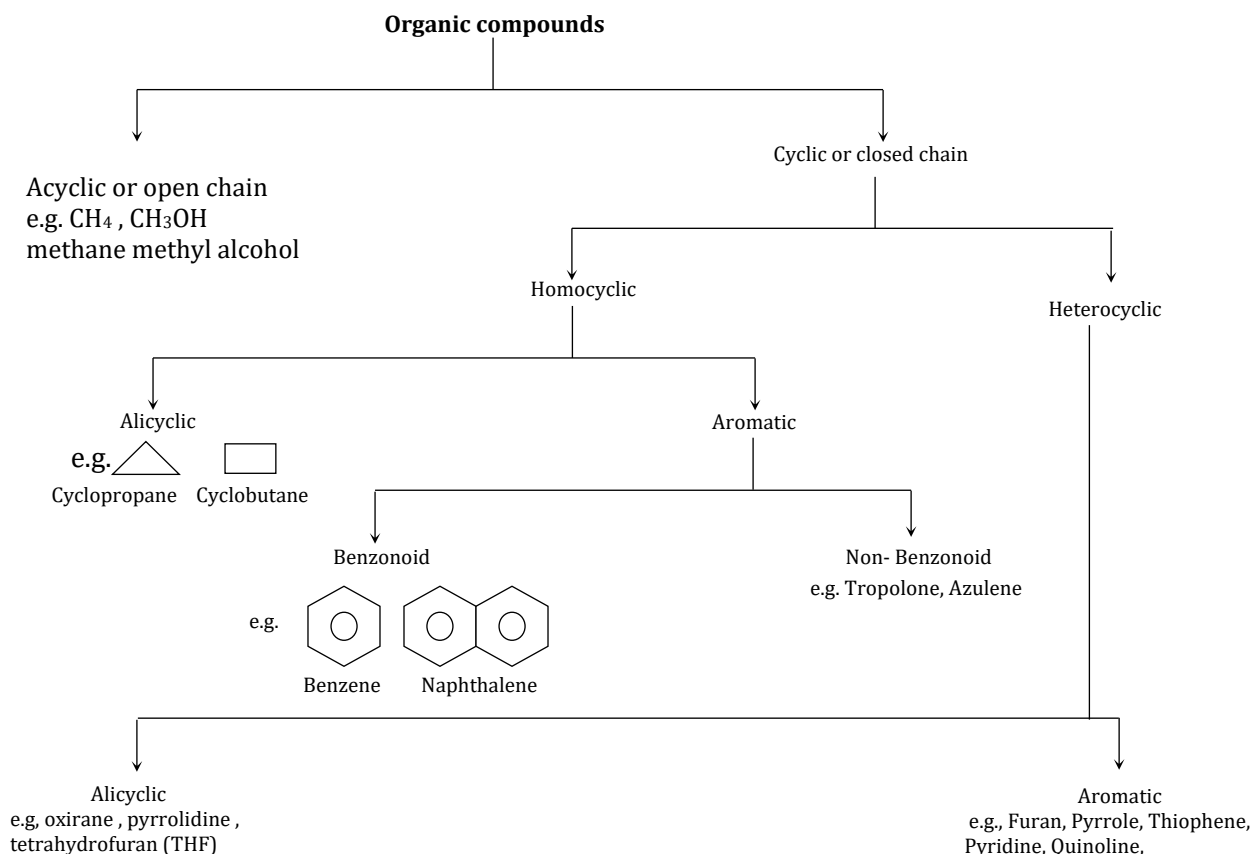


ORGANIC CHEMISTRY - SOME BASIC PRINCIPLES AND TECHNIQUES

21.2 Classification of organic compounds.

Organic compounds are infinite in number. Large number of organic compounds in due to, Remarkable catenation and isomerism property. Neither very high nor very low electronegativity of carbon (2.5). Tendency of carbon to form multiple bonds. Organic compounds can be divided into various classes as follows:

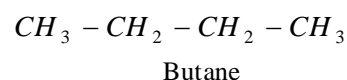
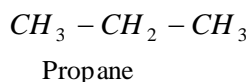
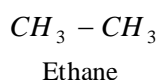


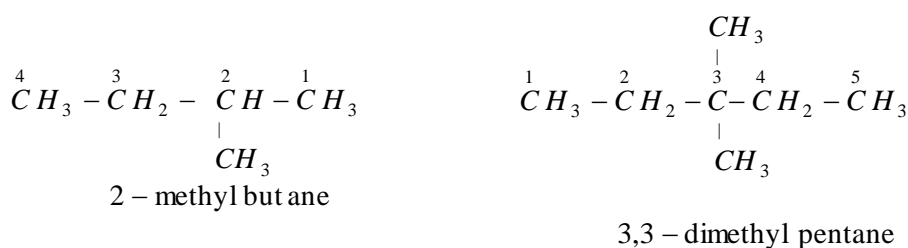
21.3 Nomenclature of organic compounds.

In order to systematize the nomenclature of organic compounds, IUPAC (International Union of Pure and Applied Chemistry) system of nomenclature was first introduced in 1947. These rules underwent modifications from time to time and the most exhaustive rules for nomenclature of organic compounds were first published in 1979 and later revised and update in 1993. The rules discussed are the latest and are based upon 1979 and 1993 editions of the IUPAC nomenclature of organic compounds.

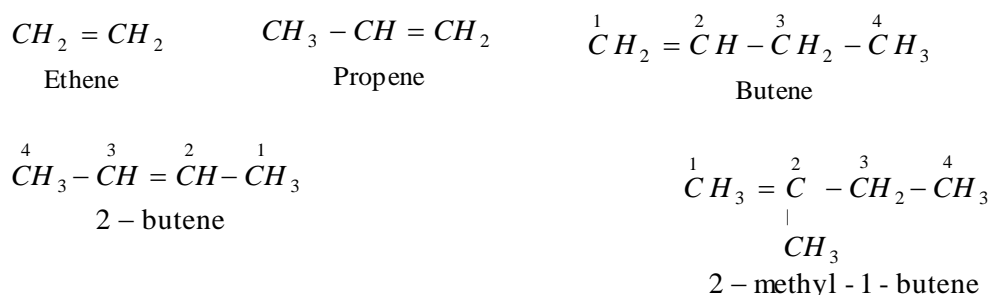
IUPAC names of Homologous series

Alkanes or Paraffins : These are represented by the general formula C_nH_{2n+2} . According to IUPAC system, they are called alkanes and the names of all **alkanes** will be ending with the suffix **-ane**. For example,

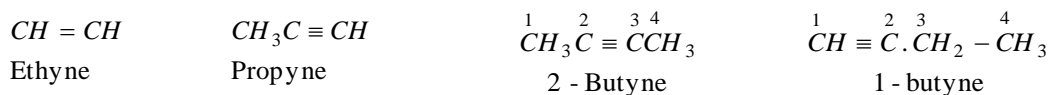




Alkenes or Olefins : These are characterised by the presence of a double bond between two carbon atoms and thus they contain two hydrogen atoms less than the corresponding alkane. They are represented by the general formula C_nH_{2n} . According to IUPAC system olefins are derived from the corresponding alkanes by replacing the suffix **-ane** by **-ene**. Thus olefins are called **alkenes**.



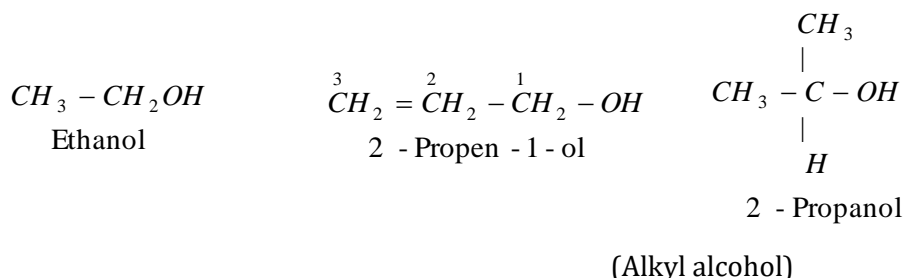
Acetylenes : According to IUPAC system acetylenes are called **alkynes**. The name is derived from the corresponding alkanes by replacing the ending suffix **-ane** by **-yne**. The position of triple bond is indicated by number.



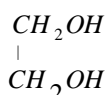
The alkynes are represented by the general formula C_nH_{2n-2} .

Alcohols : Alcohols are derived from alkanes by the replacement of one, two or three hydrogen atoms by the same number of $-OH$ groups. As a result, mono, di, and trihydric alcohols are obtained respectively.

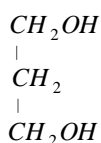
Monohydric alcohols are derived from the corresponding alkanes by replacing the **-e** in the alkane by **-ol**. Alcohols are thus known as **alkanols**. For example,



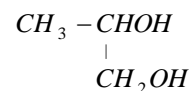
Dihydric alcohols are known as **diols**. They are obtained by adding the suffix **diol** to the name of the parent alkane. The numbers indicating the positions of the two $-OH$ groups may appear first or come between the two. For example:



1,2 Ethanediol or Ethane 1,2, diol
(Ethylene glycol)

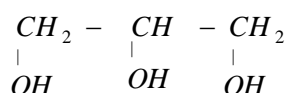


1, 3 Propanedio l or propylene 1, 3, diol
(Trimethylene glycol)



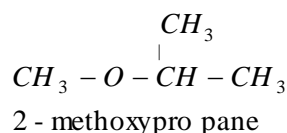
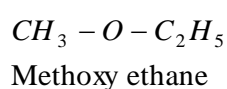
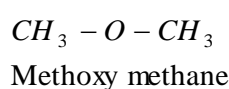
1, 2 Propanedio l or propane 1,2, diol
(Propylene glycol)

The IUPAC name of the *trihydric alcohols* is derived by adding suffix **-triol** to the name of the corresponding alkane and indicating the positions if the -OH groups by numerals. For example,



Propane-1, 2, 3-triol (Glycerol)

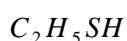
Ethers :The ethers are known as **alkoxy hydrocarbons**, i.e, hydrocarbons in which a hydrogen atom is replaced by alkoxy group, -RO. The larger alkyl group is chosen as the parent hydrocarbon, saturated or unsaturated. The name of the hydrocarbon (alkane) in prefixed by the name of the alkoxy group and position number. For example,



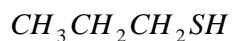
Thio alcohols : Commonly these are known as **mercaptans**. According to IUPAC system, the names are obtained by adding the suffix **thiol** to the name of the corresponding alkane. For example



Methane thiol



Ethane thiol



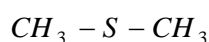
1 - Propane thiol



2 - Methylpropane thiol

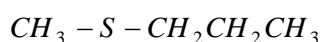
The SH group is the functional group in **thiols**. The -SH group is called **thiol group or mercapto group or sulphydryl group**.

Thioethers or Alkyl sulphides : According, to IUPAC system, thioethers are named as **alkylthio alkanes**. Smaller alkyl group to the sulphur atom is regarded as the substituent.



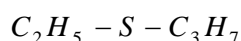
Methyl thiomethane

(Dimethyl sulphide)



1 - Methylthiopropane

(Methyl propyl sulphide)

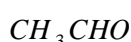


Ethyl thiopropane

(Ethyl propyl sulphide)

The characteristic functional group for thioethers is -S-.

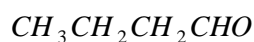
Aldehydes : In IUPAC system the name of an aldehyde is derived by replacing the ending **-e** of the corresponding alkane with **-al**. For example,



Ethanal



Propanal



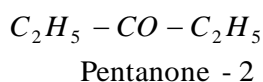
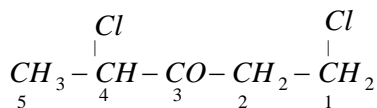
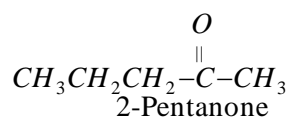
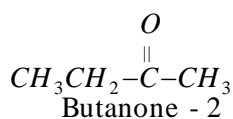
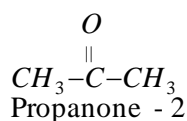
Butanal



Methanal

The general formula for aldehydes is $C_nH_{2n+1}CHO$ or $R-CHO$ and functional group is $-CHO$.

Ketones : In IUPAC system ketones are named by replacing the ending -e of the corresponding alkane with **-one**. The chain is then numbered to give the carbonyl carbon the lowest possible number. The latter is then employed to designate the position of carbonyl group.

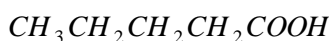
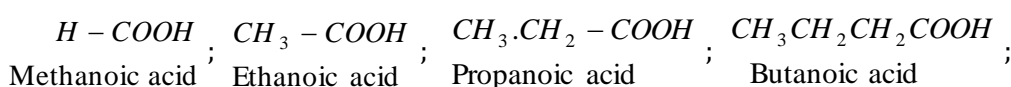


1, 4, dichloro - 3 - pentanone

Pentanone - 2

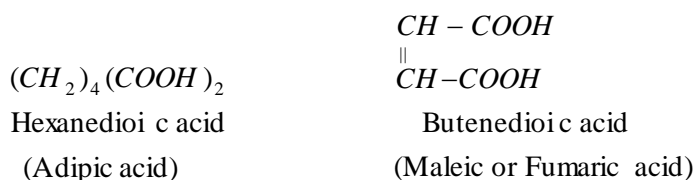
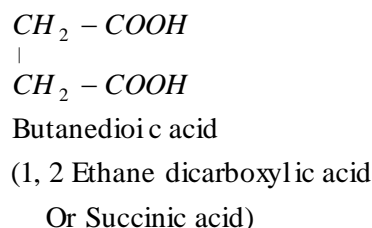
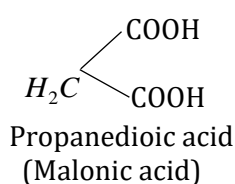
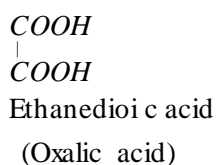
The general formula for ketones is $C_nH_{2n+1}-CO-C_nH_{2n+1}$ or $R-CO-R$ and functional group is $>C=O$.

Carboxylic acids : These are derived by replacing one or two hydrogen atoms of the alkanes by carboxylic group, $(-COOH)$. The names of monocarboxylic acids are derived from alkanes, by replacing the terminal -e by the suffix **oic acid**. For example.

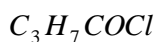
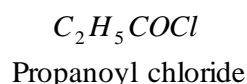
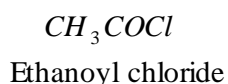
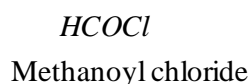


Pentanoic acid

The general formula of monocarboxylic acids is $C_nH_{2n+1}-COOH$ or $R-COOH$. The functional group is $-COOH$. In IUPAC system, dicarboxylic acids are named as **alkanedioic acids**, i.e. the suffix **dioic acid** is added to the name of parent alkane. The position of substituents is indicated by numbers.



Acid Derivatives : Acid halides or Acyl halides – The IUPAC names of these compounds are derived by replacing the -e of the alkane by **oyl halide**. They can also be obtained by replacing the suffix **oic acid** of the carboxylic acids by **-oyl halide**.



Butanoyl chloride

The general formula of acid halides is $C_nH_{2n+1}COX$ or $R-COX$ and the functional group is

Acid amides – According to IUPAC system, amides are named by replacing the final -e of the alkane by **amide**. For example,

$HCONH_2$	CH_3CONH_2	$CH_3CH_2CONH_2$	$C_3H_7CONH_2$
Methanamid e	Ethanamide	Propanamid e	Butanamide
(Formamide)	(Acetamide)	(Propionam ide)	(Butyramid e)

The general formula of amides is $C_nH_{2n+1}CONH_2$ or $R-CONH_2$.

The functional group is $-CONH_2$.

Acid anhydrides – In IUPAC system, anhydrides are named by replacing the word **acid** in the name of the parent acid by **anhydride**. For example,

$CH_3-CO-O-CO-CH_3$	$CH_3CH_2-CO-O-CO-CH_2CH_3$
Acetic anhydride (Ethanoic Anhydride)	Propionic anhydride (Propanoic Anhydride)

Esters – In IUPAC system, the names are obtained by first writing the name of the alkyl part of the $-OR$ group followed by the IUPAC name of the acid in which suffix **-ic** is replaced by **-ate**.

$HCOOCH_3$	$CH_3COOCH_2CH_3$	$CH_3CH_2COOCH_2CH_2$
Methyl formate	Ethyl acetate	Ethyl propionate
Methyl methanoate	Ethyl ethanoate	Ethyl propanoate
(IUPAC name)	(IUPAC name)	(IUPAC name)

The general formula of esters in $R-COOR'$ and functional group is $-COOR'$.

Aliphatic amines : Commonly amines are named by adding the word amine to the name of the alkyl groups attached to the nitrogen atom. For example,

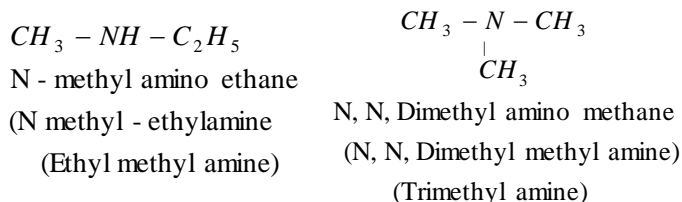
CH_3-NH_2	$CH_3-CH_2-NH_2$	$CH_3CH_2CH_2-NH_2$
Methylamine	Ethyl amine	Propyl amine

According to IUPAC system, these **primary amines** (containing $-NH_2$ group) are named as amino derivatives of alkanes. They are, therefore named after the parent alkane, and the position of $-NH_2$ group is indicated by the lowest possible number. For example,

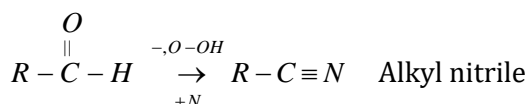
$CH_3-CH_2-NH_2$	CH_3-C-CH_3
Amino ethane	$\quad \quad \quad $
(Ethyl amine)	$\quad \quad \quad NH_2$
	2 - amino propane

CH_3
$ $
CH_3-C-CH_3
$ $
NH_2
2 - amino - 2 - methyl
Propane (tertiary butyl amine)

The general formula of primary amines is $R-NH_2$ and functional group is $-NH_2$ (amino group). The **secondary** and **tertiary amines** containing $-NH$ and N groups respectively are named as alkyl amino alkanes and dialkyl amino alkanes respectively. The general formulae of secondary and tertiary amines are $R-NH-R$ and R_3N respectively.



Alkyl Cyanides : Their common names are derived by replacing a hydrogen atom of the alkane. They can also be regarded as derivatives of carboxylic acid in which bivalent oxygen, together with monovalent $-OH$ group have been replaced by a trivalent nitrogen.

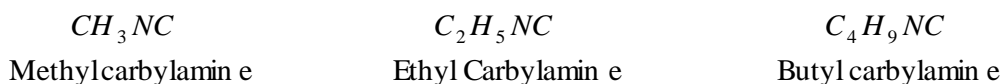


According to IUPAC system alkyl cyanides are called **nitriles**. The parent name is derived from the longest carbon chain containing the $-CN$ group. The position is indicated by a number.



The general formula of alkyl nitriles is $R - CN$ and functional group is $-CN$.

Alkyl Isocyanides : These are derived by replacing a hydrogen atom of alkanes by the isonitrile ($-NC$) group. Commonly they are known as alkyl isocyanides. According to IUPAC system the word carbylamine is added to the name of the alkyl radical.

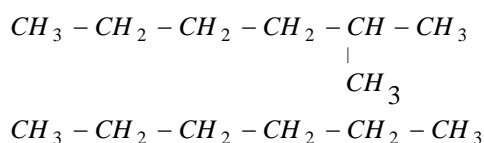


Nitroalkanes or Nitroparaffins : These are derived from alkanes by the replacement of a hydrogen atom by $-NO_2$ group. Their general formula is $R - NO_2$ and functional group is $-NO_2$. Their common and IUPAC names are generally the same and derived by adding the suffix **nitro** before the name of the corresponding alkane. For example,



IUPAC Nomenclature of Complex Compounds

According to IUPAC system of nomenclature any given organic compound can be represented by one and only one molecular structure. In general, the IUPAC system of naming an organic compound consists of three parts: **(a) Prefix(es)** **(b) Root word** **(c) Suffix(es)**. The **root word** depends on the number of carbon atoms present in a suitable chain, called the **parent chain**, containing the functional group and as many of carbon - carbon multiple bonds(s) as possible. Appropriate **suffix(es)** is then added to the root word to denote the saturated or unsaturated character of the **parent chain** and also the functional group present therein. Finally, **prefix(es)** is put to indicate the nature and position of the side chain or substituents. The basic rules for IUPAC system are: **Longest Chain Rule** - The longest possible continuous chain of carbon atoms containing the functional group and carbon - carbon multiple bonds is first selected and the root word corresponding to it is noted.



Root words

No. of carbons	Root word	No. of carbons	Root word
1	Meth –	6	Hex –
2	Eth –	7	Hept –
3	Prop –	8	Oct –
4	But –	9	Non –
5	Pent –	10	Dec –

Primary Suffix : A primary suffix is to be added to the root word to indicate saturation and unsaturation in the selected chain. The generic root word for any carbon chain is alk - (from alkane).

Chain Type	Suffix	Generic Name
Saturated	– ane	Alk + ane
Unsaturated with one double bond	– ene	Alk + ene
Unsaturated with one triple bond	– yne	Alk + yne
Alkane - 1H	– yl	Alk + yl

Secondary Suffix : A secondary suffix is added to indicate the nature of functional group, if present in the compound. Some functional groups are given below :

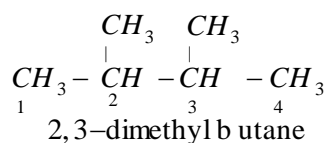
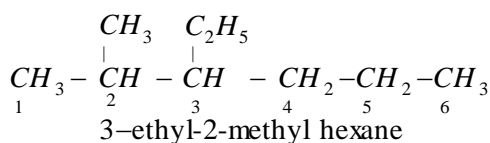
Functional Group	Secondary Suffix	Functional Group	Secondary Suffix
Alcohol (–OH)	– ol	Ester (– COOR)	– oate
Aldehyde (–CHO)	– al	Amide (– CONH ₂)	– amide
Ketone (>C = O)	– one	Acid chloride (–COCl)	– oyl chloride
Carboxylic acid (– COOH)	– oic acid		

The terminal "e" of the primary suffix is replaced by secondary suffix.

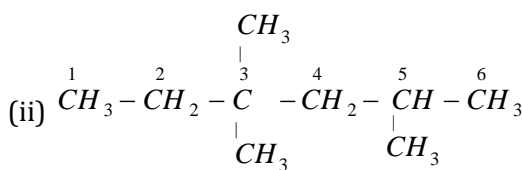
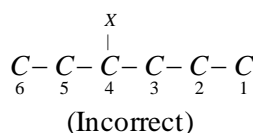
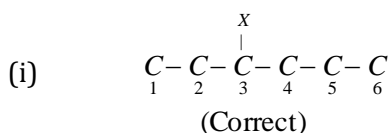
Formula	No. of carbons	Root word	Primary suffix	Secondary suffix	IUPAC Name
HCHO	1	meth –	– an	– al	Methanal
CH ₃ CH ₂ OH	2	eth –	– an	– ol	Ethanol
CH ₃ COOH	2	eth –	– an	– oic acid	Ethanoic acid
CH ₃ CH ₂ CH ₃	3	prop –	– ane	–	Propane
CH ₃ CH = CH ₂	3	prop –	– ene	–	Propene
CH ₃ – C ≡ CH	3	prop –	– yne	–	Propyne
CH ₃ COCH ₂ CH ₃	4	but –	– an	– one	Butanone

Prefixes rule : Prefixes are to be added to the **root word** to represent the **side chains** and **substituents**.

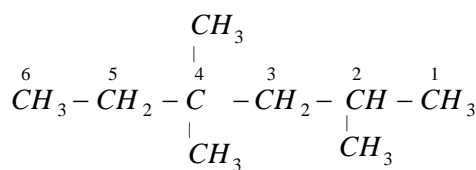
Alphabetical arrangement of Prefixes Rule : If there are more than one side chains/substituents, they should be prefixed in the alphabetical order. When two or more identical side chains/substituents are present, their location and number are represented by prefixing **di (2), tri (3), tetra (4) etc.** before the substituents/side chains.



Lowest Sum Rule : The sum of the numbers used to indicate the position of substituents should be minimum. The parent carbon chain is to be numbered from one end. The position of substituents and functional groups is indicated by the number of carbon atoms to which they are attached.

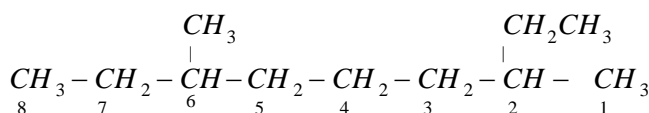


3, 3, 5 trimethyl hexane (I)(Incorrect)

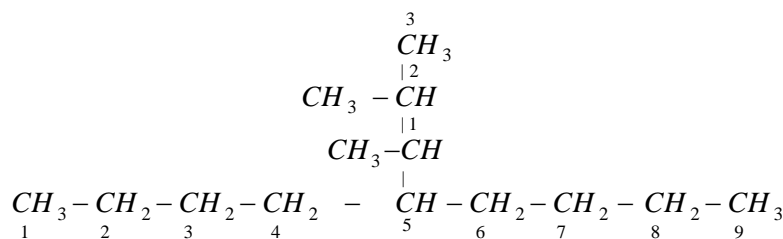


2, 4, 4 trimethy l hexane (II)(Correct)

In case of II, the sum of numbers of substituents is $2 + 4 + 4 = 10$, which is less than in I, where the number of substituents is $3 + 3 + 5 = 11$. When two or more groups are located in equivalent position in the carbon chain, the lower number is assigned to that group which is written first in the name of the compound in the alphabetical order.

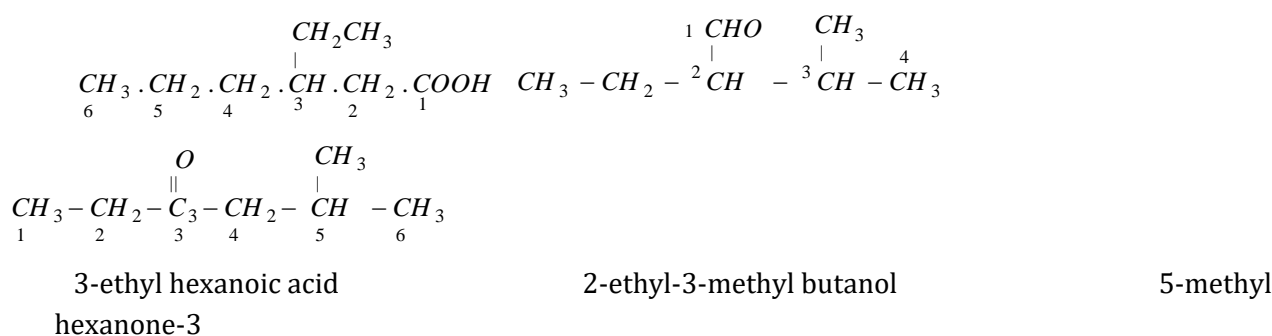


In case the substituent on the parent chain is complex (containing more than 4 carbon atoms) it is named as substituted alkyl group whose carbon chain is numbered from the carbon carbon - atom attached to the main chain.

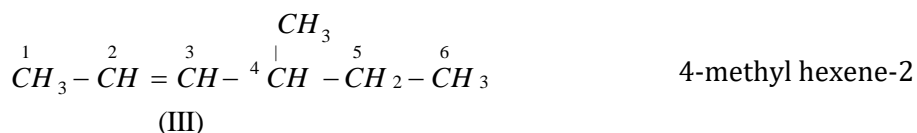


5 - (1, 2 dimethyl p ropyl) nonane

The position of a **double bond (or triple bond)** in alkenes (or alkynes) is indicated by prefixing the number of the carbon proceeding such a bond, the carbon chain being numbered from the end which assigns lower positional number to the double (or triple) bond.



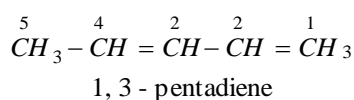
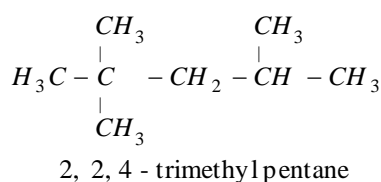
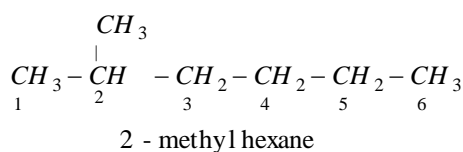
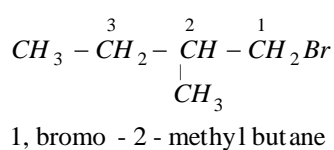
Numbering the carbon : Carbon multiple bonds : While numbering the parent chain containing carbon - carbon multiple bonds, the lower number of two carbons involved in the multiple bonds, is used to indicate the position of the multiple bond. Number 2, for example, is used to indicate the position of the double bond in the alkene, (III).



Prefix for Alicyclic compounds : The word cyclo is prefixed to the root word if the compound being named is an alicyclic compound. When alicyclic compounds contain side chains and/or substituents, they appear as secondary prefixes before the word cyclo.

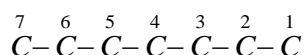
Naming polyfunctional compounds : When a compound contains two or more different functional groups, one of the functional groups is chosen as the principal functional group and the remaining functional groups (secondary functional groups) are treated as substituents in the IUPAC names. The following guidelines determine the choice of the principal and secondary functional group while giving IUPAC names to polyfunctional organic compounds.

- When two or more than two functional groups are present in a compound, the principal functional group generally gets the following order of preference: **Acids > Acid derivatives excluding nitriles > Aldehydes > Nitriles > Ketones > Alcohols > Amines > Ethers > Alkenes > Alkynes**
- While selecting the parent chain in a polyfunctional compound, it should be ensured that it includes the maximum number of functional groups present, including the principal functional group.
- While numbering the parent chain in such cases, the following is the decreasing order of preferences for giving the lowest numbers. **Principal functional group > Double bond > Triple bond > Substituents.**
- If branching alkyl groups (side chains) contain multiple bonds and functional groups, the side chain is numbered separately so that the carbon atom in the side chain which is itself bonded to the parent chain is designated as 1. **The application of these rules may be demonstrated by the following examples:**

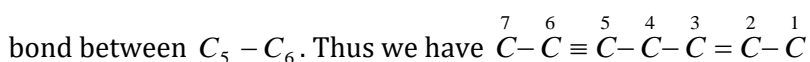


- How to derive the structure of a compound from IUPAC name - The following steps are to be followed :
- Identity the root word and write the parent carbon chain and then number it from one end.
- Identify the primary suffix and then the multiple bonds, if present. Locate them at the proper place in the parent chain,
- Now attach the functional group(s) and substituents at the specified carbons as indicated by the suffixes and prefixes of IUPAC name
- Finally required number of hydrogen atoms are placed on each carbon in the parent chain to satisfy the tetravalency of carbon.

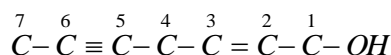
Example 1: Suppose we have to write the structure of 4-methyl hept-2- ene-5-yne-1-ol. Here the **root word** is hept. Thus the parent carbon chain contains seven carbon atoms.



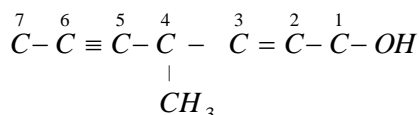
The primary suffix "ene" and "yne" indicate that a double bond is present between $C_2 - C_3$ and triple bond between $C_5 - C_6$. Thus we have



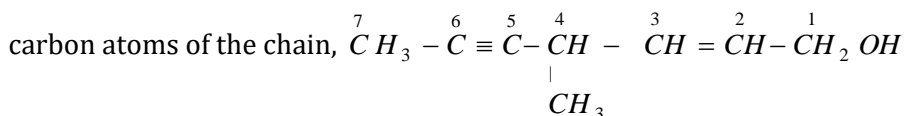
The secondary suffix - **ol** indicates that -OH group is present at C_1 .



The methyl substituent is present at carbon 4.

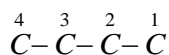


Now tetravalency of each carbon atom is completed by placing the number of hydrogen atoms at the



Example 2: To write the structure of 1-bromo-4-chloro-butane.

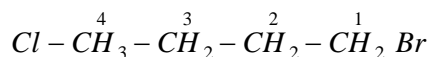
Here the root word is but-, so the parent carbon **chain** contains 4 carbon atoms.



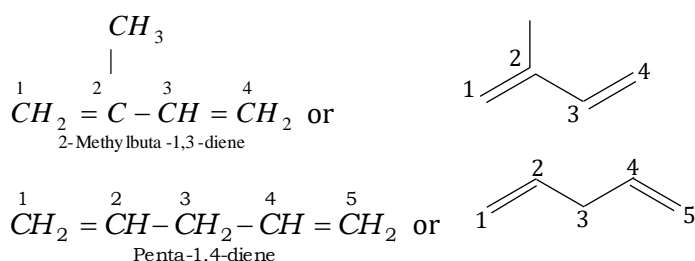
Since the substituents are present at C_1 and C_4 the lower number should be given to the group in the



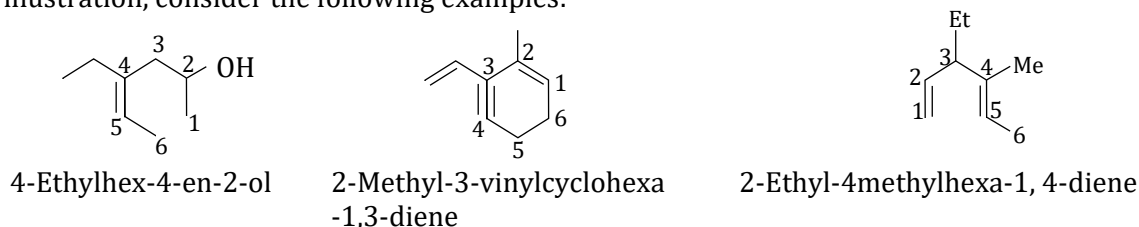
Now satisfying the tetravalency of carbon by placing hydrogen atoms at the carbon atoms, we have



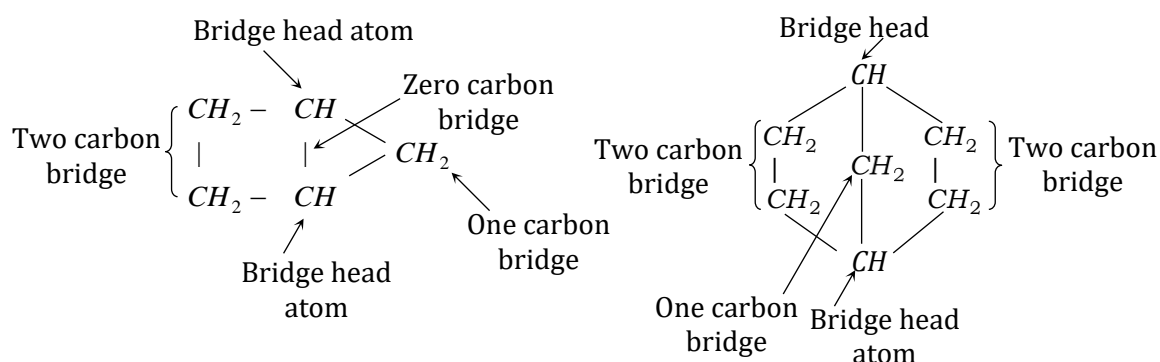
Bond line notations of organic molecules: It is a more accurate, simple, and convenient method of representing structures of organic molecules. In this notation bonds are represented by lines and carbon atoms by line ends and intersections. It is further assumed that required number of hydrogen atoms are present wherever they are necessary to satisfy the tetravalency of carbon. Sometime symbols like Me (for methyl), Et (for ethyl) are used to indicate the presence of these groups.



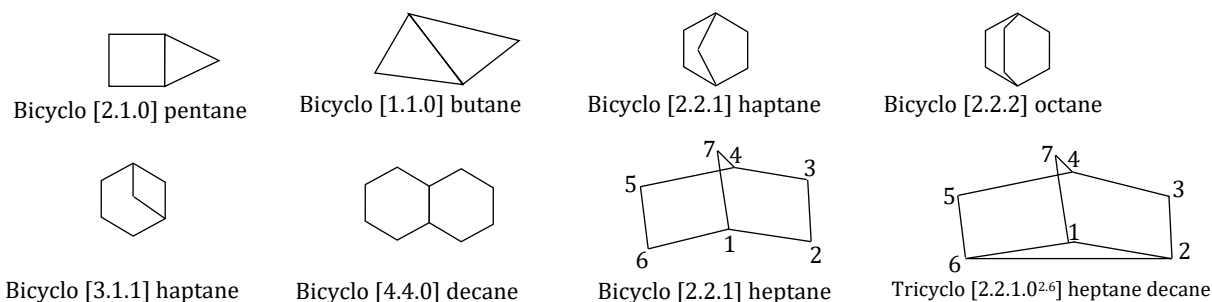
For further illustration, consider the following examples:



IUPAC rules for nomenclature of polycyclic compounds : Many a time, hydrocarbons of their derivatives contain two or more rings. The carbon atoms common to both the rings are called bridge head atoms. Each bond or chain of carbon atoms connecting both the bridge heads is called a bridge. The bridge may, contain 0, 1, 2etc., carbon atoms. This is illustrated by the following examples :

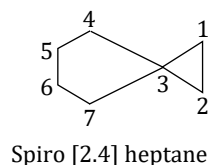
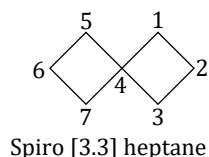
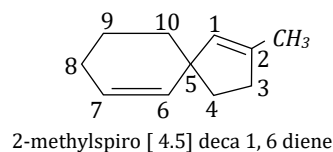
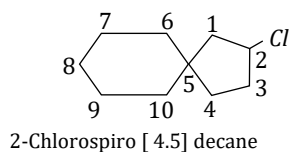


A bicyclic compound is named by attaching the prefix '*bicyclo*' to the hydrocarbon having the same total number of carbon atoms as in the two rings. The number of carbon atoms in each of these three bridges connecting the two bridge head carbon atoms is indicated by Arabic numerals i.e., 0, 1, 2, 3...etc. These Arabic numerals are arranged in descending order, separated from one another by full stops and then enclosed in square brackets. The complete name of the hydrocarbon is then obtained by placing these brackets between the prefix bicyclo and the name of the alkane. For example,



IUPAC rules for nomenclature of spiro compounds : Compounds in which one carbon atom is common to two different rings are called spiro compounds. The carbon atom common to the two rings is called the spiro atom. The IUPAC name for a spiro compound begins with the word 'spiro' followed

by brackets containing the number of carbon atoms, in ascending order, in each ring connected to the common carbon atoms and then by the name of the parent hydrocarbon containing the total number of carbon atom in the two rings. The numbering begins with the ring atom next to the spiro atom and then proceed first around the smaller ring and then to the spiro atom and finally around the large ring. This is illustrated by the following examples.

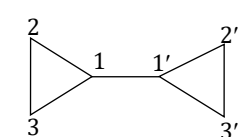


IUPAC rules for nomenclature of unbranched assemblies consisting of two or more identical cyclic hydrocarbon units joined by a single bond.

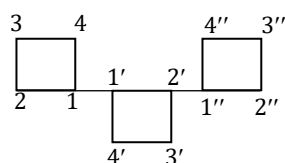
These systems are named by placing a suitable numerical prefix before the name of the repetitive hydrocarbon unit. The numerical prefixes used in this nomenclature are given below :

<i>No. of cyclic hydrocarbon units</i>	Two	Three	Four	Five
<i>Prefix</i>	bi	ter	quater	quinque

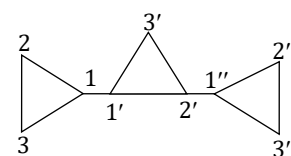
Starting from either end, the carbon atoms of each repetitive hydrocarbon unit are numbered with unprimed and primed Arabic numerals such as 1, 2, 3,...1', 2', 3',...1'', 2'', 3'',...etc. The point of attachment of the repetitive hydrocarbon units are indicated by placing the appropriate locants before the name. For example,



1, 1'-Bicyclopropane

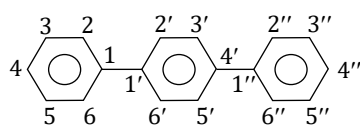


1, 1', 2' 1''-Tercyclobutane

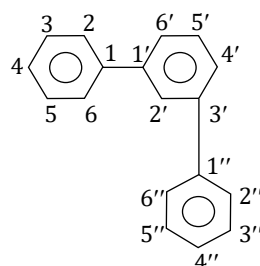


1, 1', 2', 1''-Tercyclopropane

As an exception, unbranched assemblies consisting of benzene rings are named by using appropriate prefix with the name phenyl instead of benzene. For example,

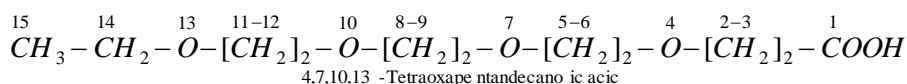


1, 1', 4', 1''-Terphenyl

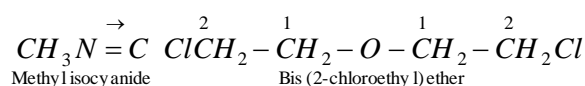


1, 1', 3', 1''-Terphenyl

Replacement nomenclature. IUPAC recommend its use in case of unsymmetrical structures with several chalcogen atoms. For example,



Functional class names of ratio-functional names. IUPAC recommend its use for naming isocyanides, ethers with substituents not having priority for citation as suffix. For example,



These names are not written as one word.

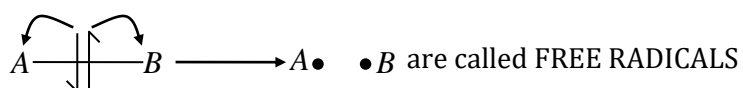
TYPE OF BOND CLEAVAGE

A covalent bond between A and B may break in two ways.

1. Homolytic bond fission
2. Hetrolytic bond fission

HOMOMYTIC BOND CLEAVAGE

It occurs when both A and B atom takes their electron from bond like

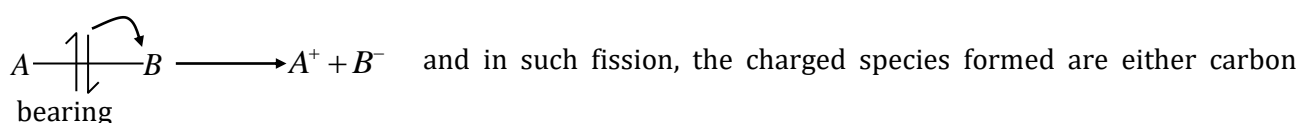


Homolytic bond cleavage mainly occurs in the following conditions

- (i) If both the atom have nearly same electronegativity.
- (ii) If we apply heat, photons, electric spark.
- (iii) If we take non-polar solvent like CCl_4 , benzene etc.
- (iv) Mainly in vapour phase.

HETROLYTIC BOND CLEAVAGE

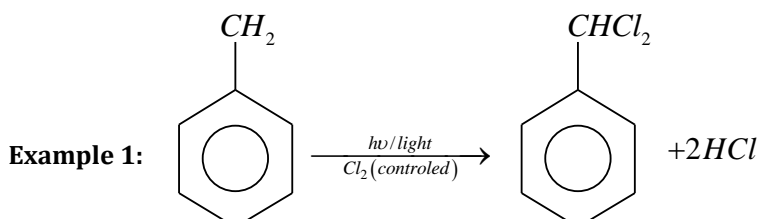
It occurs when one atom takes both the electron from bond and leaves two ions, like



positive charge called carbonations or carbon bearing negative charge called carbanion

Hetrolytic bond cleavage occurs mainly in the following conditions.

- (i) If both the atom have large difference in electronegativity.
- (ii) If we take polar solvent like H_2O , C_2H_5OH etc.
- (iii) If we take Acid, base or such Regent in reaction.
- (iv) Mainly in aqueous phase.
- (v) If metals like Fe, Zn etc are taken in reaction.



(in this reaction homolytic cleavage occurs due to $h\nu$ (photons), hence substitution CH_3 group)

Homolytic cleavage forms free radicals, while heterolytic form ions. Enthalpies for heterolytic (ionic) cleavage depend strongly on the solvent's ability to solvate the ions that result. Homolytic cleavage is used to define bond dissociation energies are always positive (endothermic)

Electronic Displacement in Covalent Bonds

The following four types of electronic effects operates in covalent bonds

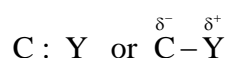
- (i) Inductive effect
- (ii) Mesomeric and Resonance effect
- (iii) Electronic effects
- (iv) Hyperconjugation

Inductive Effect

In a covalent bond between the two dissimilar atoms, the electron pair forming the bond is never shared equally between the two atoms but is attracted a little more towards the more electronegative atom of the two, e.g. The electron pair forming the C – X bond is somewhat more attracted towards the atom X with the result – it attains a partial negative charge ($-\delta$) while the carbon atoms attain a partial positive charge ($+\delta$)



On the other hand, in compounds like C – Y, where Y is an electropositive element or group i.e. C is more electronegative than Y, the electron pair forming the C – Y bond is somewhat displaced towards the carbon atom and thus C and Y gain partial negative and partial positively charged respectively.

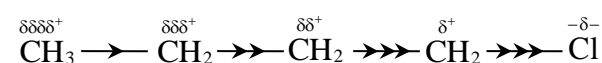


According to Ingold sign convention, the former is called as (–I) effect and the later is called as (+II) effect.

The inductive effect causes certain degree of polarity in the bond which in term renders the bond much more liable to be attacked by other charged atoms or group.

Thus, inductive effect may be defined as the **permanent displacement** of electron forming a covalent bond towards the more electronegative element or group.

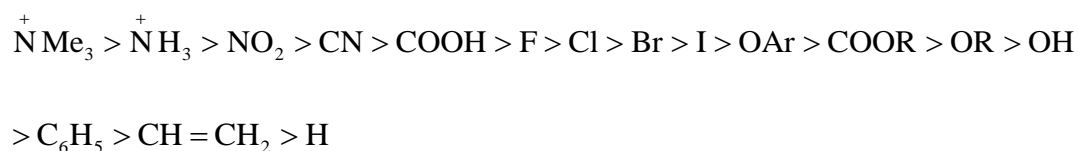
The inductive effect is represented by the symbol \rightarrow the arrow pointing towards the more electronegative element or group of elements e.g. N – butyl chloride



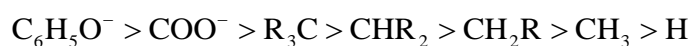
The extent of positive charge keeps on decreasing away from Cl atom and at third and fourth carbon it is almost zero for all practical purposes.

Examples of I effect groups

(a) (–I) effect group (electron attracting)



(b) (+I) effect – group (electron – repelling)

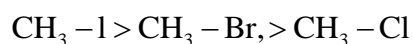


Applications of Inductive effect

(i) Effect on Bond lengths: Since the inductive effect leads to ionic character in the bond, the increase in –I effect usually decreases the bond length.

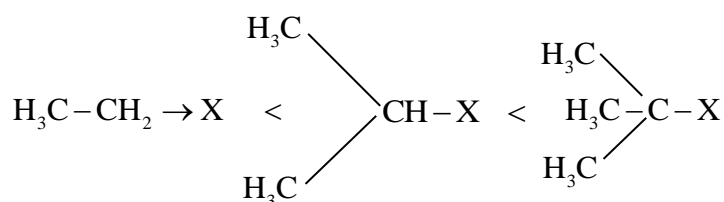
Increasing – I effect			
$\text{CH}_3 \longrightarrow \text{I}$	$\text{CH}_3 \longrightarrow \text{Br}$	$\text{CH}_3 \longrightarrow \text{Cl}$	$\text{CH}_3 \longrightarrow \text{F}$
2.14Å	1.94Å	1.78Å	1.38Å
Decrease in bond length			

(ii) Dipole moment : Since inductive effect leads to a dipolar character in the molecule, it develops some dipole moment in the molecule, which increases with the increase in the inductive effect.



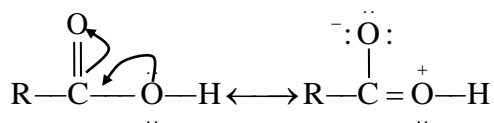
Increasing dipole moment

(iii) Reactivity of alkyl halides : Alkyl halides are more reactive than corresponding alkanes due to presence of C – X bond which is polar due to I effect; furthermore reactivity increases with increase of branching.



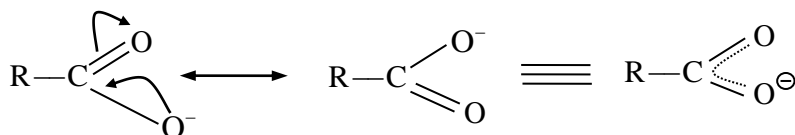
Increasing reactivity due to increasing C—X bond polarity

- (iv) **Strength of Carboxylic Acids :** Strength of an acid depends upon the ease with which an acid ionises to give proton. A molecule of carboxylic acid can be represented as a resonance hybrid of the following structures.



In the II structure, the oxygen atom of the hydroxyl group has a positive charge due to which it has a tendency to attract electron pair (inductive effect) of the O – H bond towards itself, which results in the removal of hydrogen atom as proton and hence carboxylic acids behave as acids.

Once, the carboxylate anion is formed, it is stabilised more easily by resonance than undissociated acid.



Thus, the acidity of carboxylic acid is due to inductive effect and resonance stabilization of the carboxylate anion. Thus any group or atom, which is highly electronegative help in removing the hydrogen atom as proton and the group or atom which is less electronegative than C makes the removal of proton difficult.

Hence (-I) effect group increases acidic strength and (+I) effect groups decreases the acidic strength of carboxylic acid.

Basic strength of Amines

The basic character of amines is due to presence of unshared electron pair on nitrogen atom which accepts proton; the readiness with which the lone pair of electron available for protonation determines the relative strength of amines.

Due to +I effect of alkyl group, the nitrogen atom becomes rich in electrons with the result the lone pair of electron on nitrogen atom in amines is more easily available than in ammonia and hence generally, amines are stronger bases than ammonia.

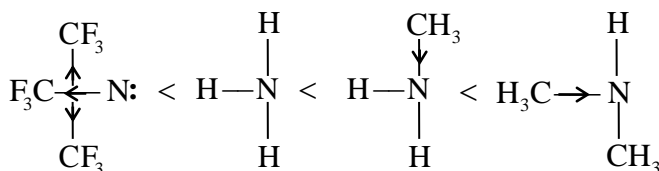
On the other (–I) groups or electron groups attached to nitrogen atom makes it difficult for protonation.

Note : Relative basic strength of amines is not in total accordance with the inductive effect, other factor like steric and stabilisation of cation by hydration also play important role determine the basic strength of amines.

Illustration Compare the basic strength of the following

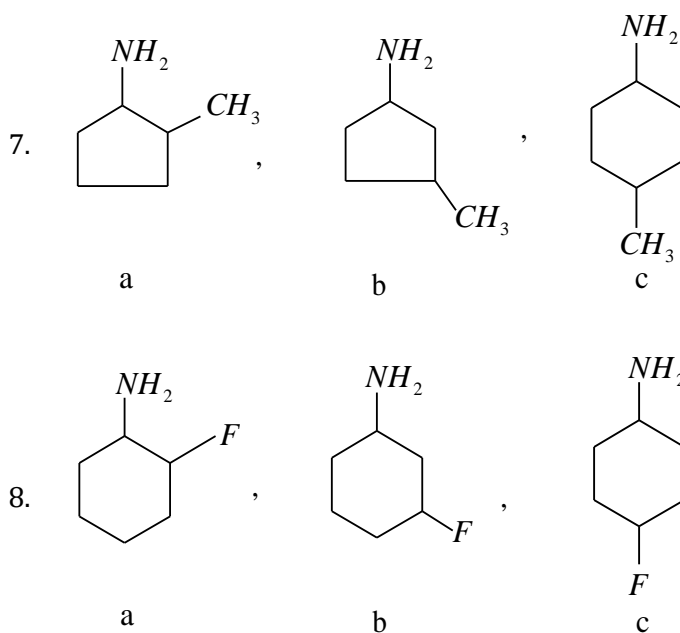


Solution The increasing order of basic strength is as follows.



CF_3 group being $-I$ effect group attracts the electron pair of nitrogen makes protonation difficult in primary and secondary amine due to presence of $+I$ effect group (CH_3) which makes protonation easy. Hence the increasing order of basic strength is as follows.

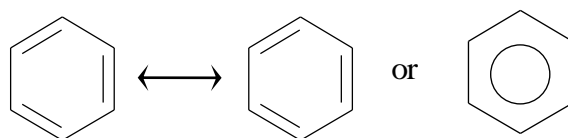
Arrange Basic strength



Resonance or Mesomeric Effect

The phenomenon, in which two or more structures, involving identical position of atoms, can be written for a particular compound, is called resonance. The various structures are called as resonating structure or contributing structures.

The benzene molecule can be expressed as a resonance hybrid of the two contributing Kekule structure. Such contributing structures are commonly known as canonical structures.

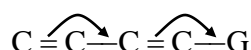


This canonical structure of a system is a set various structures which are sufficient to define all the possible electron distributions.

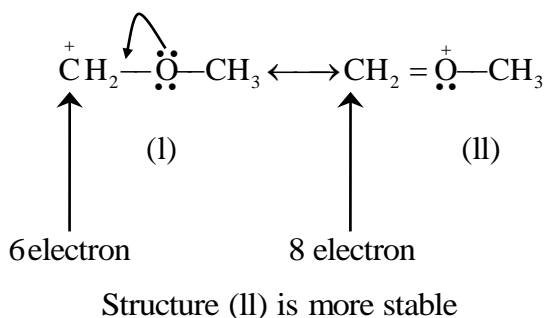
- (i) Presence of a conjugate system (alternate double, single bond or single, multiple bond)



- (ii) Conjugated system, attached to electron deficient atom with vacant p-orbital.

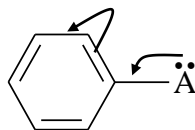


- (b) Structures in which all of the atoms have a complete valence shell of electrons are especially stable and make large contribution to the hybrid



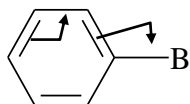
Mesomerism: It is the resonance effect of certain compounds under the influence of particular group attached to the conjugated system. M – effect is very popular in aromatic compounds having one or more groups attached with aromatic nucleus. It is of two types.

+M : When the movement of electron starts from the group. (When group has a lone pair or an extra electron).



$A = -NH_2, ^-OH, X, -OR$ etc.

–M : When the movement of electrons takes place towards the group



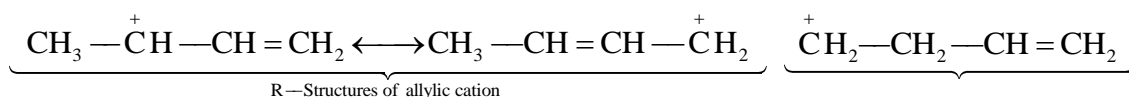
$B = -NO_2, -SO_3H, -C=O, -C\equiv N, CHO$ etc.

Note : Mesomeric effect is permanent in nature

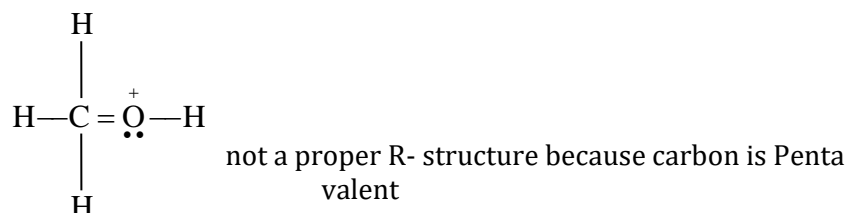
Rules for writing Resonance structures

- (a) **No Real existence:** Resonance structures exist only on paper. Resonance structures are useful because they allow us to describe molecules, radicals, and ions for which a single Lewis structure is inadequate. We write two or more Lewis structures, calling them resonance structures or resonance contributors. We connect these structures by double-headed arrows (\longleftrightarrow) and we say that the real molecule, radical or ion is a hybrid of all of them.
- (b) **In writing resonance structures, we are only allowed to move electrons**

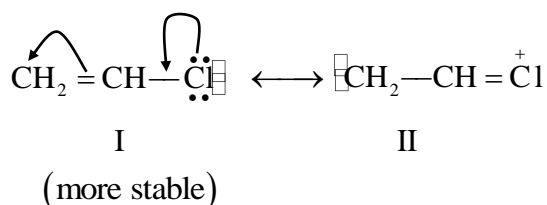
Position of nuclei of the atoms must remain the same in all resonance structures e.g.



- (c) **Lewis structures:** All the structures must be proper lewis structures

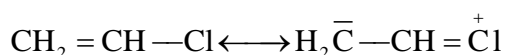


- (d) Charge separation should be low since, to separate, charge energy is required, therefore, structure in which opposite charges are separated have greater energy and hence less stable.



Effect of Resonance

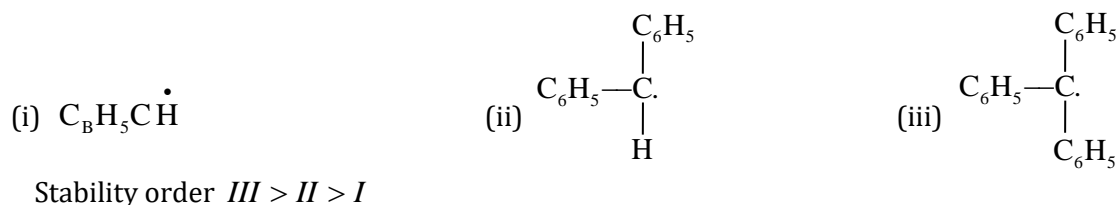
- (a) Dipole moment : Dipole moment of certain compounds can be explained by resonance eg. Vinylchloride



$$\mu = 1.4\text{D}$$

- (b) Bond length : the phenomenon of resonance explain the abnormal bond length between C—C, C=C, C=O, etc in compounds exhibiting resonance e.g. in benzene C—C bond length acquires a value which lies between C—C single bond length (1.54Å) and C=C (double bond) length (1.33Å)

Stability of free radicals and carbonium ions

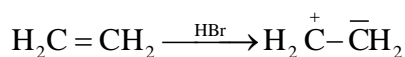


Similarly we can explain the stability of carbonium ions.

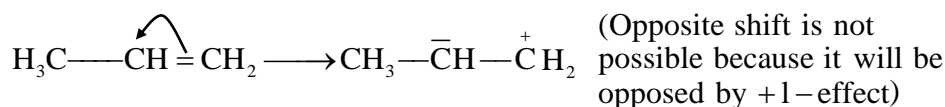
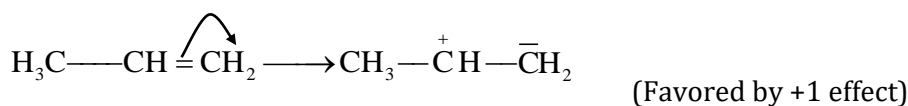
Electrometric Effect

It is a temporary effect in which a shared pair of electron (π -electron pair) is completely transferred from a double bond or triple bond to one of the atoms joined by the bond at the requirement of attacking reagent.

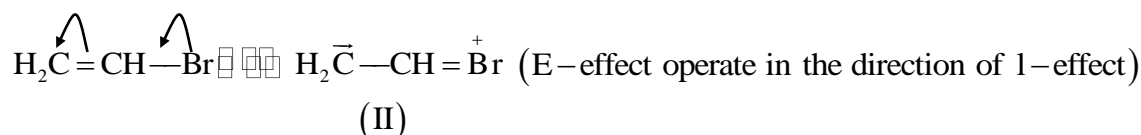
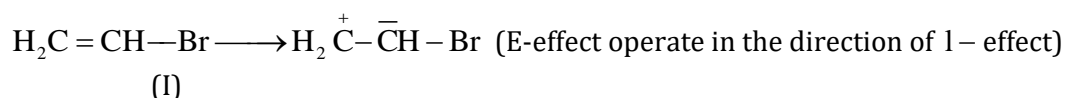
- Case I :** When multiple bonds is present between two similar atom (symmetric alkenes or alkynes) electronic shift can take place in any direction



Note 1 : If two carbon atoms are different (asymmetric alkenes or alkenes) then the direction of electronic shift is determined by the direction of the inductive effect of the group present at doubly or triply bonded atom e.g.....



Note 2 : When inductive and electromeric effects oppose each other, in such cases, electromeric effect usually overcome inductive effect e.g.



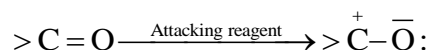
Conjugate effect



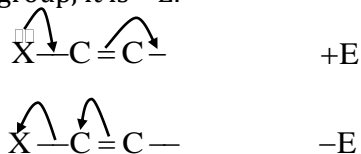
Since conjugate effect is stronger, it suppresses the I - effect and hence vinyl bromide undergoes electromeric effect as (II)

Conjugate effect: When an electron transfer takes place from octet of an atom to that of another atom without breaking its bond, it is known as conjugate effect.

Case II : When multiple bond is present between two different atoms electromeric shift takes place towards more electronegative atom.



+E and - E effect : When electron displacement takes place away from the atom or group it is said to be +E and it is towards the group, it is - E.

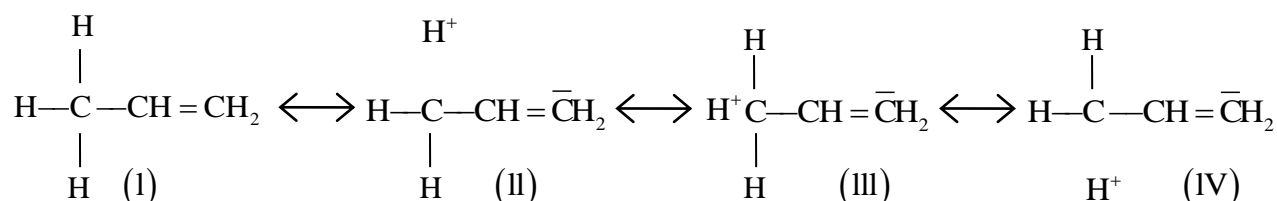


Hyperconjugation : It is the delocalization of sigma electron. Also known as sigma – pi conjugation or no bond resonance

Occurrence : Alkene, alkynes. Free radicals (saturated type) carbonium ions (saturated type)

Conditions : Presence of α – H with respect to double bond, triple bond, carbon containing positive charge (in carbonium ion) or unpaired electron (in free radicals)

Example :

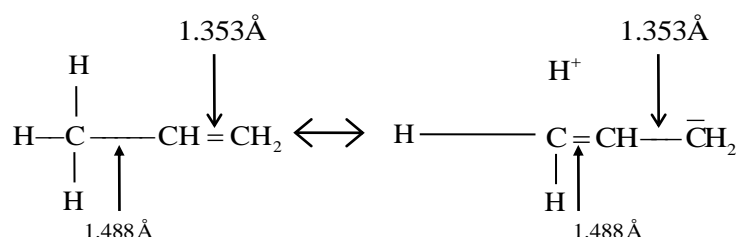


Note : Number of hyperconjugative structures = number of α – Hydrogen hence, in above examples structures ii, iii, iv are hyperconjugative structures (H-structures).

Hyperconjugation is a permanent effect

Effects of hyperconjugation

- (i) **Bond Length**: Like resonance, hyperconjugation also affects bond lengths because during the process the single bond in compound acquires some double bond character and vice – versa. E.g. C—C bond length in propene is 1.488 Å as compared to 1.334 Å in ethylene.

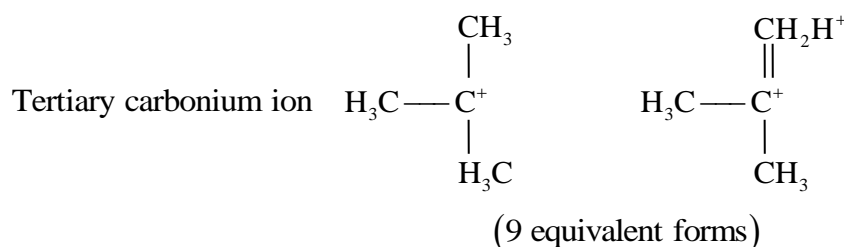


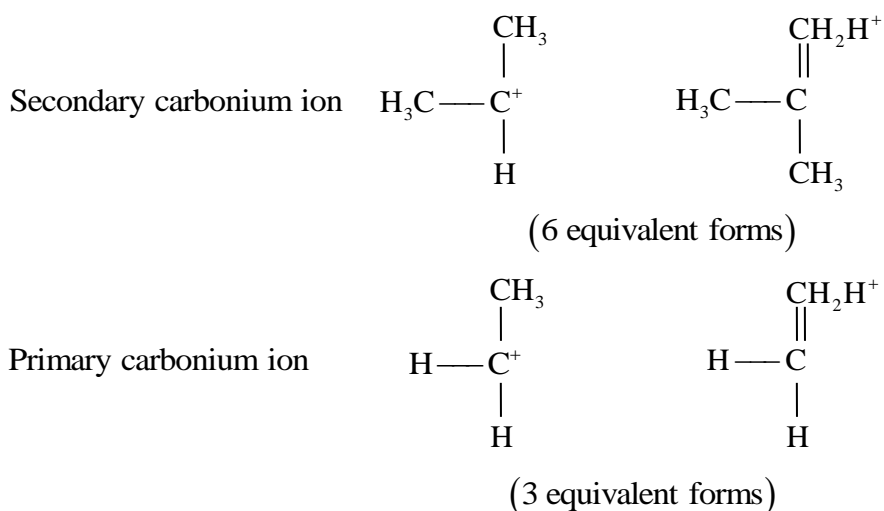
- (ii) **Dipole moment**: Since hyperconjugation causes the development of charges, it also affects the dipole moment of the molecule.
- (iii) **Stability of carbonium ions**

The order of stability of carbonium ions is as follows

Tertiary > Secondary > Primary

Above order of stability can be explained by hyperconjugation. In general greater the number of hydrogen atoms attached to α – carbon atoms, the more hyperconjugative form can be written and thus greater will be the stability of carbonium ions.



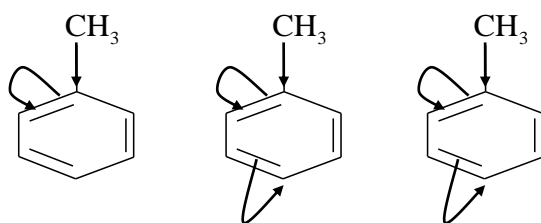


(iv) Stability of free radicals:

Stability of free radicals can also be explained as that of carbonium ion

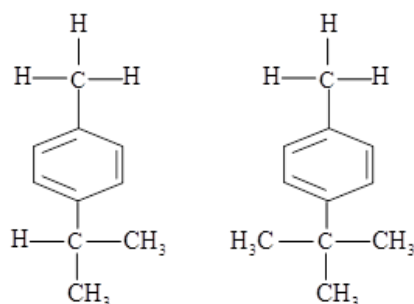


(v) Orientation influence of methyl group: The o, p-directing influence of the methyl group in methyl benzenes is attributed partly to inductive and partly to hyperconjugation effect.



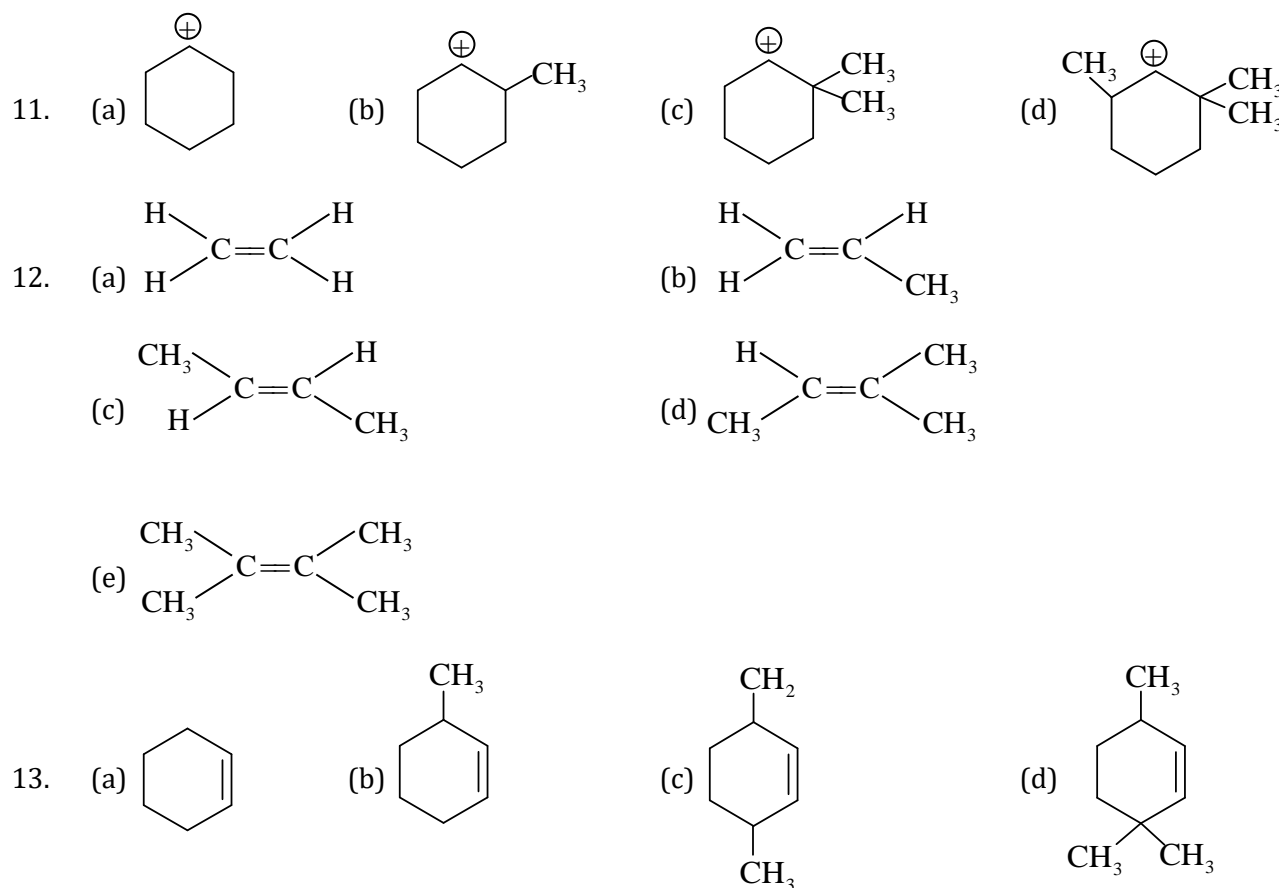
(Orientation influence of the methyl group due to +I effect)

The role of hyperconjugation in o, p, - directing influence of methyl group is evidenced by the fact that nitration of p-isopropyl toluene and p-tert butyl toluene from the product in which $-\text{NO}_2$ group is introduced in the ortho position with respect to methyl group and not to isopropyl or t-butyl group although the latter groups are more electron donating than



Methyl groups i. e., The substitutions takes place contrary to inductive effect. Actually this constitutes an example where hyperconjugation overpowers inductive effect.

Arrange the stability of following carbocation:



Reactive intermediates

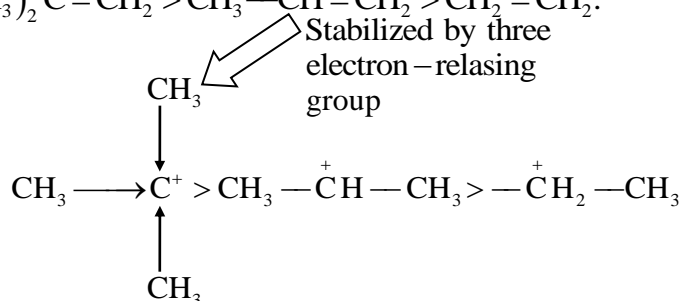
Synthetic intermediate are stable products which are prepared, isolated and purified and subsequently used as starting materials in a synthetic sequence. Reactive intermediate, on the other hand, are short lived and their importance lies in the assignment of reaction mechanisms on the pathway from the starting substrate to stable products. These reactive intermediates are not isolated, but are detected by spectroscopic methods or trapped chemically or their presence is confirmed by indirect evidence.

Carbocations

Carbocations are the key intermediates in several reactions and particularly in nucleophilic substitution reactions.

(a) **Structure :** Generally, in the carbocations the positively charged carbon atom is bonded to three other atoms and has no nonbonding electrons. It is sp^2 hybridized with planar structure and bond angles of about 120° . There is a vacant unhybridized p orbital which in the case of CH_3^+ lies perpendicular to the plane of C—H bonds .

(b) **Stability :** There is an increase in carbocation stability with additional alkyl substitution. Thus one finds that additions of HX to three typical olefins decreases in the order $(CH_3)_2C=CH_2 > CH_3-CH=CH_2 > CH_2=CH_2$.

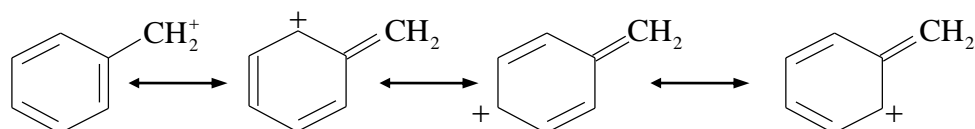


This is due to the relative stabilities of the carbocations formed in the rate determining step which in turn follows from the fact that the stability is increased by the electron releasing methyl group (+I), three such groups being more effective than two, and two more effective than one.

Stability of carbocations $3^\circ > 2^\circ > 1^\circ > \text{CH}_3^+$

Electron release : Disperses charge, stabilizes ion

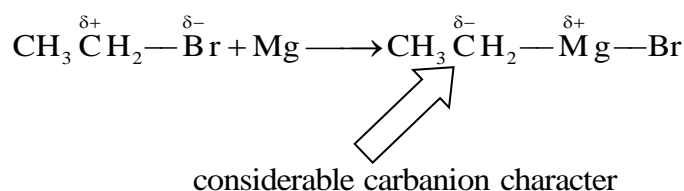
Further, any structural feature which tends to reduce the electron deficiency at the tricoordinated carbon stabilizes the carbocation. Thus when the positive carbon is in conjugation with a double bond, the stability is more. This is so, because due to resonance the positive charge is spread over two atoms instead of being concentrated on only one. This explains the stability associated with the allylic cation. The benzylic cations are stable, since one can draw canonical forms as for allylic cations.



The benzyl cation stability is affected by the presence of substituents on the ring. Electron donating p-methoxy and p-amino groups stabilize the carbocation by 14 and 26 kcal/mole, respectively. The electron withdrawing groups like p-nitro destabilize by 20 kcal/mol.

Carbanions

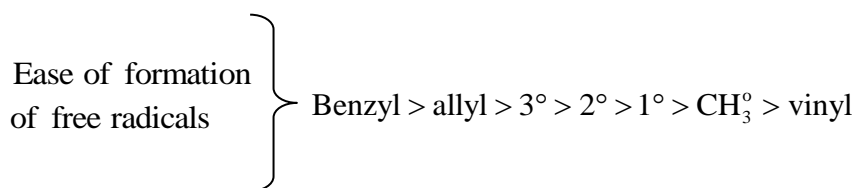
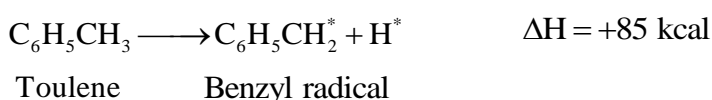
- (a) **Structure :** A carbanion possesses an unshared pair of electron and thus represents a base. The best likely description is that the central carbon atom is sp^3 hybridized with the unshared pair occupying one apex of the tetrahedron. Carbanions would thus have pyramidal structures similar to those of amines. It is believed that carbanions undergo a rapid interconversion between two pyramidal forms. There is evidence for the sp^3 nature of the central carbon and for its tetrahedral structure. At bridgehead a carbon does not undergo reactions in which it must be converted to a carbocation. However, the reactions which involve carbanions at such centres take place with ease, and stable bridgehead carbanions are known. In case this structure is correct and if all three R groups on a carbanion are different, the carbanion should be chiral. All reaction therefore, which involve the formation of chiral carbanion should give retention of configuration. However, this never happens and has been explained due to an umbrella effect as in amines. Thus the unshared pair and the central carbon rapidly oscillate from one side of the plane to the other.
- (b) **Stability and Generation :** The Grignard reagent is the best known member of a broad class of substances, called organometallic compounds where carbon is bonded to a metal lithium, potassium sodium, zinc mercury, lead, and thallium – almost any metal known. Whatever the metal it is less electronegative than carbon, and the carbon metal bond like the one in the Grignard reagent highly polar. Although the organic group is not a full – fledged carbanion – an anion in which carbon carries negative charge, it however, has carbanion character. Or organometallic compounds can serve as a source from which carbon is readily transferred with its electrons. On treatment with a metal, in RX the direction of the original dipole moment is reversed (reverse polarization).



Free radicals

- (a) **Structure and geometry:** A free radical is a species which has one or more unpaired electrons. In the species where all electrons are paired the total magnetic moment is zero. In radicals, however, since there are one or more unpaired electrons, there is a net magnetic moment and the radicals as a result are paramagnetic. Free radicals are usually detected by electron spin resonance, which is also termed electron paramagnetic resonance.

Stability: As in the case of carbocation, the stability of free radicals is tertiary > secondary > primary and is explained based on hyperconjugation. The stabilizing effects in allylic radicals and benzyl radicals is due to vinyl and phenyl groups in terms of resonance structures. Bond dissociation energies shown that 19 kcal/mol less energy is needed to form the benzyl radical from toluene than the formation of methyl radical from methane. The triphenyl methyl type radicals are no doubt stabilized by resonance; however, the major cause of their stability is the steric hindrance to dimerization.

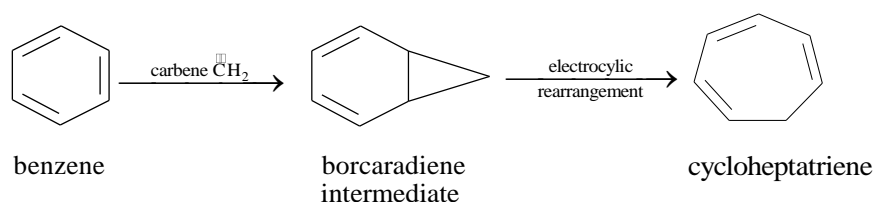


Carbenes

Carbenes are neutral intermediates having bivalent carbon, in which a carbon atom is covalently bonded to two other groups and has two valency electrons distributed between two non bonding orbitals. When the two electrons are spin paired the carbene is a singlet, if the spins of the electrons are parallel it is triplet.

- (a) **Structure:** A single carbene is thought to possess a bent sp² hybrid structure in which the paired electrons occupy the vacant sp² orbital. A triplet carbene can be either bent sp² hybrid with an electron in each unoccupied orbital, or a linear sp hybrid with an electron in each of the unoccupied p-orbital. It has however, been shown that several carbenes are in a non-linear triplet ground state. However, the dihalogenocarbenes and carbenes with oxygen, nitrogen and sulphur atoms attached to the bivalent carbon exist probably as singlets. The singlets and triplet state of a carbene display different chemical behaviour. Thus addition of singlet carbenes to olefinic double bond to form Cyclopropane derivative is much more stereoselective than addition of triplet carbenes.
- (b) **Generation :** Carbenes are obtained by thermal or photochemical decomposition of diazoalkanes. These can also be obtained by α-elimination of hydrogen halides from a haloform with base, or of a halogen from a gem dihalide with a metal.
- (c) **Reactions :** These add to carbon double bonds and also to aromatic system and in the later case the initial product rearranges to give ring enlargement products (a carbenoids – organometallic or complexed intermediates which, while not free carbenes afford products expected from carbenes are usually called carbenoids).

When a carbene is generated in a three membered ring allenes are formed by rearrangement. However, a similar formation at a Cyclopropylmethyl carbon gives ring expansion. Carbenes are also involved in Reimer – Tiemann reaction.



Nitrenes

Isomerism

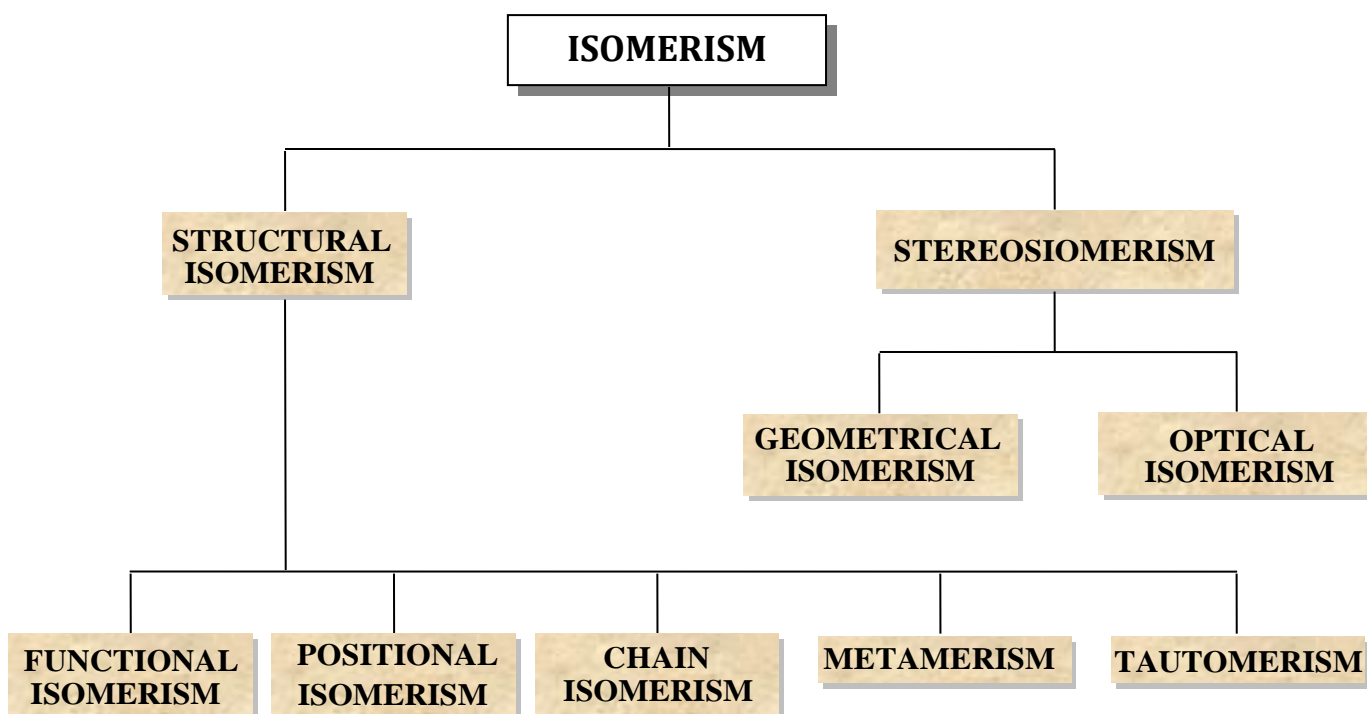
In the study of organic chemistry, we come across many cases when two or more compounds are made of equal number of like atoms. A molecular formula does not tell the nature of organic compound; sometimes several organic compounds may have same molecular formula. These compounds possess the same molecular formula but differ from each other in physical or chemical properties, are called isomers and the phenomenon is termed isomerism (Greek, isos = equal; meros = parts). Since isomers have the same molecular formula, the difference in their properties must be due to different modes of the combination or arrangement of atoms within the molecules. Broadly speaking, isomerism is of two types.

- (i) Structure Isomerism
 - (ii) Stereoisomerism
- (i) Structure isomerism:** When the isomerism is simply due to difference in the different arrangements of atoms within the molecule without any reference to space, the phenomenon is termed structural isomerism. In other words, while they have same molecular formulas, they possess different structural formulas. This type of isomerism which arises from difference in the structure of molecules includes:
- (a) Chain or Nuclear isomerism;
 - (b) Positional isomerism
 - (c) Functional isomerism
 - (d) Metamerism and
 - (e) Tautomerism.
- (ii) Stereoisomerism :** When isomerism is caused by the different *attunements* of atoms or groups in space, the phenomenon is called Stereoisomerism (Greek, Stereos = occupying space). The stereoisomers have the same structural formulas but differ in the spatial arrangement of atoms or groups in the molecules. In other words, stereoisomerism is exhibited by such compounds which have identical molecular structure but different configurations.

Stereoisomerism is of two types :

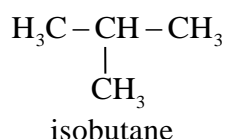
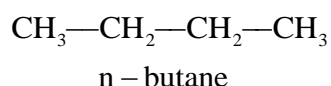
- (a) Geometrical or cis-trans isomerism; and
- (b) Optical isomerism.

Thus various types of isomerism could be summarized as follows :

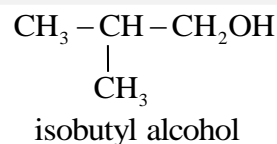
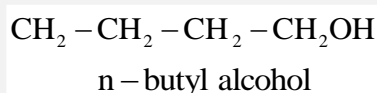


Chain or Nuclear isomerism

This type of isomerism arises from the difference in the structure of carbon chain which forms the nucleus of the molecules. It is therefore, named as chain, nuclear isomerism or Skeletal isomerism. For example, there are known butanes which have the same molecular formula (C_4H_{10}) but differ in the structure of the carbon in their molecules.

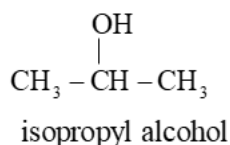
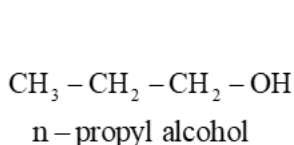


Thus n-butyl alcohol and isobutyl alcohol having the same molecular formula $C_4H_9\text{OH}$ are chain isomers.

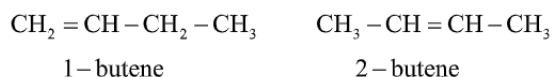


Positional isomerism

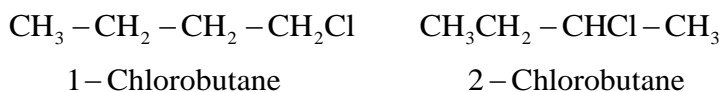
It is the type of isomerism in which the compounds possessing same molecular formula differ in their properties due to the difference in their properties due to difference in the position of either the functional group or the multiple bond the branched chain attached to the main carbon chain. For example, n-propyl alcohol and isopropyl alcohol are the positional isomers.



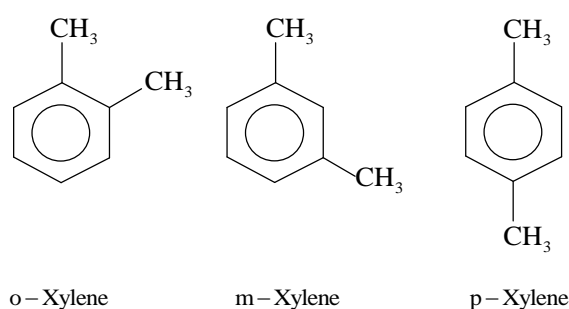
Butene also has two positional isomers:



1-Chlorobutane and 2-Chlorobutane are also the positional isomers:



Xylene $\text{C}_6\text{H}_4(\text{CH}_3)_2$, exists in the following three forms which are positional isomers.



Functional isomerism

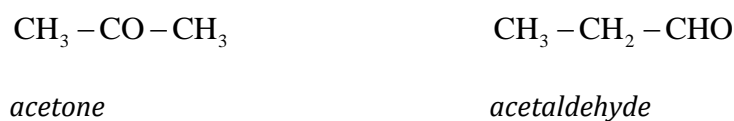
When any two compounds have the same molecular formula but possess different functional groups, they are called functional isomers and the phenomenon is termed functional isomerism. In other words, substances with the same molecular formula but belonging to different classes of compounds exhibit functional isomerism. Thus,

1. Diethyl ether and butyl alcohol both have the molecular formula $\text{C}_4\text{H}_{10}\text{O}$, but contain different functional groups.



Thus functional group in diethyl ether is $(-\text{O}-)$, while in butyl alcohol it is $(-\text{OH})$.

2. Acetone and propionaldehyde both with the molecular formula $\text{C}_3\text{H}_6\text{O}$ are functional isomers.



In acetone the functional group is $(-\text{CO}-)$, while in acetaldehyde it is $(-\text{CHO})$.

3. Cyanides are isomeric with isocyanides;



Alkyl cyanide

Alkyl isocyanide

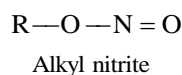
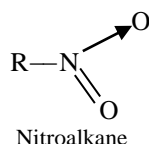
4. Carboxylic acids are isomeric with esters.



Propanoic acid

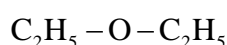
Methyl ethanoate

5. Nitroalkanes are isomeric with alkyl nitrites:



Metamerism

This type of isomerism is due to the unequal distribution of carbon atoms on either side of the functional group in the molecule of compounds belonging to the same class. For example, methyl propyl ether and diethyl both have the same molecular formula.

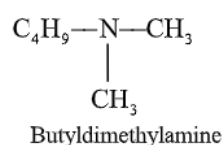
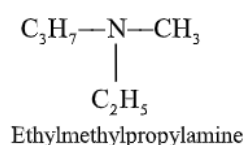
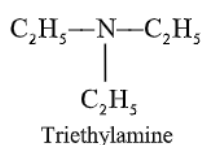


Methyl propyl ether

diethyl ether

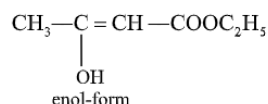
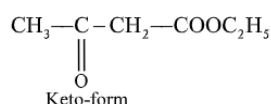
In methyl propyl ether the chain is 1 and 3, while in diethyl ether it is 2 and 2. This isomerism known as **Metamerism** is shown by members of classes such as ethers, and amines where the central functional group is flanked by two chains. The individual isomers are known as **Metamers**.

Example :



Tautomerism

It is the type of isomerism in which two functional isomers exist together in equilibrium. The two forms existing in equilibrium are called as tautomers. For example, the compound acetoacetic ester has two tautomers – one has a keto group and other has an enol group:



Out of the two tautomeric forms, one is more stable and exists in larger proportion. In above normally 93% of the keto form (more stable) and only 7% of the enol form (less stable i.e. labile) exist.

The equilibrium between the two forms is dynamic, i.e. if one form is somehow removed by making a reaction, some of the amount of the other form changes into the first form so that similar equilibrium exists again. Thus, whole of the acetoacetic ester show the properties of both ketonic group as well as the enolic groups. Thus, it adds on HCN, NaHSO_3 etc. due to the presence of $>\text{C}=\text{O}$ group and it

decolourises bromine water and gives dark colouration with FeCl_3 due the presence of $\geq \text{C}-\text{OH}$ group. Due to the presence of keto and enol form this type of tautomerism is known as keto - enol tautomerism. It is the most observed type of tautomerism.

Keto - enol tautomerism is generally observed in those compounds in which either a methyl (CH_3-), methylene ($-\text{CH}_2-$), or a methyne ($-\text{CH}-$) group is present adjacent to a carbonyl

($-\text{CO}-$) group as in acetoacetic ester above. In other words, it can be said that keto-enol tautomerism is possible in only those carbonyl compounds in which atleast one α - hydrogen atom is present so that it may convert the carbonyl group to enol group.

A hydroxy group attached to a carbon which is itself attached to another carbon atom by a double bond is known as enolic (en for double bond, ol for alcohol). Its nature becomes acidic as in phenol and unlike OH groups in alcohol which is neutral or only very slightly acidic ($\text{C}_2\text{H}_5\text{OH} + \text{Na} \rightarrow \text{C}_2\text{H}_5\text{ONa} + \frac{1}{2}\text{H}_2$). In the above two examples migration of a proton from one carbon atoms to another takes place with simultaneous shifting of bonds.

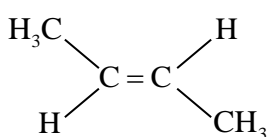
Hydrocyanic acid, $\text{H}-\text{C} \equiv \text{N}$ and Isohydrocyanic acid $\text{H}-\text{N} \equiv \text{C}$ are also tautomeric isomers or tautomers.

Difference between Tautomerism & Resonance

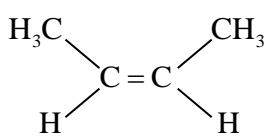
- In tautomerism, an atom changes place but resonance involves a change of position of pi-electrons or unshared electrons.
- Tautomers are different compounds and they can be separated by suitable methods but resonating structure cannot be separated as they are imaginary structures of the same compound.
- Two tautomers have different functional group but there is same functional group in all canonical structure of a resonance hybrid.
- Two tautomers are in dynamic equilibrium but in resonance only one compound exists
- Resonance in a molecule lowers the energy and thus stabilises a compound and decreases its reactivity. But no such effects occur in tautomerism.

The stereoisomerism has been classified into two main categories. These are :

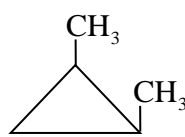
- Geometrical isomerism** Due to the restricted motion within the molecule. For examples, 2-butene and 1, 2-dimethylcyclopropane.



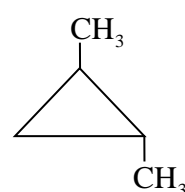
trans-2-butene



cis-2-butene



cis-1, 2-dimethylcyclopropane



trans-1, 2-dimethylcyclopropane

In *cis* form, similar groups are on the same side whereas in *trans* form, they are on the opposite side.

- (b) *Optical isomerism* Differ in the capacity to rotate the plane polarized light in the opposite directions.

The following terms are used to describe isomers.

1. *Optically active molecule* A molecule that cannot be superimposed on its mirror image. It is also called chiral molecule.
2. *Asymmetric or chiral carbon* A carbon atom that is bonded to four different groups.
3. *Enantiomers* The optical isomers which are mirror images of each other.
4. *Dextrorotatory isomer* or *(+)-isomer* An isomer which rotates the plane of polarized light to the right (clockwise direction).
5. *Laevorotatory isomer* or *(-)-isomer* An isomer which rotates the plane of polarized light to the left (anticlockwise direction).
6. *Racemic mixture* An equimolar mixture of the two isomers. Since the optical rotatory powers of two isomers are equal in magnitude but opposite in sign, the racemic mixture does not rotate the plane of polarized light. The two isomers in a racemic mixture cannot be separated by ordinary laboratory methods as the two isomers resemble each other closely in all properties except optical. They can, however, be separated if they are made to combine with another optically active compound.

Racemisation The phenomenon of conversion of one enantiomer into the other such that a mixture containing 50% of each is formed is known as racemisation.

10. *Resolution* The separation of a racemic mixture into its two optically active components is known as resolution.

Number of Optical Isomers The number of optically-active and optically-inactive isomers of a compound containing n chiral carbons may be computed from the expressions given below.

1. If the molecule is not divisible into two equal and similar halves.

$$N = 2^n \quad + 0 \quad = 2^n$$

(Optically active) (optically inactive)

Example: $\text{OHCCH}^*(\text{OH})\text{CH}^*(\text{OH})\text{CH}_2\text{OH}$; $N = 2^2 = 4$.

2. If n is even and the molecule is divisible into two equal and similar halves

$$N = 2^{(n-1)} \quad + 2^{(n-2)/2}$$

(optically active) (optically inactive)

Example: $\text{HO}_2\text{CCH}^*(\text{OH})\text{CH}^*(\text{OH})\text{CO}_2\text{H}$; $N = 2^{(2-1)} + 2^{(2-2)/2} = 3$

3. If n is odd and the molecule is divisible into two equal and similar halves via the central atom

$$N = \left[2^{(n-1)} - 2^{(n-1)/2} \right] \quad + 2^{(n-1)/2}$$

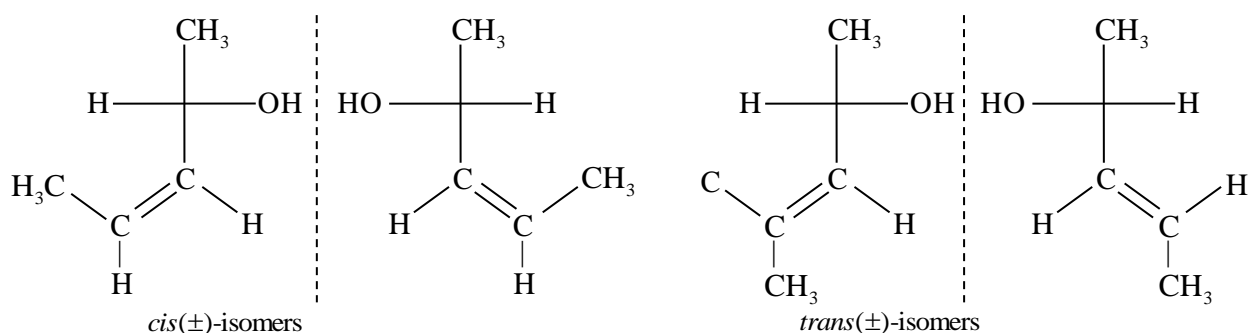
(optically active) (optically inactive)

Example : $\text{HO}_2\text{CCH}^*(\text{OH})\text{CH}^*(\text{OH})\text{CH}^*(\text{OH})\text{CO}_2\text{H}$; $N = \left[2^{(3-1)} - 2^{(3-1)/2} \right] + 2^{(3-1)/2} = 4$

4. If the molecule contains a double bond and the chiral atom is away from the terminal carbon of the double bond.

The total number of stereoisomers will be double the number of optical isomers computed from the above expressions.

Example : $\text{H}_3\text{CCH}^*(\text{OH})\text{CH}=\text{CHCH}_3$; $N = 2 * 2^1 = 4$. These are

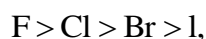


Examples

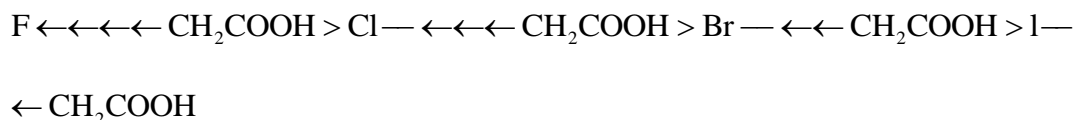
Problem 1 Can you think acidic nature of



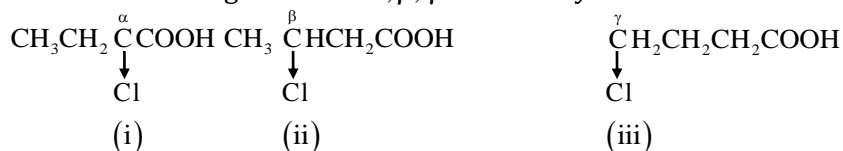
Solution As we have stated (–I) effect (electron – withdrawing nature) is in order



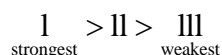
Hence (a) is strongest acid and (d) is weakest acid out of (a), (b), (c) and (d).



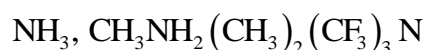
Problem 2 Take the following isomeric α, β, γ chlorobutyric acid



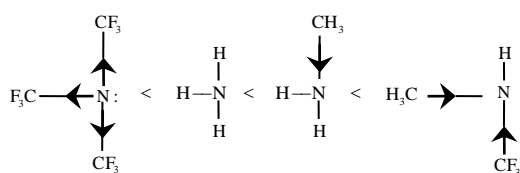
Solution As we have stated, as we go away from the source, electron – withdrawing tendency decreases, hence acidic nature also decrease. Thus



Problem 3 Compare the basic strength of the following



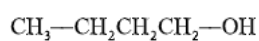
Solution The increasing order of basic strength is as follows



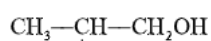
CF_3 group being - I effect groups attracts the electron pair of nitrogen makes protonation difficult in primary and secondary amine due to presence of +I effect group $\text{k}(\text{CH}_3)$ which make protonation easy. Hence the increasing order of basic strength is as follows.

Problem 7 Write all possible structural isomers of the compound with molecular formula $\text{C}_5\text{H}_{12}\text{O}$.

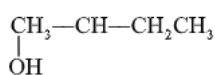
Solution Total number of structural isomers = 7



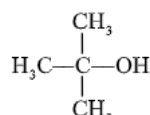
(i)



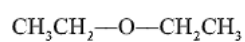
(ii)



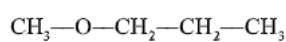
(iii)



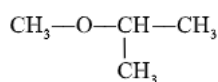
(iv)



(v)



(vi)



(vii)

Problem 9 Arrange the following species in increases order of dipole moment.

Cis - 2, 3 - Dichloro - 2 - Butene, Cis - 1, 2 - dichloroethene,

(i)

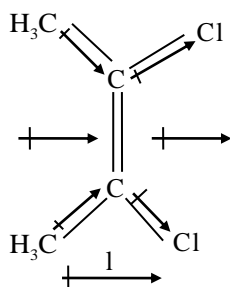
(ii)

Cis - 1, 2 - dibromo - 1, 2 - dichloroethene, trans - 1, 2 - dichloroethene

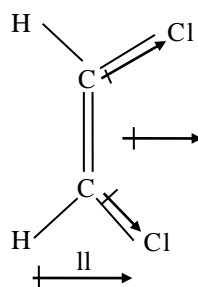
(iii)

(iv)

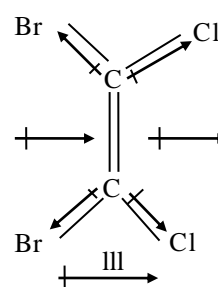
Solution



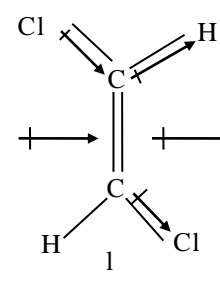
Resultant vector



Resultant vector



Resultant vector



Nonet resultant vector

In I, there is addition of vector

In II, there will neither be addition nor subtraction of vector

In III, there is subtraction of vector

In IV, the vector almost cancel each other.

So the increasing order of dipole moment is $IV < III < II < I$.