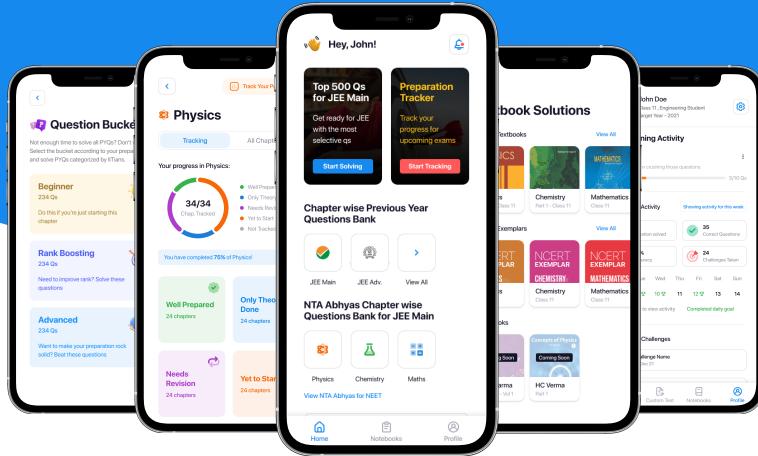




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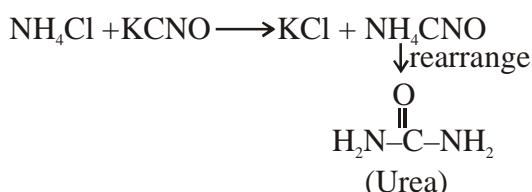
General Organic Chemistry & Isomerism

Vital force theory :

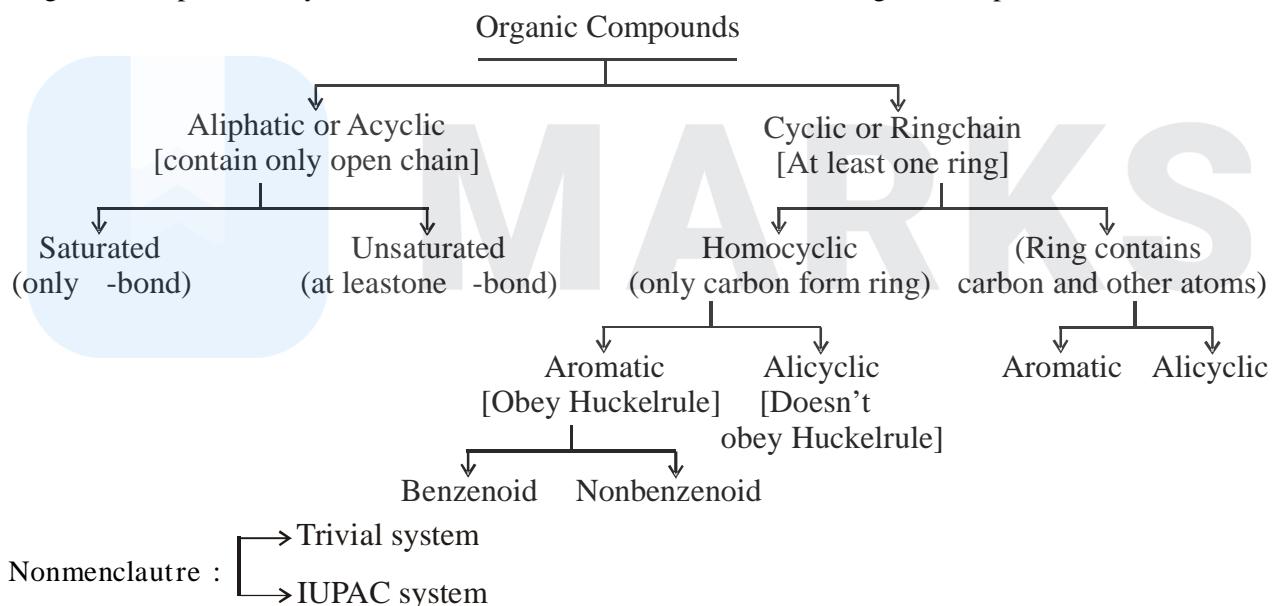
Organic compounds can be made only from natural sources. It was given by Berzelius.

Wholer synthesis :

He made urea, the first organic compound made in Laboratory from inorganic sources.

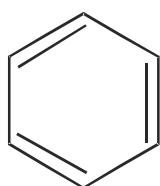


Organic Compound : Hydrocarbon and their derivatives are called as organic compounds.



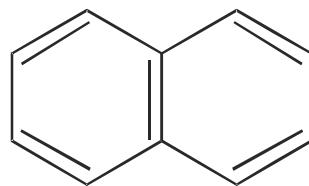
Aromatic Compounds :

Earliear, compounds with pleasant smell were called Aromatic compounds. Now a days the term aromatic means planar cyclic molecule or ion containing delocalised π -electrons, must follow Huckel's rule ie $(4n+2)\pi$ electrons, resist addition reaction, gives electrophilic substitution reaction. In Huckel's rule $n = \text{any whole number}$ ie 0, 1, 2,



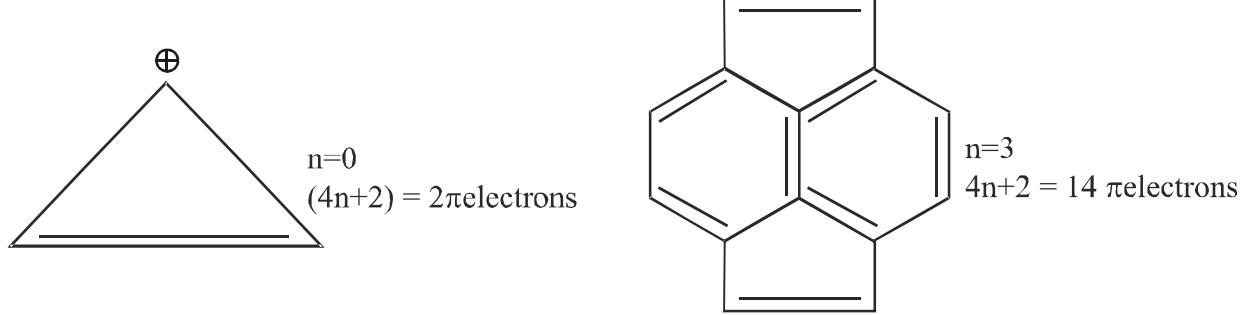
$n=1$
 $4n+2 = 6\pi$ electrons

Benzene



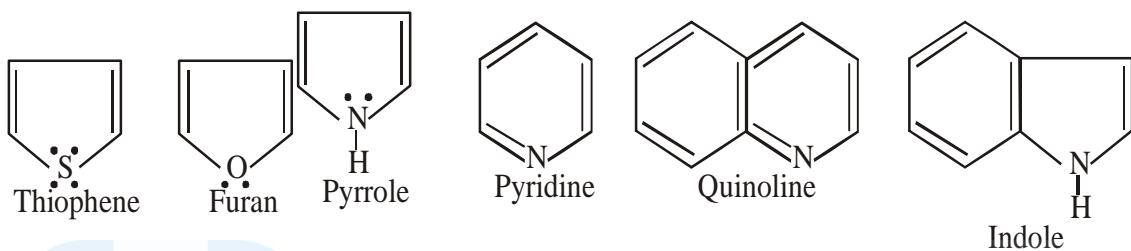
$n=2$
 $4n + 2 = 10\pi$ electrons

Naphthalene



Aromatic Heterocyclic Compounds :

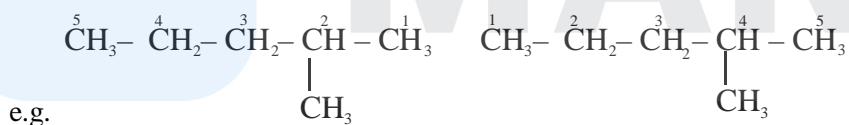
Atomatic compounds which contain a hetero atom (O, S, N etc.) in the ring are called heterocyclic compound e.g.



A. Numbering of the carbon atoms of the longest chain :

(a) Lowest individual number or lowest locant rule :

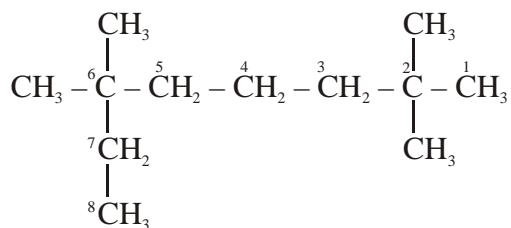
The carbon atoms carrying the first substituent get the lowest possible number.



2-Methylpentane (Correct) 4-Methylpentane (wrong)

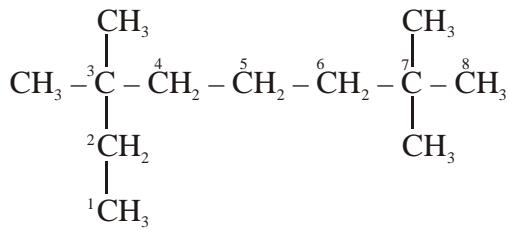
(b) Lowest Sum Rule :

When many substituents are present, the numbering is done from the end where upon the sum of locants is the lowest.



2, 2, 6, 6-Tetramethyloctane (correct)

Sum of locants = $2 + 2 + 6 + 6 = 16$

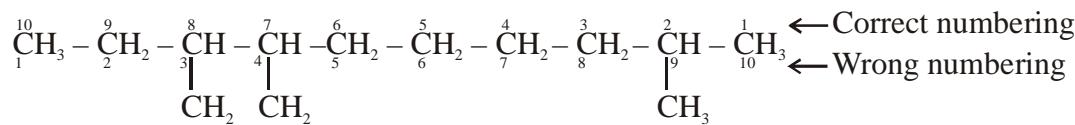


3,3,7,7-Tetramethyloctane (wrong)

$$\text{Sum of locants} = 3 + 3 + 7 + 7 = 20$$

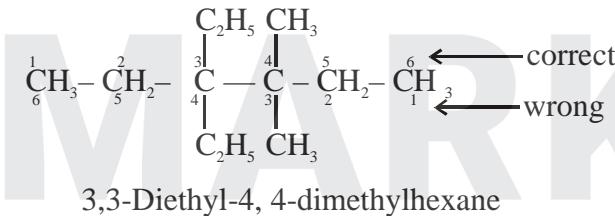
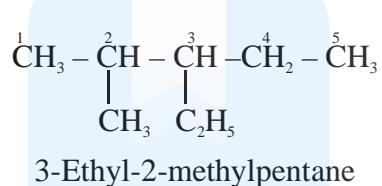
(c) First point of difference rule :

For a very long carbon chain, the set of locant is preferred which has a lower number at the first point of difference even, if it violates the lowest sum rule.



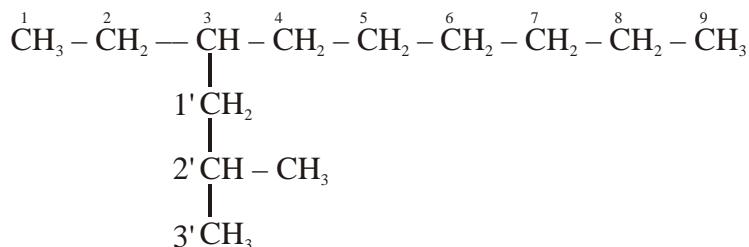
(d) Alphabetical order of simple substituents :

If there are different alkyl substituents attached to the parent chain, their names are written in the alphabetical order.



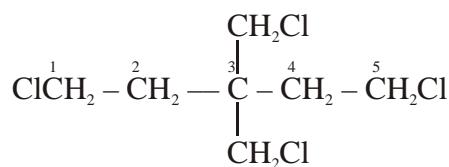
B. Naming the Complex Alkyl Substituents

When the substituents on the parent chain is itself branched chain, it is named as substituted alkyl group and its carbon chain is separately numbered in such a way, that the carbon atom directly attached to the parent chain is given number 1'. The name of this complex substituents is written in brackets.



3-(2'methylpropyl)nonane

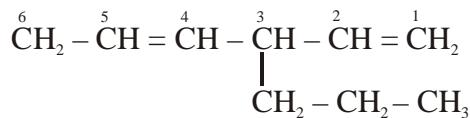
Note : The numerical prefixes 'bis', 'tris', 'tetrakis' etc. are used to indicate a multiplicity of substituted substituent.



3,3-Bis (Chloromethyl)-1,5-dichloropentane

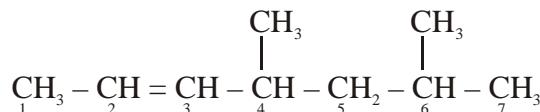
C. Rules ;for having complex unsaturated Aliphatic Hydrocarbons

- (i) Longest chain : The longest chain of carbon atoms (parent chain) is so selected as to include the double or triple bond even if it is not the actual longest chain of carbon atoms.



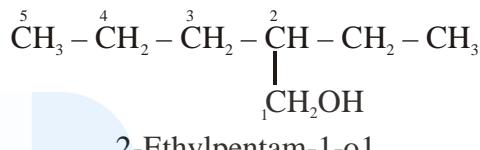
3 – Propylhexa - 1,4-diene

- (ii) Numbering of carbon chain : The parent carbon chain is numbered in such a manner so as to give lowest number to that carbon atom linked by double or triple bond even if it violates the rules of saturated hydrocarbons.



4,6-Dimethylhept-2-ene

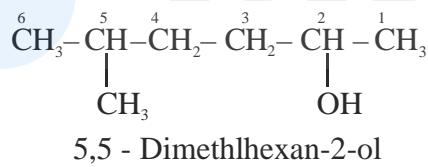
D. Rules for Naming Complex Aliphatic Compounds Containing one Functional Group :



2-Ethylpentam-1-ol

Numbering of Parent Chain

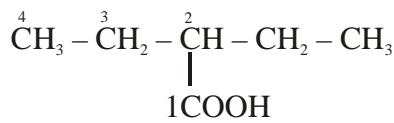
The numbering of the parent carbon chain is done in such a way that the carbon linking to functional group gets the lowest number even if there is violation of saturated hydrocarbon rules.



5,5 - Dimethylhexan-2-ol

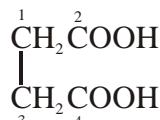
Note:

- (i) When a chain terminating group such as $-\text{CHO}$, $-\text{COOH}$, $-\text{COOR}$, $-\text{CONH}_2$, $-\text{C}\equiv\text{N}$, etc is present as the functional group, it must be assigned number 1. This does not apply to non-terminal groups such as $>\text{CO}$, $-\text{NH}_2$ and $-\text{OH}$ from first position may or may not be assigned.

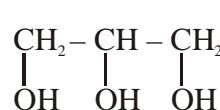


2-Ethylbutanoic acid

- (ii) Numerical prefixes di-, tri-, tetra etc are attached before the designations of functional group if two or more identical groups are present. e.g.

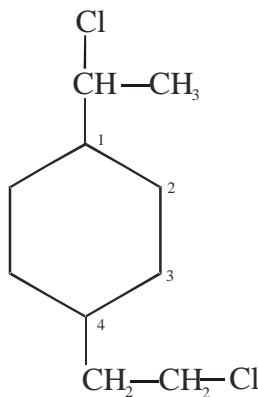


Butane-1,4-dioic acid



Propane – 1,2,3 - triol

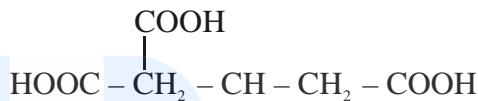
- (iii) When two or more prefixes consists of identical roman letters, priority is given to the group which contains the lowest locant at the first point difference. e.g.



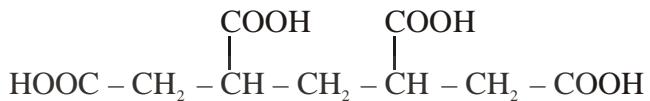
1-(1'-chloroethyl)-4-(2'-chloroethyl) cyclohexane

Here 1'-chloroethyl gets priority over 2'-chloroethyl.

- (iv) If unbranched chain is linked directly to more than two carboxyl groups, these groups are named by substitutive use of suffix "tricarboxylic acid" etc. The principal chain selected should be linked directly to maximum possible number of carboxyl groups e.g.

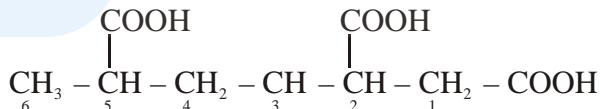


Butane 1, 2, 3-tricarboxylic acid



Pentane-1,2,4,5-tetracarboxylic acid

- (v) The carboxylic groups which are not directly linked to the principal chain are expressed as carboxyalkyl prefixes e.g.



3-(carboxymethyl)hexane-1,2,5-tricarboxylic acid

Similarly, the substitutive prefixes for aldehyde, cyanides, acylchlorides and amides are carbaldehyde carbonitrile, chlorocarbonyl and carboxamide respectively.

E. Rules for Naming Aliphatic Compounds Having Polyfunctional Groups

A compound containing more than one functional group is called polyfunctional compound. In IUPAC system, one of the functional groups is chosen as the principal function group (secondary suffix) and the remaining functional groups (secondary functional groups) are treated as substituents and indicated by prefixes.

The choice of the principal functional group is made on the basis of the following order of preference.

Carboxylic acid > sulphonic acid > acid anhydrides > esters > acid chlorides > acid amides > cyanides > aldehydes . ketones > alcohols, phenols, thiols > amines > alkenes > alkynes > halo, nitro, alkyl

Seniority Table for Principal groups

(Highest priority group at the top)

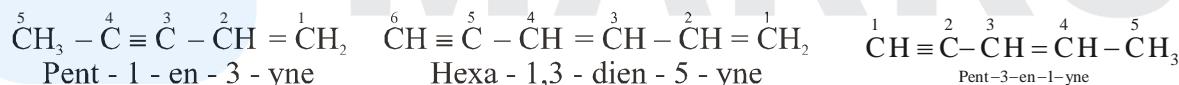
Group	Prefix Name	Suffix Name
-COOH	Carboxy	-oic acid
-SO ₃ H	Sulpho	Sulphonic acid

-COOR	Alkoxy carbonyl or Carbalkoxy	oate
-COX	Haloformyl or Halocarbonyl	-oyl halide
-CONH ₂	Carbamoyl	amide
-CN	Cyano	nitrile
-NC	Isocyano	Carbylamine
-CHO	Formyl or aldo	-al
>C = O	Keto or oxo	-one
-OH	Hydroxy	-ol
-SH	Mercapto	Thiol
-NH ₂	Amino	amine
>C = C<	-	-ene
-C ≡ C -	-	yne

1. The first step in the naming of polyfunctional compounds is the selection of principal functional group which gives the class name of the structure.
2. The second step is the selection of parent chain as such it includes the maximum number of functional group including the principal group.
3. The third step is the numbering of parent chain. Which is done from the side of principal functional group i.e. it gets lowest number. The following decreasing order of preference for giving the lowest numbers is followed.
Principal functional group > Double bond or Triple bond > Substituents.

Note :

- (a) If a molecule contains both carbon-carbon double and triple bonds, preference of numbering is generally given from the double bond side. But in one case when triple bond is present at the terminal position and double bond at any where in central position, then numbering should be done from triple bond side.



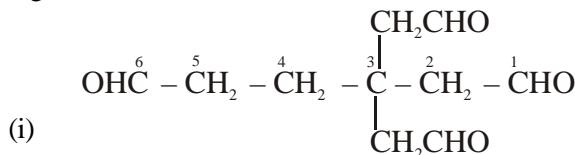
- (b) In case two substituents of same seniority occupy identical position in relation to the end of the chain, the lower number should be given to the substituent in alphabetical order.



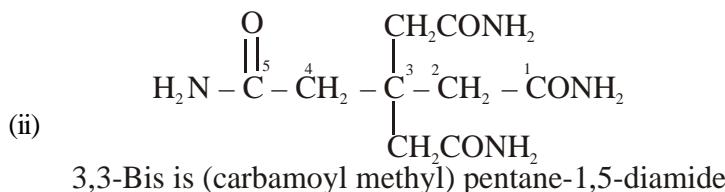
1-Bromo-3-Chloropropane

4. If all the like groups are not directly linked to the unbranched carbon chain, the carbon atoms of the two like groups are included in the present chain while the third which forms the side chain is considered substituent group.

e.g.



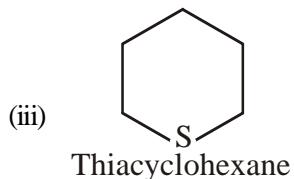
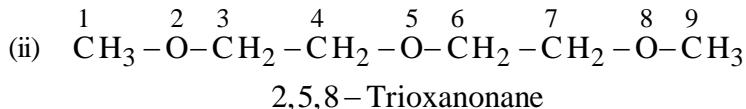
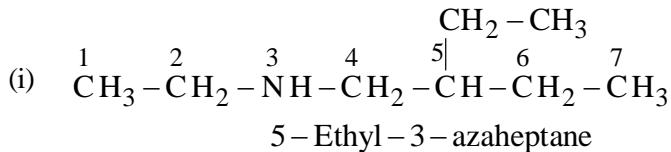
3,3-Bis (formylmethyl) hexane-1, 6-dial



F. Replacement Nomenclature

In this system, ethers, sulphides, selenides and amines are named as oxa, thia, selena and aza derivatives of alkane corresponding to the total number of carbon and oxygen or sulphur or selenium or nitrogen atoms.

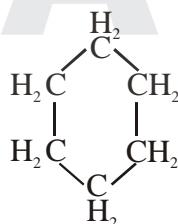
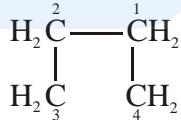
The location of these hetero atoms on the carbon chain are indicated by numerals in accordance with lowest set of locant rule.



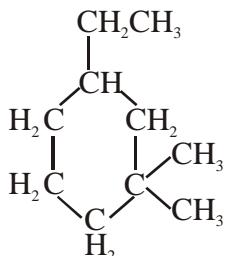
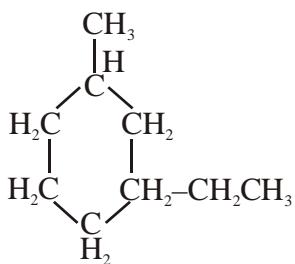
IUPAC NOMENCLATURE OF ALICYCLIC COMPOUNDS

1. Cycloalkanes

In cycloalkanes, carbon atoms are arranged in a ring.

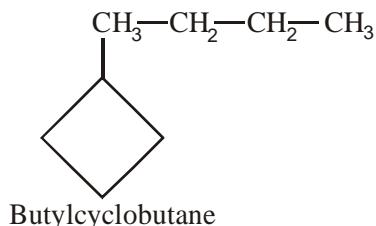


Substituted cycloalkanes are named as alkyl cycloalkanes. The substituent which comes first in the alphabetical order is given the lowest possible number provided it does not violate the lowest set of locants rule.

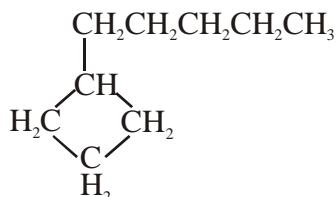


1-Ethyl-3-methylcyclohexane 3-Ethyl-1,1-dimethylcyclohexane

When the ring contains more or equal number of carbon atoms than the alkyl group attached to it, then it is named as a derivative of cycloalkane and the alkyl group is treated as substituent.

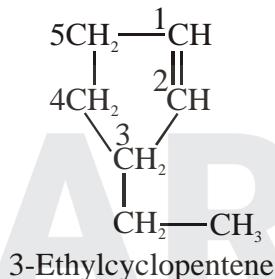
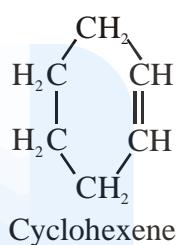


In case the diphatic chain contains greater number of carbon atoms than present in the ring, the compound is considered as derivative of alkane and the ring is designated as substituent.

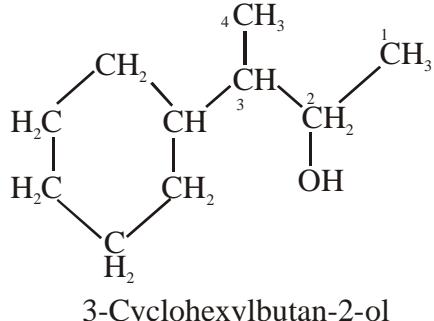
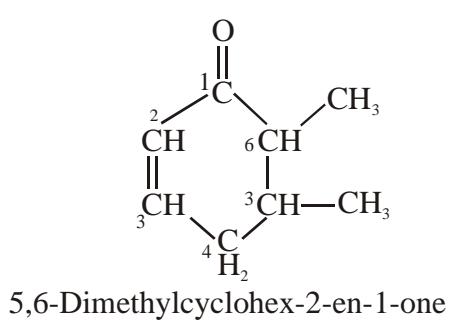
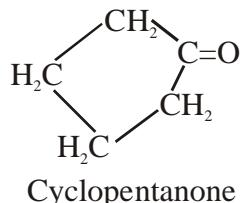
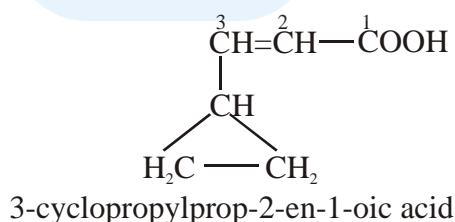


1-Cyclobutylpentane

2. Cycloalkenes and Cycloalkynes :

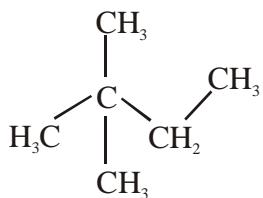


3. Alicyclic compounds containing functional group

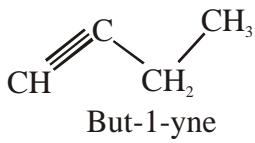


Note : If the side chain contains a multiple bond or a functional group, the alicyclic ring is treated as substituent irrespective of the size of the ring.

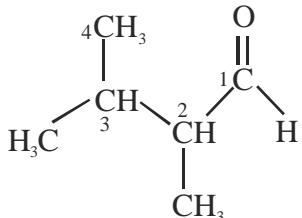
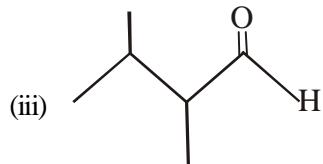
The structure of the compound is represented by bond line. The free end is occupied by C-atom group and bent portion is occupied by $-\text{CH}_2$ group. C-atom. Rest valency of carbon is satisfied by adding H-atom.



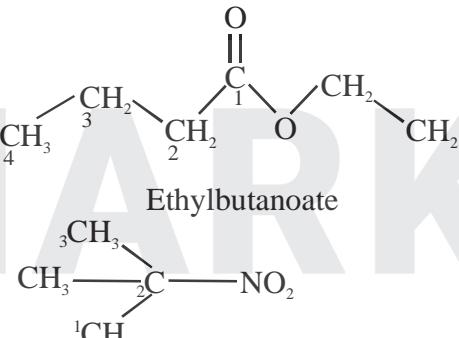
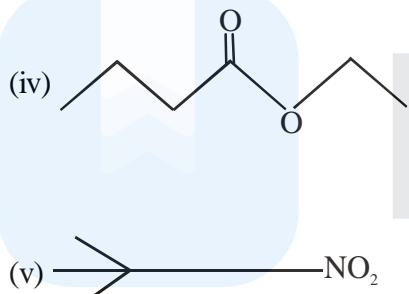
2,2-Dimethylbutane



But-1-yne



2,2-Dimethylbutanal

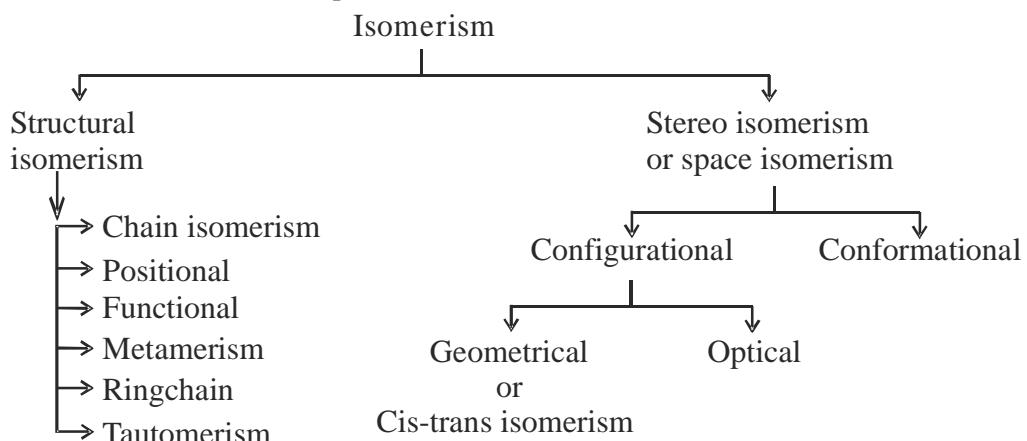


Ethyl-2-nitropropane

ISOMERISM

Definition:

The different organic compounds having same molecular formula but different physical or chemical or both the properties are called isomers and the phenomenon is called Isomerism.

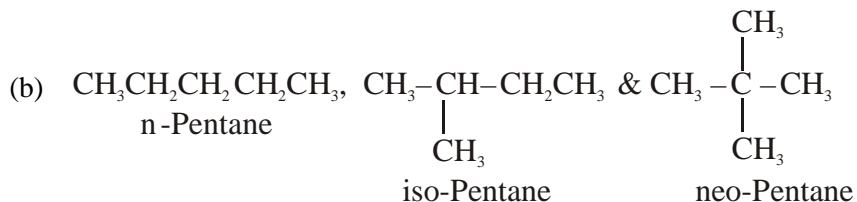
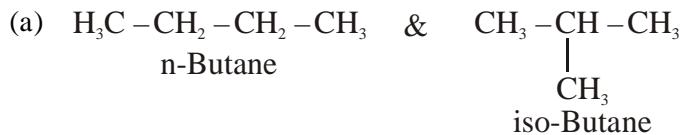


A. STRUCTURAL ISOMERISM

Arises due to the difference in the manner of linkage of atom to atom.

1. Chain isomerism/Skeleton/Nuclear :

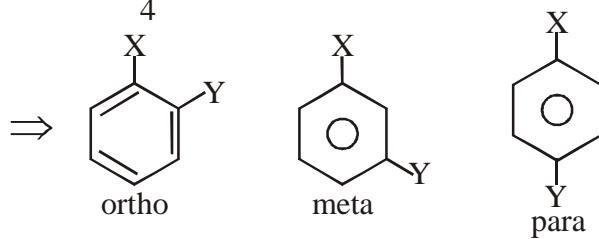
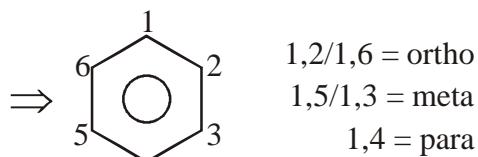
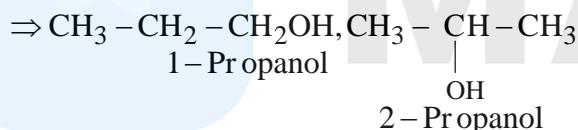
The structural isomerism which arises due to the difference in the length of C-chain is called chain isomerism.



2. Positional Isomerism :

The structural isomerism which arises due to the difference in the position of

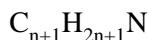
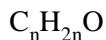
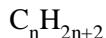
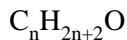
- (a) Double bond
- (b) Triple bond
- (c) Same functional groups



3. Functional Isomerism :

The isomerism which arises due to the difference in their functional group is called as functional isomerism.

General Formula



Homologous Series

Alcohol

Aldehyde

Acid

Cyanide

Homologous Series

Ether

Ketone

Ester

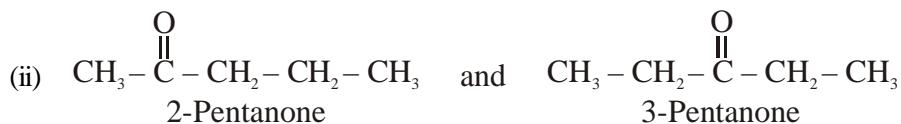
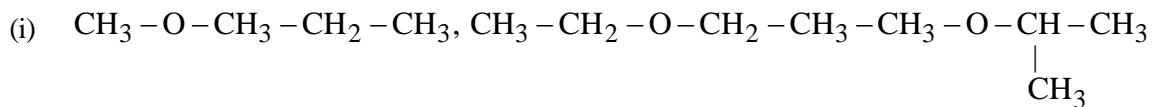
Isocyanide (carbylamine)



4. Metamerism :

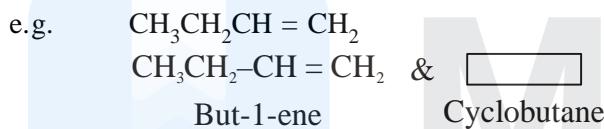
- The structural isomerism which arises due to the difference in the distribution of C-atom on the either or both sides of same functional group.
- Metamers can also be chain and position isomers.

Some examples of Metamerism



5. Ring Chain Isomerism

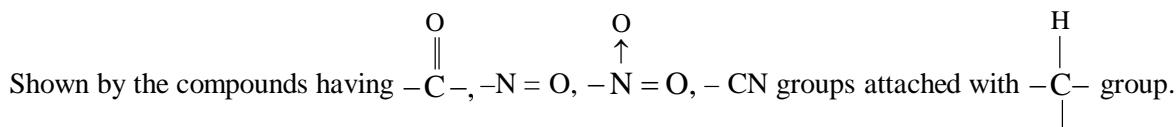
Shown by unsaturated hydrocarbons and alicyclic compounds.



* Ring chain isomers are actually a type of functional isomers.

6. Tautomerism :

- It is special type of functional isomerism in which two functional isomers interconvert due to the movement of an acidic H-atom between two poly valent atoms. Here two isomers exist in dynamic equilibrium and hence it is also known as desmotropism/kryptomerism/Alleotropism.



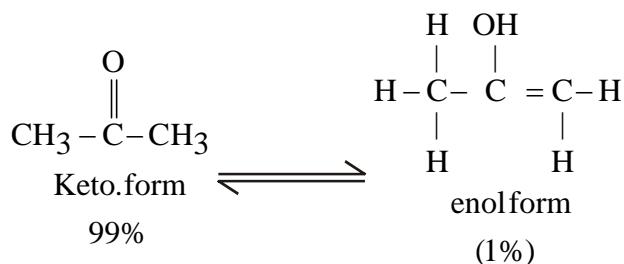
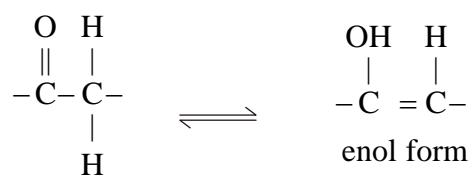
- Tautomerism arises due to shift of an atom from one site in the molecule to another equivalent site in the same molecule.

SOME EXAMPLES OF TAUTOMERISM :

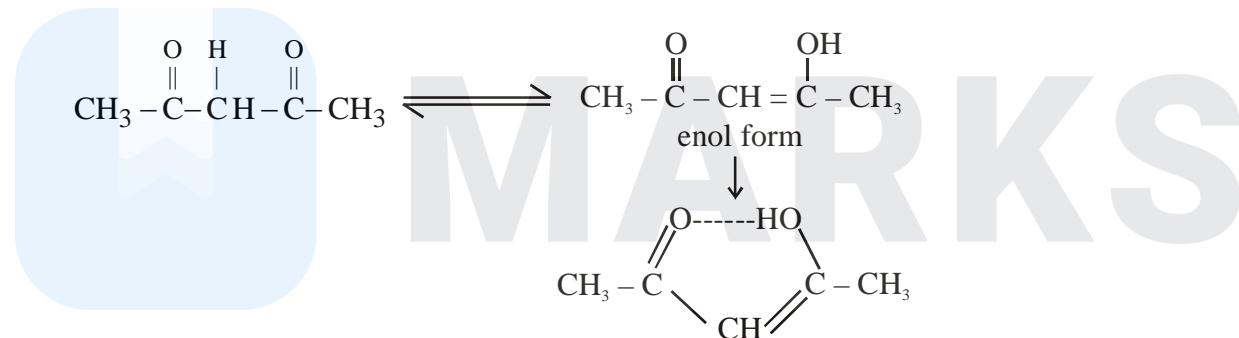
(i) Keto-enol tautomerism :

- Aldehydes and ketones containing $-\text{C=O}-\text{CH}_2-$ group shows tautomerism.

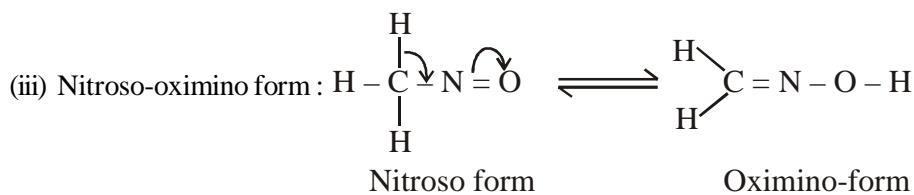
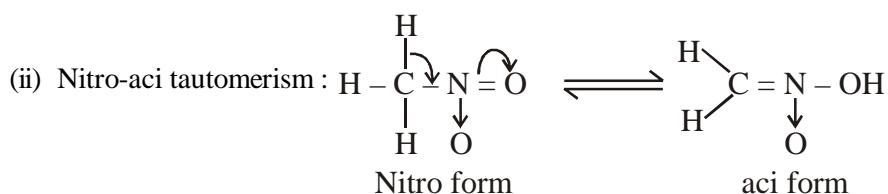
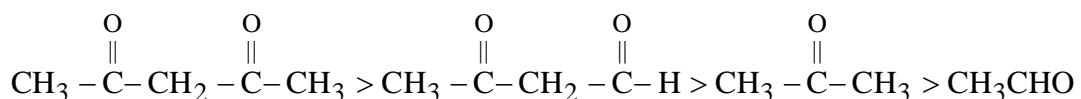
- Enol containing $\text{---C}(\text{OH})=\text{C}---$ group shows tautomerism.



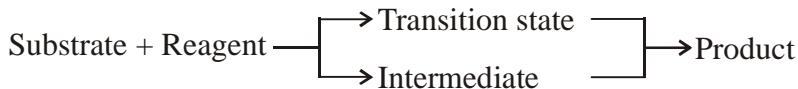
- β -diketones have more enolic content due to the formation of chelation.



Order of enol-content of some molecule :



MECHANISM

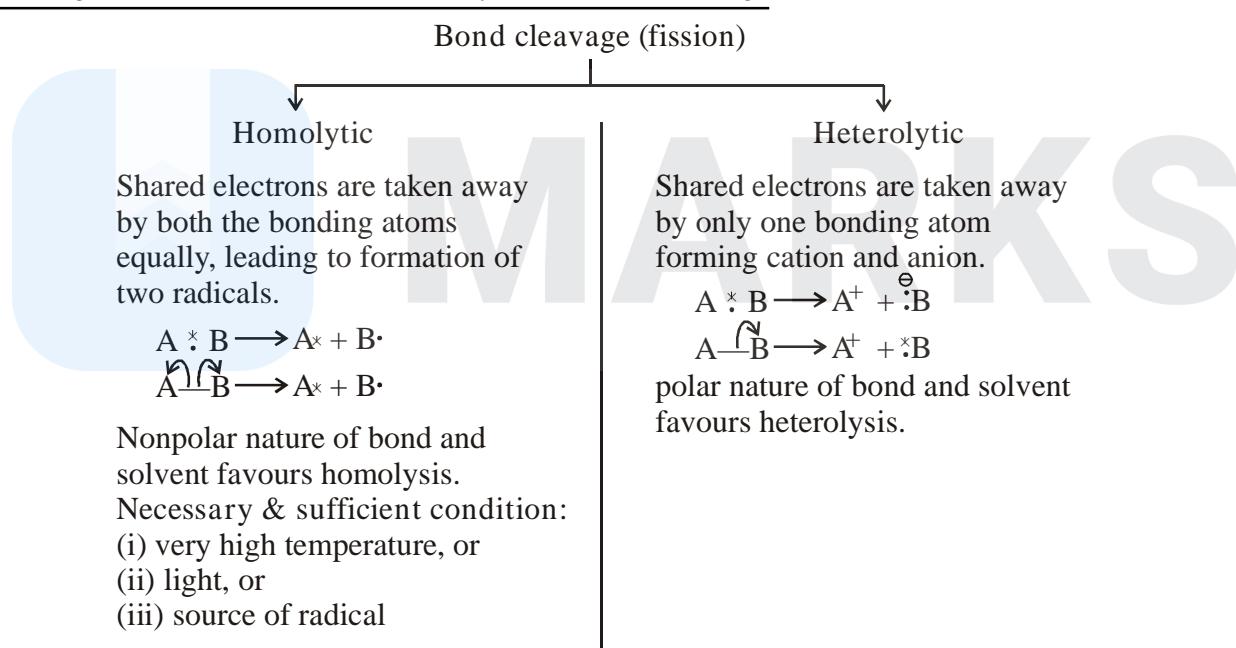


Substrate : Part of reactant which is underattack.

Reagent : Part of reactant which attacks over substrate.

Reagents		
Electrophile	Nucleophile	Free radicals
Electron pair seeking groups. e.g. ${}^+ \text{CH}_3$, ${}^+ \text{H}$, ${}^+ \ddot{\text{Cl}}$: AlCl_3 , BF_3 , And all lewis acids	Electron pairdonors. e.g. :CH_3 , :H , :Cl^- : :NH_3 , $\text{H}_2\ddot{\text{O}}$: And all lewis bases	Species having at least one unpaired e^- . E.g. $\cdot \text{H}$, $\cdot \text{CH}_3$, $\cdot \ddot{\text{Cl}}^-$

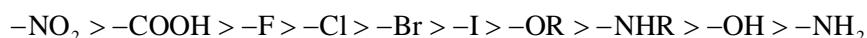
When reagent attacks over substrate they cause bond cleavage



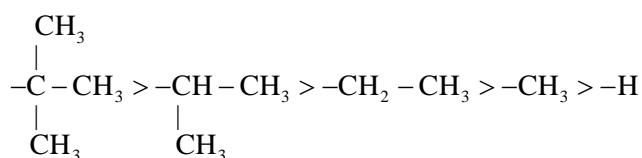
ELECTRON DISPLACEMENT :

Inductive effect : - Permanent effect in which polarisation of one bond induces polarisation in all the neighbouring bonds but with the decreasing efficiency as we move farther from the group is called as inductive effect.

-I group : Electron withdrawing groups.

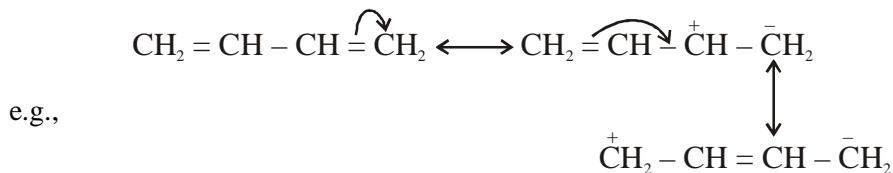


+I group : Electron repelling groups :



Mesomeric Effect :

Shifting of π -electrons in conjugate system giving permanent polarity on the chain.



Delocalisation of π -electrons as a result of mesomeric effect giving a number of resonance structures. Due to this effect terminal carbon is almost as positive as the first carbon. This is quite different from Inductive effect due to which charge decreases as one moves away from the source.

Types :

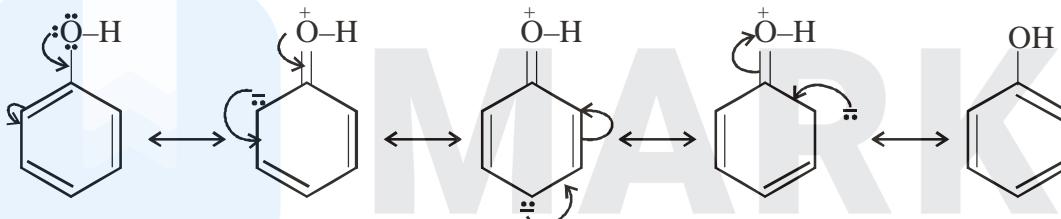
(a) Positive Mesomeric Effect (+M) :

- The direction of electron displacement is away from the group or atom having lone pair of electrons.
- They release the electron pair for conjugation with an attached conjugated system.

e.g. $-\ddot{\text{O}}\text{H}$, $-\ddot{\text{O}}\text{R}$, $\ddot{\text{N}}\text{H}_2$, $-\ddot{\text{S}}\text{R}$, $-\ddot{\text{X}}$: etc. show +M effect.



- | In case of aromatic compound they are ortho and para directors. (Ring activators)

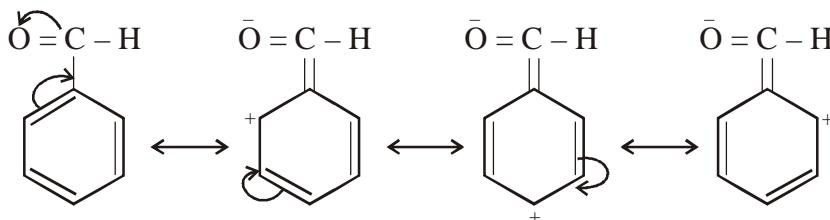


Note : Electron density increases at o & p-positions, electrophile attacks at o and p positions.

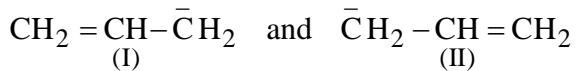
(b) Negative Mesomeric effect (-M effect)

- Displacement of π -electron takes place away from conjugate system.
- -M effect deactivates the conjugate system for S_E (Electrophilic substitution reaction)
- -M effect decreases electron density in the conjugate system thus in case of aromatic compound these are meta director.

- | Eg. $-\text{CN}$, $-\text{CHO}$, $-\text{COOH}$, $-\text{NH}_3^+$, etc show -M effect.

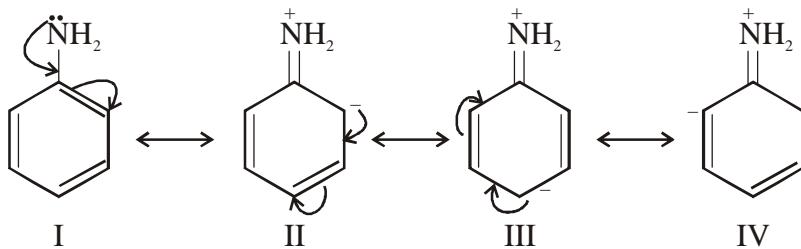


Note : Conjugate compounds can be represented by two or more than two possible structures due to the delocalisation of conjugated electrons. These possible structures are known as Resonating structures. The real structure of conjugated compounds is a hybrid of all resonating structures. This phenomenon is known as resonance. Thus resonance is hybridisation of resonating structures.



I and II are Resonating structures of allyl carbanion.

- Resonating structures are not the real structures of conjugated compounds.



I to IV are the resonating structures of aniline. The real structure of aniline will be a resonance hybrid of all these four structures.

Effect of resonance on the conjugate functional group of the compound.

- (a) Resonance decreases bond length of functional group thus increases bond energy.

$$(b) \text{ Bond length of functional group} \propto \frac{1}{\text{No.of resonating structures}}$$

- (c) Bond strength \propto No. of resonating structures.

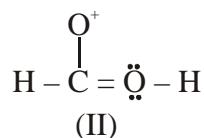
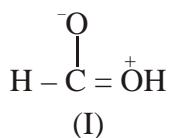
$$(d) \text{ Reactivity of functional group due to bond breaking} \propto \frac{1}{\text{No.of resonating structures}}$$

- (e) Stability of conjugated compounds \propto No. of resonating structures.

Contribution of Resonating Structures :

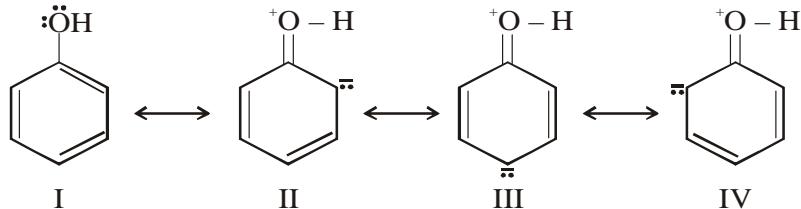
It depends upon the stability of structure and the stability depends upon

- (i) Neutral species is more stable than the charged (or dipolar species).
- (ii) Species having complete octet is more stable than the species having incomplete octet.
- (iii) If all structures have formal charge, the most stable one is that in which the positive and negative charges reside on the most electropositive and most electronegative atoms of the species respectively.



- (iv) Resonating structure with a greater number of covalent bonds is more stable.

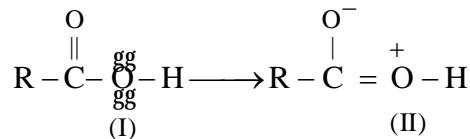
- (v) Increase in charge separation decreases the stability of a resonating structure.



$\text{I} > \text{II} \equiv \text{IV} > \text{III}$ (stability order)

Conditions of Resonating Structures :

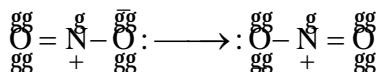
- All resonating structures must have the same arrangement of atomic nuclei



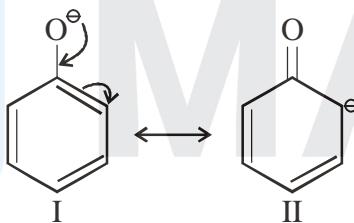
- N. B.: Position of atomic nuclei in (I) and (II) are same,



- Position of H-nuclei in (III) and (IV) are different, hence (III) and (IV) are not the resonating structures.
- The resonating structures must have the same numbers of paired and unpaired electrons. However, they differ in the way of distribution of electrons.

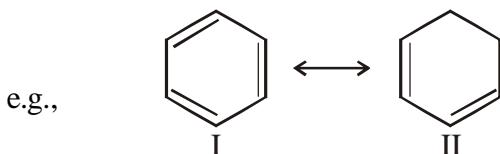


- The energies of the different resonating structures must be the same or nearly the same.
- All atoms that are part of the delocalisation system must be planar.
- All atoms of the resonating structures should follow the octet rule.



- Bond order in compounds which exhibit resonance

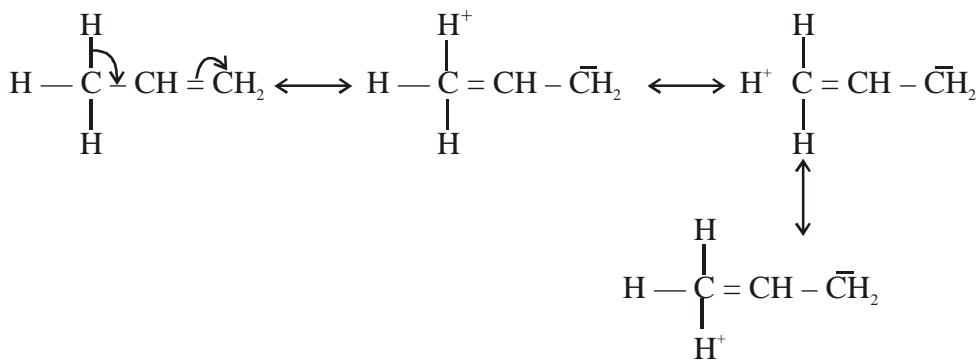
$$= \frac{\text{Total no. of bonds on central atom among all resonating structures}}{\text{No. of resonating structures}}$$



$$\text{Bond order of carbon in benzene} = \frac{2+1}{2} = 1.5$$

Hyperconjugation/No Bond Resonance/Baker - Nathan Effect/}\sigma - \pi\text{ Conjugation

- When sp^3 carbon containing at least one H is in conjugation with sp^2 carbon.
- Compound should have at least one sp^2 -hybrid carbon of either alkene, alkyl carbocation or alkyl free radical.
- Resonating structures due to hyperconjugation may be written involving “no bond” between the alpha carbon and H-atoms.
- No bond resonance can be represented as



Electromeric Effect (Temporary effect) :

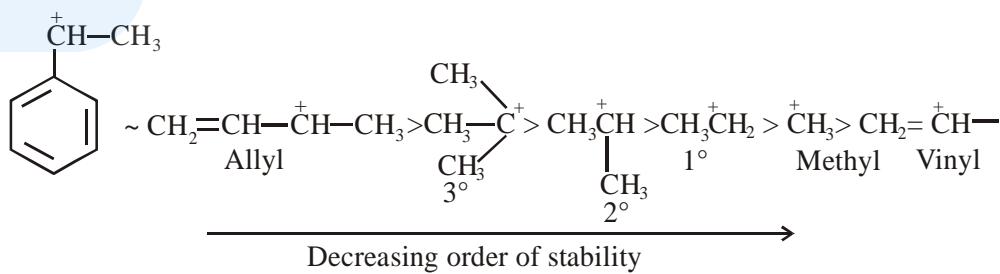
When a compound having π bond is approached by a charged reagent (electrophile or nucleophile), the electrons of the bond are completely polarised or displaced towards one of the constituent atoms due to electrostatic attraction or repulsion.

Type of reactions :

Organic Reaction Intermediates

1. Carbon Free Radicals :

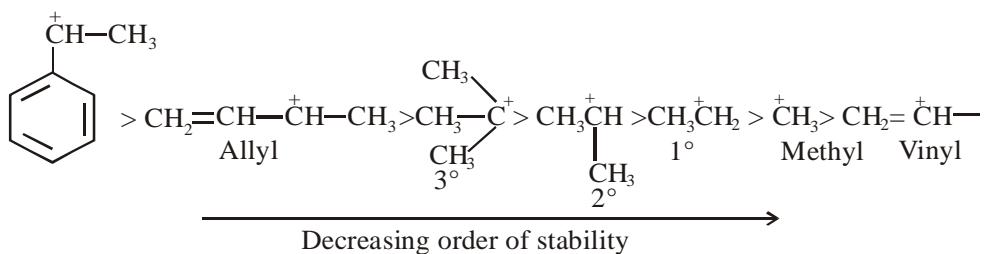
- Formed due to homolytic fission
- Carbon atom having one odd electron.
- Incomplete octet so highly reactive towards other free radicals.
- Carbon free radical is sp^2 hybridised.
- H-C-H bond angle in $\dot{C}H_3$ is 120° and three C-H coplanar.
- Stability order of different types of carbon free radicals are



Note : (i) Greater the stability easier will be formation of that species.
(ii) Stability of allyl and benzyl carbon free radical is explained by resonance and stability of 3° , 2° , and 1° carbon free radicals is explained by hyperconjugation i.e. number of hyperconjugation effect \propto stability.

2. Carbocation / Carbonium Ion :

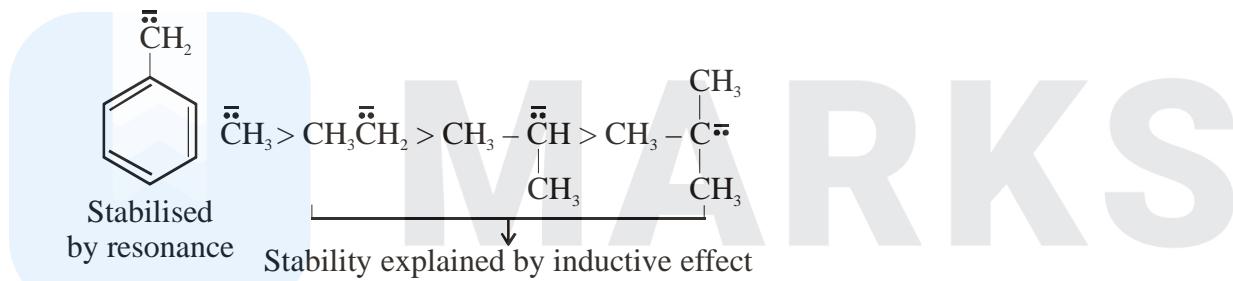
- * Results due to heterolytic fission.
- * Carbon atom having positive charge
- * Incomplete octet thus reactive towards electron rich species (Nucleophiles).
- * Stability order of different types of carbocations.



Note : Stability of allyl and benzyl carbocation is explained by hyperconjugation and inductive effect. Number of hyperconjugation effect \propto stability

3. Carbanion :

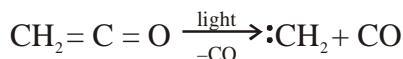
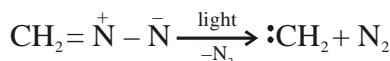
- * An organic ion with a pair of available electrons and a negative charge on the central carbon atom is called a carbanion.
 - Carbanion is sp^3 hybridised. Its geometry is pyramidal like NH_3 . It is an electron rich species, thus reactive towards electron deficient species (electrophiles).
 - Stability order of different types of carbanions:



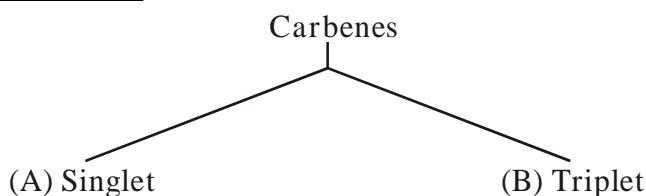
- Presence of electron-attracting group (-CN , NO_2) increases stability and presence of electron-releasing group (-CH_3) etc decreases stability of carbanion.

4. Carbenes :

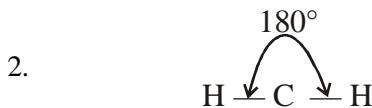
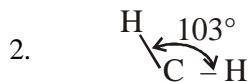
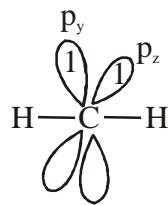
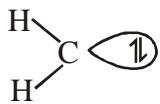
- Obtained by photolysis of either diazomethane (CH_2N_2) or keten ($\text{CH}_2=\text{C=O}$)
 - Incomplete octet thus highly reactive.



- Exists in two forms.



1. In this case unshared electrons are paired (sp^2 hybridised)
 2. Unshared electrons are not paired (sp hybridised) These are present in two unhybridised p-orbital.



3. Bond length between C–H is 1. 12 Å.

3. Bond length between C–H is 1. 12 Å.

4. Less stable

4. More stable

5. an electrophile

5. A free diradical

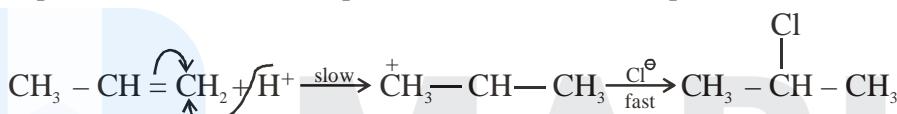
DIFFERENT REACTION

1. Addition reactions:

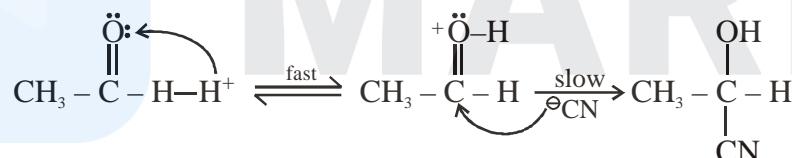
Formation of two new σ -bonds due to breaking of a π -bond.

It is of three types :

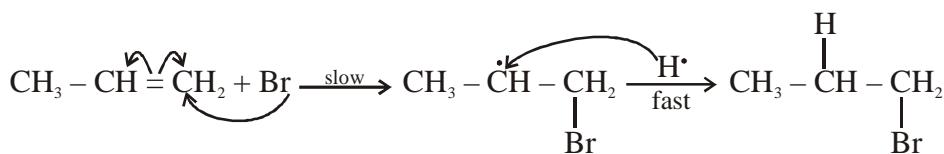
(i) Electrophilic addition : If electrophile attacks in the slow step while addition, it is electrophilic addition.



(ii) Nucleophilic addition : If nucleophile attacks in the slow step while addition.

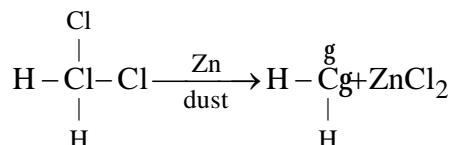


(iii) Radical addition : If radical attacks in the slow step while addition.

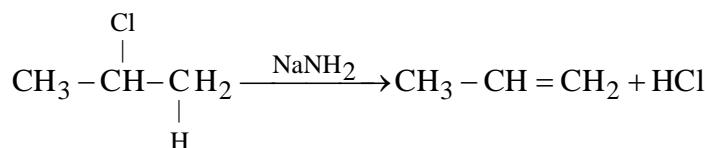


2. Elimination reaction : If two σ -bonds are broken from any molecule, reaction is called as elimination reaction. It is of three types :

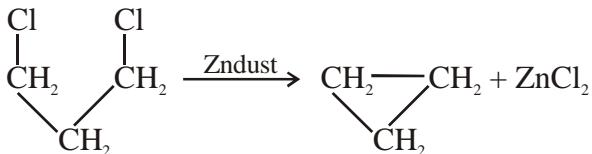
(i) α -elimination : Two σ -bonds are broken from the same atom forming a carbene.



(ii) β -elimination : Two σ -bonds are broken from consecutive atoms, forming a π -bond.



(iii) γ -elimination : Two σ -bonds are broken from alternate atoms, forming a three membered ring.

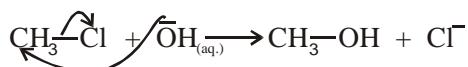


3. Substitution reaction :

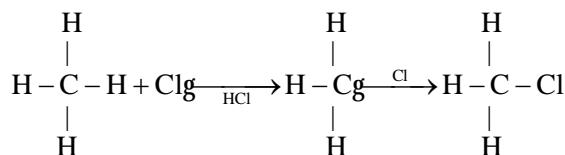
When any group comes in place of another group, reaction is called as substitution group.

It is of three types :

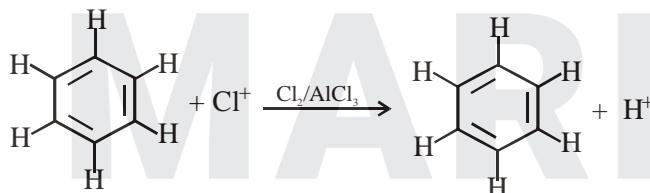
(i) Nucleophilic Substitution (S_N) : When any nucleophile replaces another nucleophile.



(ii) Radical Substitution (S_R) : When any radical replaces another radical.



(iii) Electrophilic Substitution (S_E) : When any electrophile replaces another electrophile.



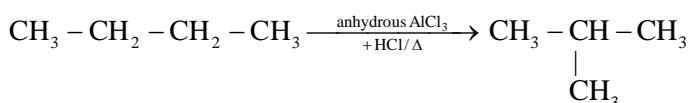
4. Condensation Reaction :

Two or more reactants are combined to form a product with or without the elimination of simple molecules like H_2O , HCl , NH_3 , R-OH etc.



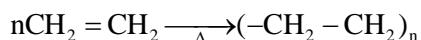
5. Rearrangement reaction :

Structure is rearranged.



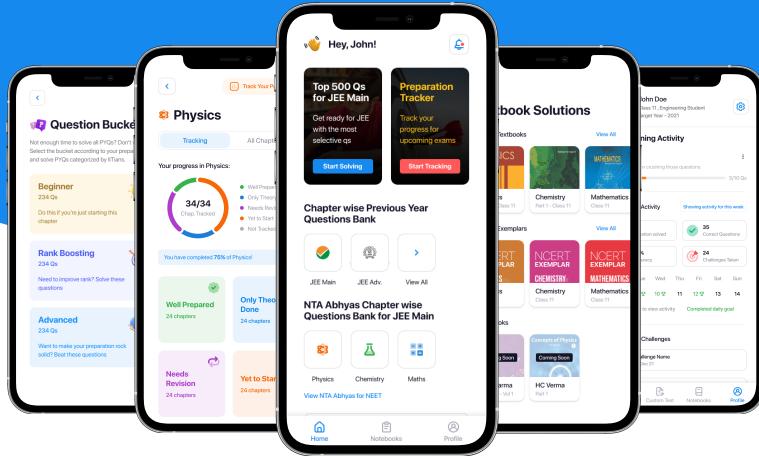
6. Polymerisation reaction :

Smaller molecules are combined to form bigger molecule.





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