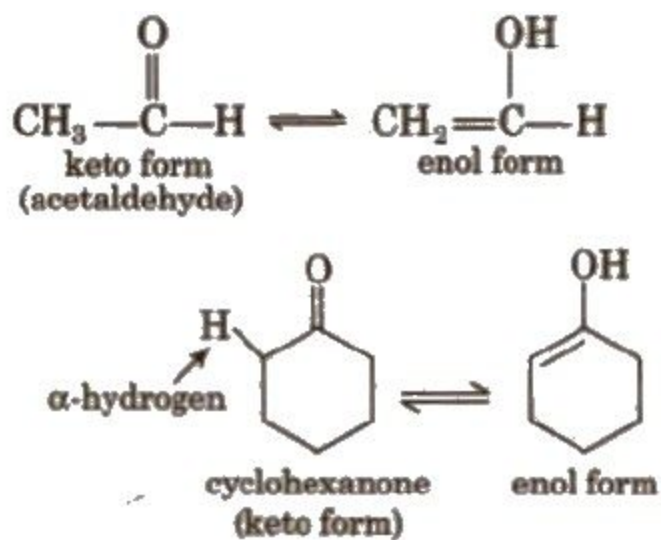
(iv) Metamerism

It arises due to different alkyl groups on either side of the same functional group in a molecule, e.g.,



(v) Tautomerism

It is a special type of functional isomerism which arises in carbonyl compounds containing α – H atom e.g.,



2. Stereoisomerism

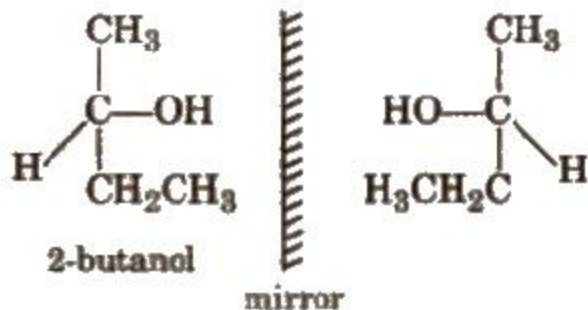
The compounds having same molecular formula but different spatial arrangement of

atoms or groups are called stereoisomers and the phenomenon is called stereoisomerism.

Stereoisomerism is of three types : optical isomerism, geometrical isomerism and conformations.

(i) Optical Isomerism

Compounds having similar physical and chemical properties but. differ only in behaviour towards plane polarised light are called enantiomer & or optical isomers and the phenomenon is known as optical isomerism. e.g.,



The isomer which rotate +ve plane of polarised light towards right (clockwise) is known as dextrorotatory or d-form while that which rotates towards left (anticlockwise) is known as laevorotatory or l-form.

Types of Geometrical Isomers

(a) **Cis-trans isomers** In cis-isomer, similar groups are present on the same side of the

double bond and in trans- isomer, similar groups are present on the opposite side of the double bond. E.g.

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