

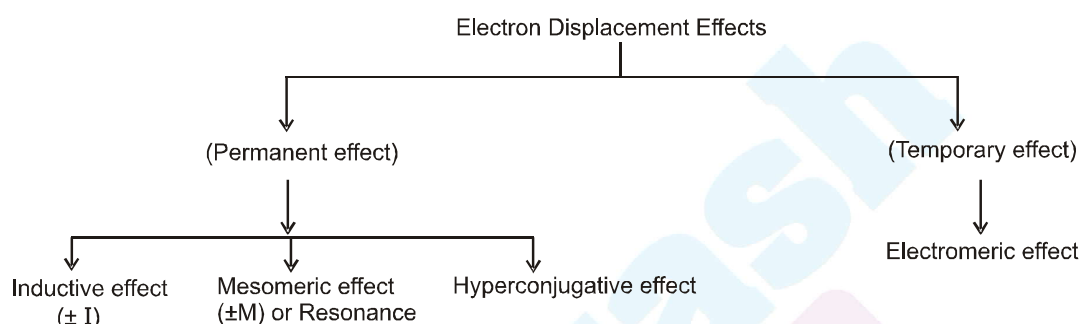


GENERAL ORGANIC CHEMISTRY

ELECTRONIC EFFECT

The effect which appears due to electronic distribution is called electronic effect.

Classification of electronic effect :



Electronic Displacement effect :

The displacement of electrons within the same molecule is known as electronic displacement. These effects affect the stability of a specie or compound and it also affects its the acidic & basic strength.

Electronic Displacement Effect is divided into two parts:

(1) Permanent effect (2) Temporary effect

(1) Permanent effect :

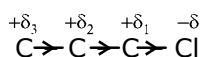
- (i) Inductive effect
- (ii) Mesomeric (resonance) effect
- (iii) Hyperconjugation

(2) Temporary effect:

- (i) Electromeric effect (ii) Inductomeric effect

(i) Inductive effect:

It is an effect in which permanent polarisation arises due to partial displacement of σ -electrons along carbon chain or partial displacement of sigma-bonded electrons toward more electronegative atom in carbon chain.



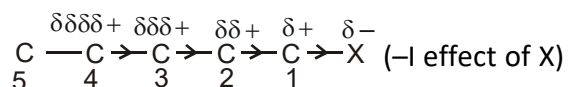
Magnitude of partial positive charge

$$+\delta_1 > +\delta_2 > +\delta_3 = -\delta$$



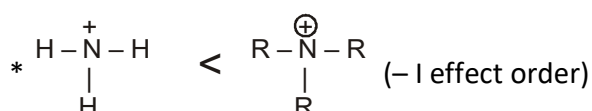
(net charge remain constant in a molecule having inductive effect)

It is a permanent effect.



if X i.e more electronegative

(After carbon no. 3, the effect disappears)



* $\text{O}^- < \text{O} < \text{O}^+$ (-I effect order)

- It is a permanent effect
- It is caused due to electronegative difference.
- It operates via σ bonded electron.
- It is distance dependent effect.
- As distance increases, its effect decreases.
- It can be neglected after third carbon.
- It is a destabilising effect.
- It is divided into 2 parts. (On the basis of electronegativity w.r.t. hydrogen atom)

(1) +I effect (2) -I effect

If any atom or group has electronegativity greater than that of hydrogen, then it is considered to show -I effect and vice-versa.

+I effect

- It is shown by e^- releasing group.
- Groups that have electronegativity less than H.
- Those group which are showing +I effect, disperses partial +ve charge on the C-chain

-I effect

- It is shown by e^- accepting group.
- Electronegativity greater than H
- Those group showing -I effect disperses -ve charge on the C-chain

Eg. $\text{CH}_3 - \text{CH}_2 - \text{Cl}$ (-I of Cl)

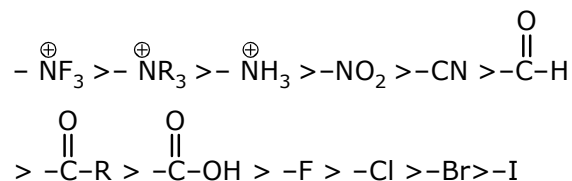
Eg. $\text{CH}_3 - \text{CH} = \text{CH}_2$ (-I of $-\text{CH}=\text{CH}_2$ & +I of $-\text{CH}_3$)

Eg. $\text{CH}_3 - \text{CH}_2 - \text{C} \equiv \text{CH}$ (-I of $-\text{C} \equiv \text{CH}$ & +I of $-\text{CH}_2-\text{CH}_3$)

Eg. $\text{CH}_2 = \text{CH}-\text{C}_6\text{H}_5$ (-I of -Ph)

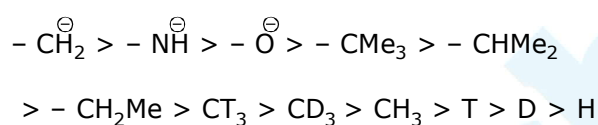


Order of -I effect showing group:



(-I order) $-\text{C}\equiv\text{CH} > -\text{CH}=\text{CH}_2$

Order of + I effect showing group



Bond Strength : $\text{CT}_3 > \text{CD}_3 > \text{CH}_3$ (+ I of $\text{T} > \text{D} > \text{H}$)

($\text{T} = {}_1^3\text{H}$ & $\text{D} = {}_1^2\text{H}$ are isotopes of hydrogen)

Mesomeric effect : (Resonance effect)

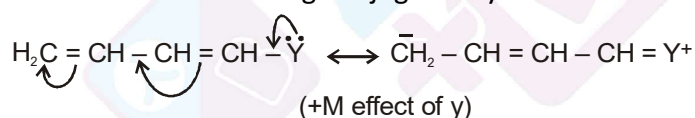
Delocalisation of π electrons in any conjugated system is known as mesomeric effect

Types

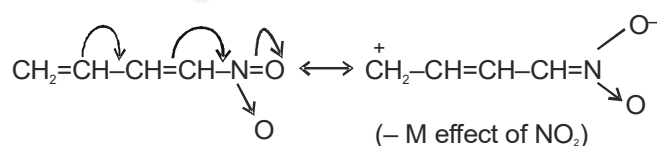
1 + M effect (+R)

2 - M Effect (-R)

* Consider the following conjugated system

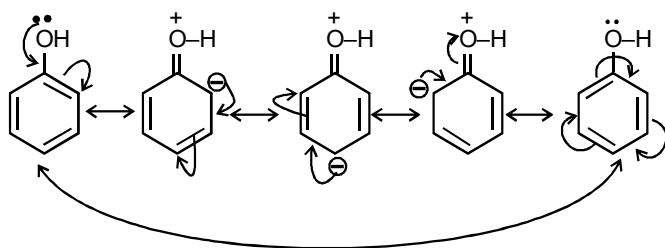


* Consider another conjugated system

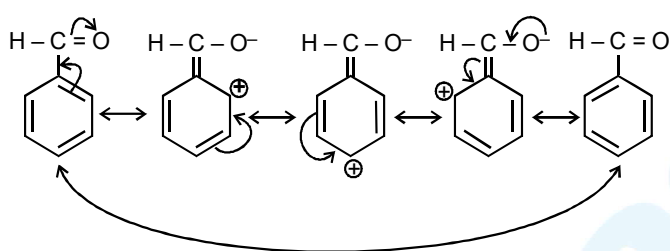




Mesomeric effect in phenol (+M effect)

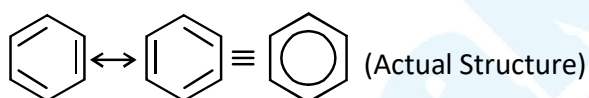


If the movement of e^- is towards ring \Rightarrow (+M effect)
 This effect increases the electron density on benzene ring.
 * -M effect in Benzaldehyde



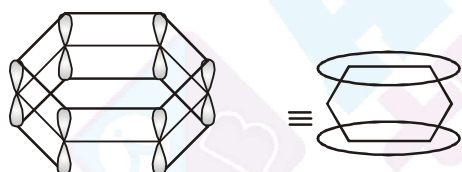
Resonance

Delocalisation of π -electrons in conjugation is known as resonance.



OR

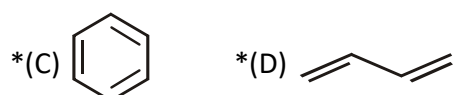
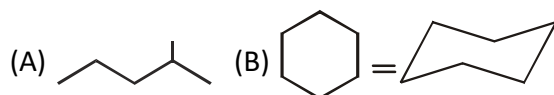
(Resonating structures) (Resonance hybrid)



Condition for showing resonance

1. Molecule should be planar, nearly planar or a part of it is planar

Q.1 Which are planar?





Because all carbon atoms are sp^2 hybridised.

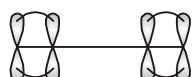
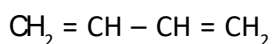
2. Molecule should have conjugated system.

Conjugated System :

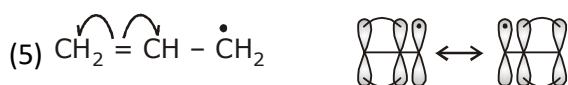
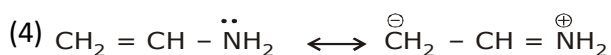
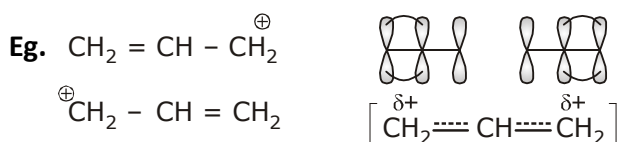
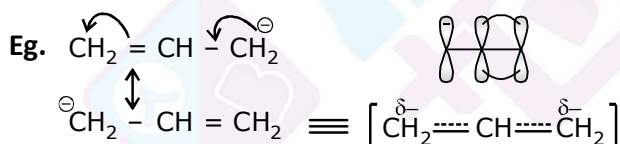
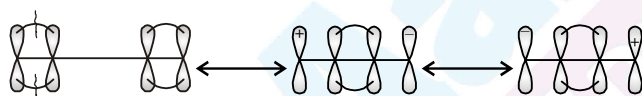
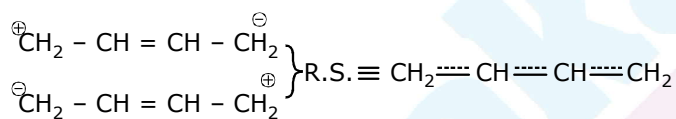
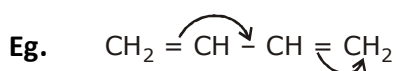
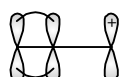
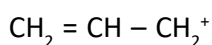
Continuous unhybridised p-orbital parallel to each-other.

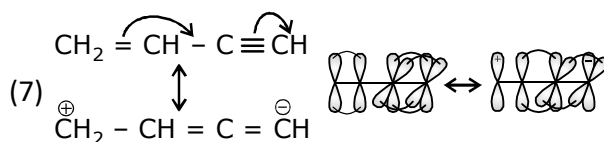
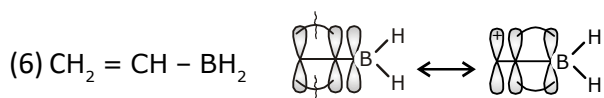
Types of Conjugated System:

(1) π -bond alternate to π -bond



(2) π -bond alternate to + charge

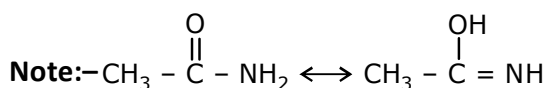




1. Resonance takes place due to delocalization of πe^- .

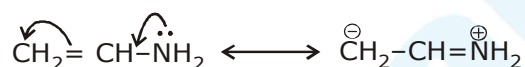


2. Position of the atoms remains the same, only delocalization of πe^- takes place.

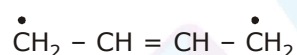
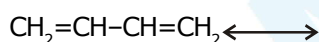


[They are not resonating structure rather they are **tautomer**]

3. Bond pair get converted into lone pair and lone pair get converted into bond pair



4. In Resonance, number of unpaired electrons remains the same.



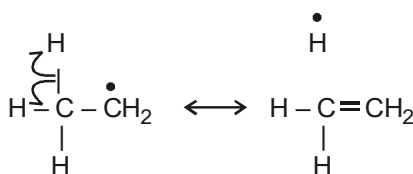
(They are not resonating structure)

Resonating structures :

- (1) Resonating structures are hypothetical structures which exist only on paper.
- (2) The energy difference b/w different resonating structure is very small.
- (3) All resonating structures contribute towards the formation of resonance hybrid (Their contribution may differ).
- (4) A single resonating structures can't explain each & every property of that particular compound.

Hyperconjugation :

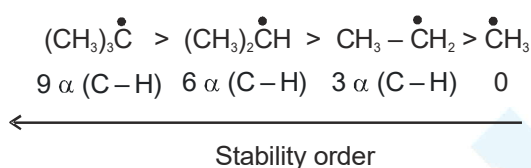
Permanent polarisation caused by delocalisation of σ -electrons into π -molecular orbital is known as hyperconjugation.



Hyperconjugation is called "No bond Resonance".

* More the number of α C – H bond, more will be the no bond resonating structures (Hyperconjugation)

• More α (C – H) bond, more will be the stability of free radical.



Reaction intermediates :

1. Free radical

Properties of Free Radical

1. It is a neutral specie.
2. It has one unpaired electron that's why it is paramagnetic in nature.

Structure :

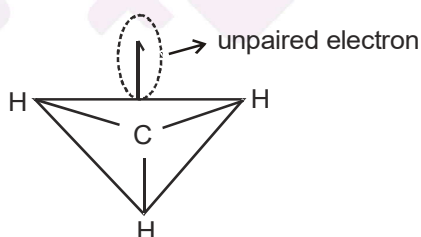
$\dot{\text{C}}\text{H}_3 \rightarrow$ Methyl free Radical

$\dot{\text{C}}\text{H}_3\text{CH}_2 \rightarrow$ Ethyl free radical

3. Its hybridisation is sp^2 and triangular planar shape.

Note :

Unpaired electron is not counted while calculating the hybridisation state.



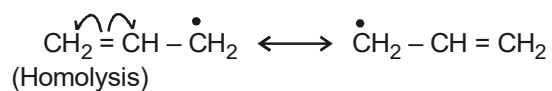
(Unpaired electron stay perpendicular to the plane of molecule)

Stability of free Radical :

Its stability can be determined with the help of hyperconjugation as well as resonance effect.

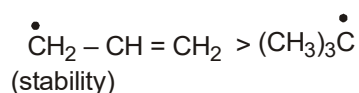


Allylic Free Radical

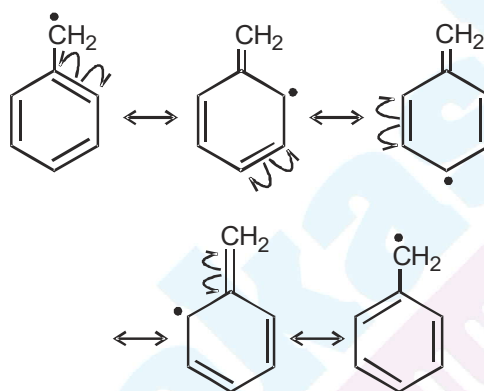


(Free Radical is on carbon adjacent to doubly bonded carbon atom)

Effect of Resonance > Hyperconjugation

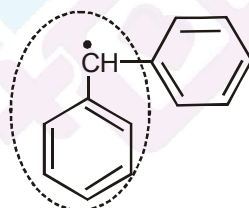


Benzylic free radical



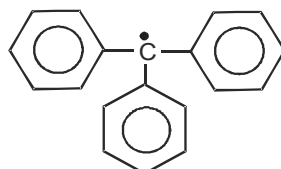
(5 Resonating structure)

* More resonating structure, more will be the stability of the free radical.



(di-benzylic free radical)

Number of resonating structures = 7

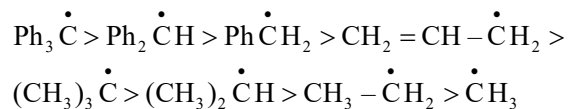


(Tri-benzylic free radical)

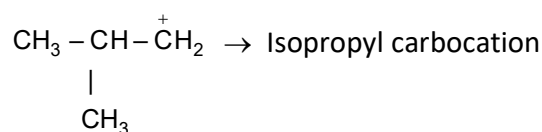
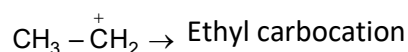
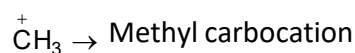
Number of resonating structures = 10



Stability Order :



Carbocation



Properties of Carbocation :

1. It is positively charged species.
2. It has sextet of electrons i.e. diamagnetic.
3. It is formed by heterolysis.
4. It is generally stable in polar solvent.

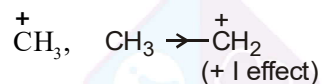
Structure :

(sp²) Triangular planar

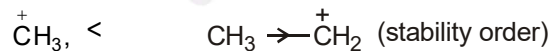
Stability :

Its stability can be determined with the help of inductive effect, hyperconjugation and resonance effect.

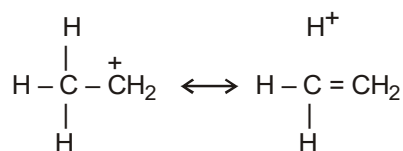
Stability of Carbocation :

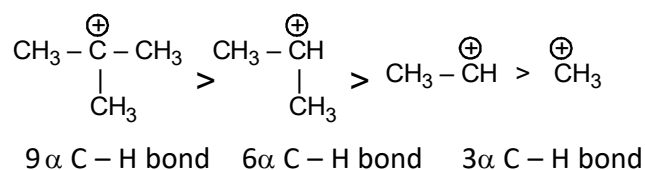


$$\text{charge} \propto \frac{1}{\text{Stability}}$$

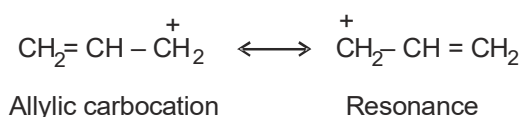


Stability of carbocation can also be determined by hyperconjugation (no bond resonance)

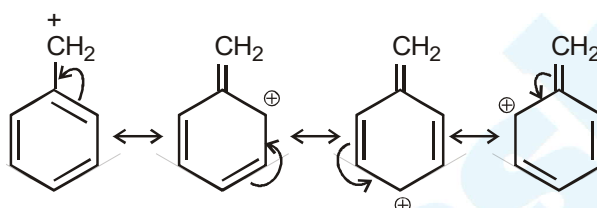




Allylic carbocation



Benzylic carbocation

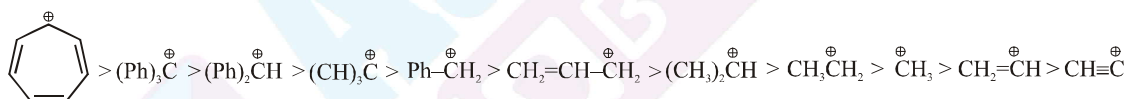


$\text{Ph}_2\overset{\oplus}{\text{C}}\text{H} \rightarrow 7$ Resonating structure

$\text{Ph}_3\overset{\oplus}{\text{C}} \rightarrow 10$ Resonating structure

$\text{Ph}_3\overset{\oplus}{\text{C}} > \text{Ph}_2\overset{\oplus}{\text{C}}\text{H} > (\text{CH}_3)_3\overset{\oplus}{\text{C}} > \text{Ph}\overset{\oplus}{\text{C}}\text{H}_2$

Stability of carbocation



Carbanion

1. It is a $-ve$ charged species.
2. It has octet of electrons.
3. Diamagnetic in nature.

Structure :

* If $-ve$ charge is in resonance then the hybridisation of carbanion is sp^2 (Triangular planar shape)

* If $-ve$ charge is not in resonance then the hybridisation of carbanion is sp^3 (Pyramidal)

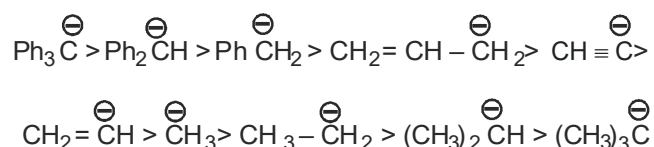


Stability :

Its stability can be determined with the help of

- (1) Inductive effect
- (2) Resonance effect

* Stability of the carbanion is as follows



Acidic strength \propto stability of the anion conjugate base formed. As we know $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$
 $\Rightarrow \text{HI} > \text{HBr} > \text{HCl} > \text{HF}$

Order of electronic effect

Mesomeric > Hyperconjugation > Inductive effect

Alcohol

- Solubility of alcohol increase with increase in branching
 $n < \text{iso} < \text{neo}$ (isomeric)
- Relative order of reactivity
 - (i) $1^\circ > 2^\circ > 3^\circ$ (O-H bond fission)
 - (ii) $3^\circ > 2^\circ > 1^\circ$ (C-O bond fission)
 - (iii) $3^\circ > 2^\circ > 1^\circ$ (Dehydration)

Reaction mechanism

1. All the +ve charge species are electrophile except H_3O^+ and NH_4^+
2. Relative electron withdrawing order (-I order)
 $-\text{NO}_2 > -\text{CN} > -\text{COOH} > -\text{F} > -\text{OR} > -\text{OH} > -\text{C}_6\text{H}_5 > -\text{CH}=\text{CH}_2$
3. +I order
 $-\text{NH}^- > -\text{O}^- > -\text{COO}^- > 3^\circ\text{alkyl} > 2^\circ\text{alkyl} > 1^\circ\text{alkyl}$
4. Greater the number of α -Hydrogen, more stable is carbocation and free radical due to hyperconjugation.



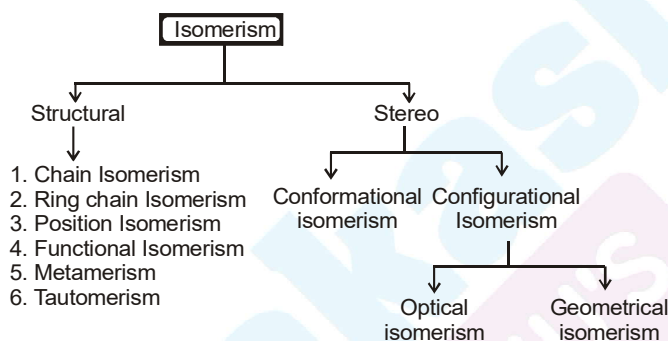
GENERAL ORGANIC CHEMISTRY

ISOMERISM

Definition

Compounds having same molecular formula (M.F.) but differ in their properties are known as **isomers** and this phenomenon is known as **isomerism**.

Classification



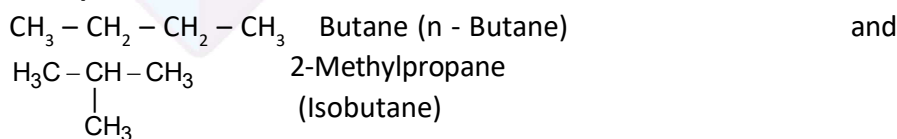
Structural isomersm

Compounds having same molecular formula but differ in connectivity of atom (Structure is different).

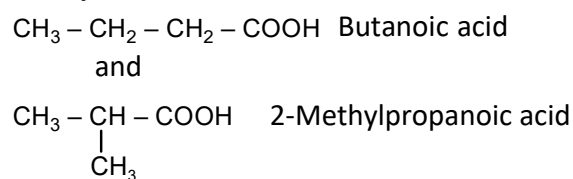
Chain Isomerism

Compounds having same molecular formula but differ in the length of the parent chain.

Example 1 :



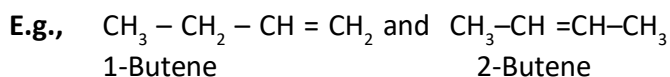
Example 2 :



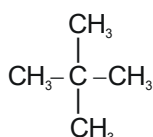


Position isomerism

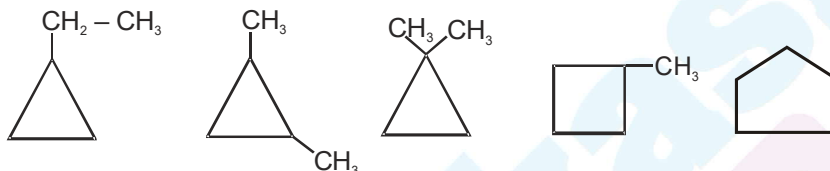
Compounds having same molecular formula and same parent chain but differ in the position of functional group, multiple bond and substituent group are known as position isomers.



An alkane having molecular formula C_5H_{12} can give only one product on monochlorination. Find the IUPAC name of the alkane.



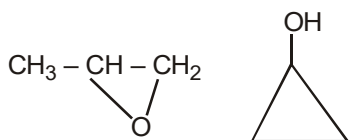
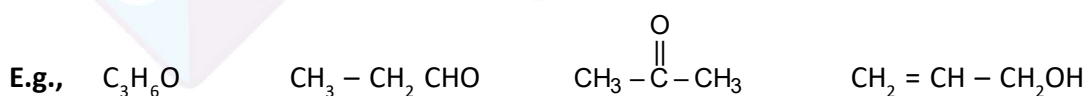
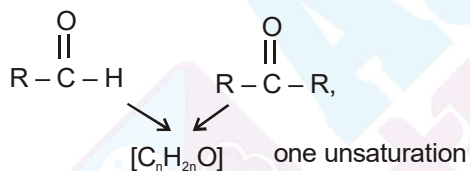
* To form cyclic structural we should always start with 3 carbon ring.



Total structural isomers = 5 + 5 = 10

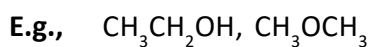
Functional isomerism

Compound having same molecular formula but differ in functional group are known as functional isomers.

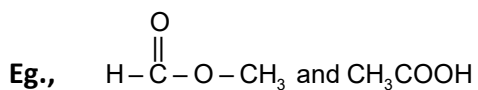


* Aldehyde, Ketone, cyclic ethers, cyclic alcohol, unsaturated alcohol etc are functional isomers to each other.

* Alcohol and ether functional isomers of each other.



* Acids and ester are functional isomers to each other.



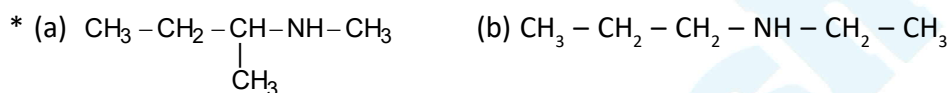
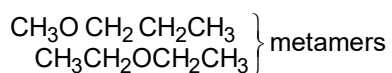
* Cyanide and Isocyanide are functional isomer to each other but HCN and HNC are tautomers of each other.

* 1°, 2° and 3° amine are functional isomer to each other.

Metamerism

This type of isomerism is found in those types of compounds which have polyvalent atoms or polyvalent functional group, e.g. ether, 2^o amine, ester etc.

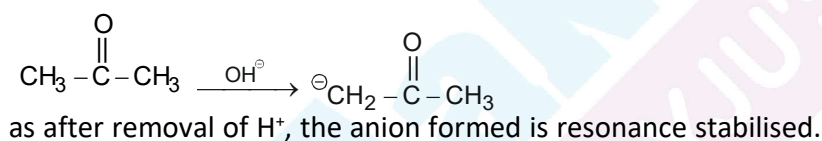
Compound having same molecular formula but differ from the nature of alkyl group directly attached with polyvalent atom or polyvalent functional group



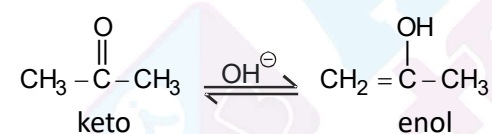
a & b are metamers

Tautomerism

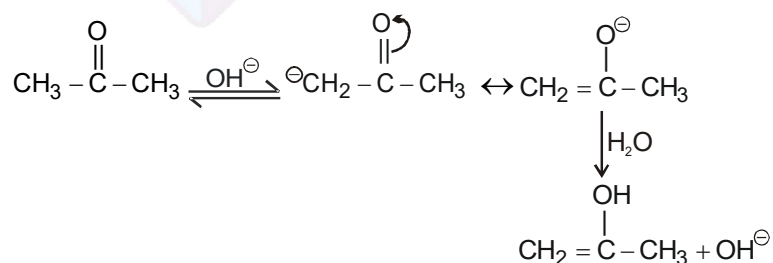
Compound having same molecular formula but different due to oscillation of an atom (usually H⁺) are known as tautomers.



Keto enol Tautomerism



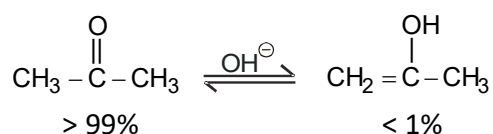
Mechanism



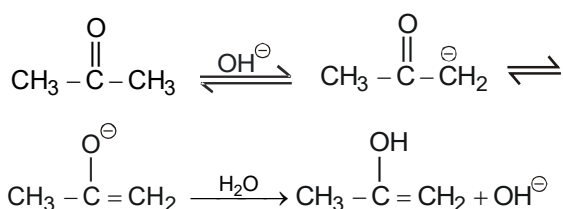
* OH[⊖] acts as catalyst.



Base catalysed tautomerism

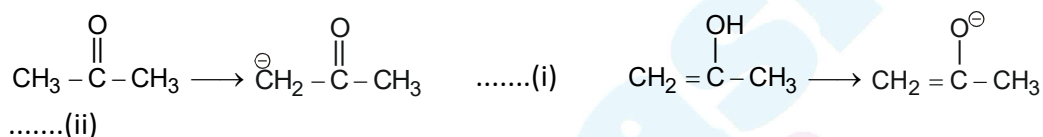


Mechanism



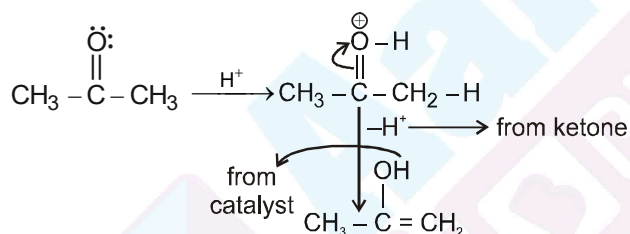
* enol is more acidic than keto.

* After removal of H⁺ from both form.



In I -ve charge is on C and in II -ve charge is on O therefore (ii) is more stable than (i) hence enol form is more acidic than keto form.

Acid Catalysed Tautomerism



Generally, keto form is more stable than enol but in some cases the stability of enol form is greater than keto. This is due to:

1. Intramolecular H-bonding
2. Aromatic character
3. Extended conjugation
4. Steric factor

E.g.,

Ring-chain isomerism

If one isomer has open chain structure and the other has cyclic structure then isomers are known as ring-chain isomers and isomerism between them is known as ring-chain isomerism.

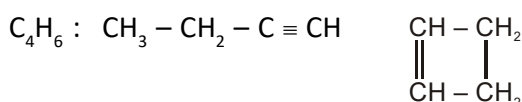


For examples :

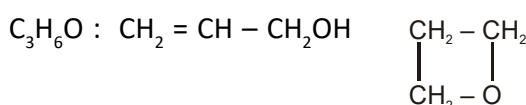
1. Alkene and cycloalkane, (C_nH_{2n})



2. Alkyne and cycloalkene, (C_nH_{2n-2})



3. Alkenols and cyclic ethers, ($C_nH_{2n}O$)



Note

Ring-chain isomers are always functional isomers.

Geometrical isomerism

Definition

Isomers which possess the same molecular and structural formula but differ in the arrangement of atoms or groups in space due to restricted rotation are known as geometrical isomers and the phenomenon is known as geometrical isomerism.

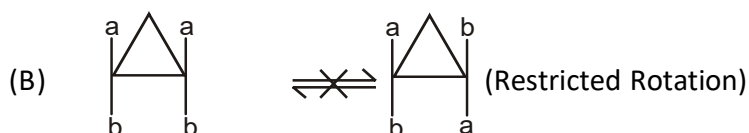
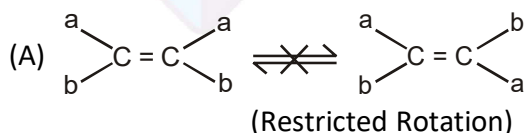
Conditions of geometrical isomerism

1. Geometrical isomerism arises due to the presence of a double bond or a ring structure.

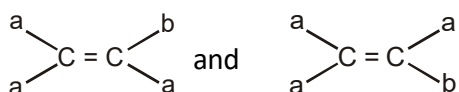
(i.e. $\begin{array}{c} \diagup \\ C \\ \diagdown \end{array} = \begin{array}{c} \diagdown \\ C \\ \diagup \end{array}$, $\begin{array}{c} \diagup \\ C \\ \diagdown \end{array} = N -$, $- N = N -$ or ring structure)

Due to the rigidity of double bond or the ring structure to rotate at the room temperature the molecules exist in two or more orientations. This rigidity to rotation is described as restricted rotation / hindered rotation / no rotation.

E.g.,

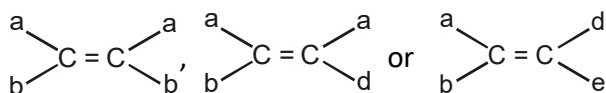


2. Different groups should be attached at each doubly bonded atom. For example,



are identical but not geometrical isomers.

On the other hand, following types of compounds can exist as geometrical isomers :



Configurational nomenclature in geometrical Isomerism

| Configuration | Criteria | Remarks |
|---------------|----------------------|--|
| cis / trans | Similarity of groups | If the two similar groups are on same side of restricted bond the configuration is cis otherwise trans. |
| E/Z | Seniority of groups | If the two senior groups are on same side of restricted bond the configuration is Z (Z = zusammen = together) otherwise E (E = entgegen = opposite). |

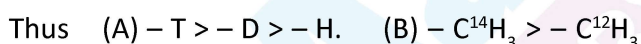
Sequence rules : (Cahn - Ingold - Prelog sequence rules)

For deciding the seniority of groups following rules are applied :

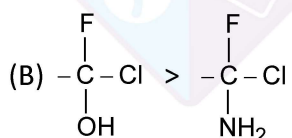
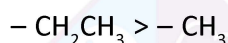
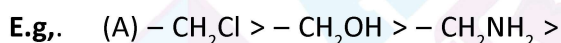
Rule I : The group with the first atom having higher atomic number is senior. According to this rule the seniority of atom is :



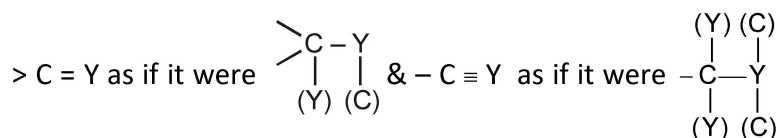
Rule II : The higher mass isotope is senior.



Rule III : If the first atom of group is identical then second atom is observed for seniority.



Rule IV : Groups containing double or triple bonds are assigned seniority as if both atoms were duplicated or triplicated.



Rule V : Bond pair gets priority over lone pair.

Rule VI : $Z > E$ & $R > S$.


Number of Geometrical Isomers :

Number of geometrical isomers can be found by calculating the number of stereocentres in the compound. (Stereocentre is defined as an atom or bond bearing groups of such nature that on interchange of any two group will produce a new stereoisomer).

| Nature of Compound | No. of G.I. (n = no. of Stereocentres) | Example | No. of Isomers | Isomers |
|---|---|--|----------------|---|
| (I) Compound with dissimilar ends | 2^n | $\text{CH}_3\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{C}_2\text{H}_5$ | 4 | I : (cis, cis) II : (trans, trans) III : (cis, trans) IV : (trans, cis) |
| (II) Compound with similar ends with even stereocentres | $2^{n-1} + 2^{\frac{n}{2}-1}$ | $\text{CH}_3\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$ | 3 | I : (cis, cis) II : (trans, trans) III : (cis, trans) (trans, cis) |
| (III) Compound with similar ends with odd stereocentre | $2^{n-1} + 2^{\frac{n-1}{2}}$ | $\text{CH}_3\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$ | 6 | I : (cis, cis, cis) II : (cis, cis, trans) (trans, cis, cis) III : (cis, trans, trans) (trans, trans, cis) IV : (trans, trans, trans) V : (cis, trans, cis) VI : (trans, cis, trans) |

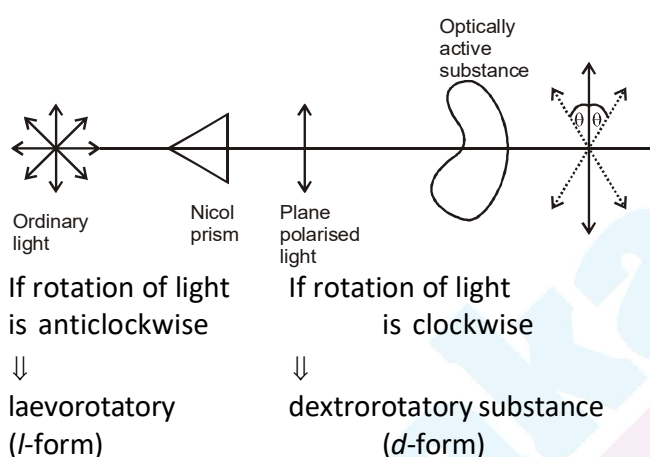
Physical Properties of Geometrical Isomers :

| Physical Properties | | Remarks |
|---------------------------------------|----------|--|
| | | |
| Dipole moment | $I > II$ | cis-isomer has resultant of dipoles while in trans isomer dipole. |
| Boiling point | $I > II$ | Molecules having higher dipole moment have higher boiling point due to large intermolecular force of attraction. |
| Solubility (in H_2O) | $I > II$ | More polar molecules are more soluble in H_2O . |
| Melting point | $II > I$ | More symmetric isomers have higher melting points due to better packing in crystalline lattice and trans isomers are more symmetric than cis. |
| Stability | $II > I$ | The molecule having more vander waal's strain are less stable. In cis isomer the bulky groups are closer they have larger Vander Waals strain. |



| | | |
|----------------------------------|---|---|
| Physical Properties | $\begin{array}{c} \text{H}_3\text{C} \nearrow \\ \text{H} \searrow \\ \text{C} = \text{C}^* \\ \text{H} \nearrow \\ \text{Br} \searrow \\ \text{I} \end{array}$ | $\begin{array}{c} \text{H}_3\text{C} \nearrow \\ \text{H} \searrow \\ \text{C} = \text{C}^* \\ \text{H} \nearrow \\ \text{Br} \searrow \\ \text{H} \end{array}$ |
| Dipole moment | I > II | |
| Boiling point | I > II | |
| Solubility (in H ₂ O) | I > II | |
| Melting point | I > II | |
| Stability | I > II | |

Optical isomerism

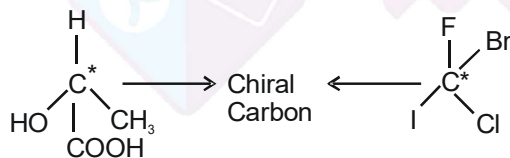


☞ If there is no rotation of light then substance is called optically inactive.

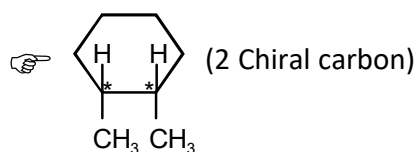
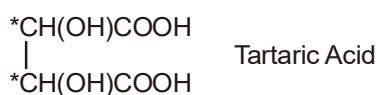
Chiral carbon

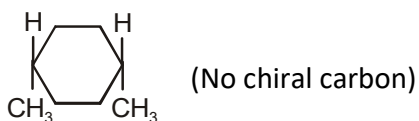
If all the four valencies of carbon are satisfied by four different atom or four different group atom then carbon is known as chiral carbon.

E.g.,



(Lactic acid)

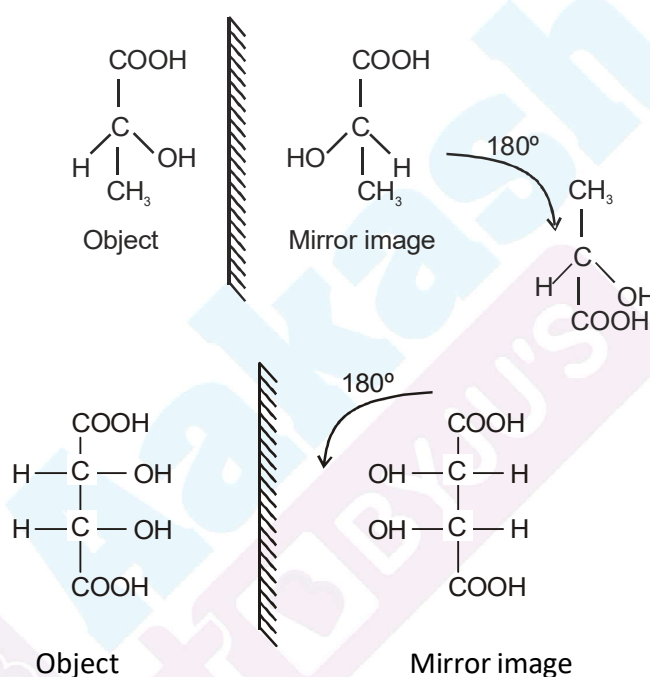




☞ For optically active isomer the object and its mirror image must be non superimposable.

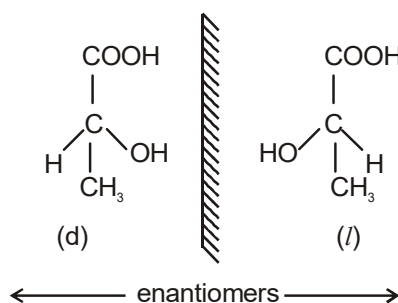
☞ If image and object are superimposable then they are not optically isomer to each other.

☞ To check, superimposable either of object or mirror image is rotated 180° along the mirror. After that mirror image is checked for superimposable.



⇒ After 180° rotation, mirror image and object are identical. (mirror image of meso compound will be identical)

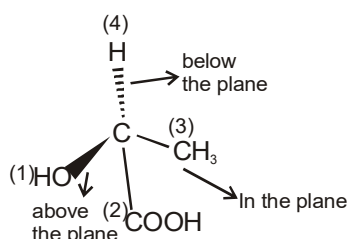
☞ If the compound have only one chiral carbon then it will be certainly optically active.



Object and its non-superimposable mirror image are called enantiomer to each other



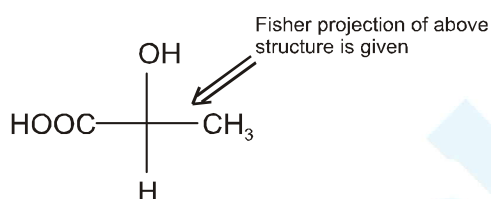
Wedge dash structure



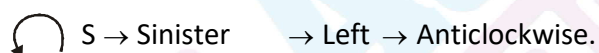
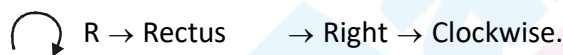
Fourth priority order can be eliminated during checking of clockwise and anticlockwise.

To draw Fisher projection of such structure:

1. Dotted group is placed below
2. The group attached by dark line is placed on the top.
3. Remaining group are placed according to their clock wise or anticlockwise position w.r.t. group in dark line.



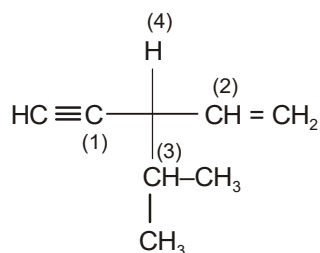
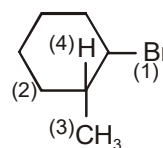
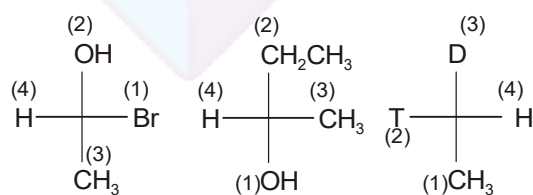
R and S form



Priority order

Higher the atomic number of the element, greater will be its priority.

E.g.,





⇒ Mirror image of R is S

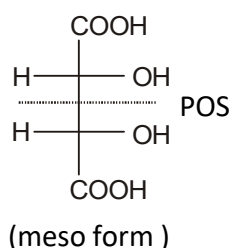
If lowest priority element is in horizontal then exact order is obtained by reversing the form (i.e. it comes R then exact form will be S and vice versa).

Racemic mixture

It is an equimolar mixture of R and S or d and l. Racemic mixture is optically inactive.

☞ A compound is optically active due to

1. Absence of plane of symmetry (POS)
2. Absence of centre of symmetry (COS)



☞ Plane of symmetry is an imaginary plane where if we place a mirror, mirror image will exactly overlap the other half.

☞ For meso form, there must be at least two identical chiral carbon.

Identical carbon ⇒ Chiral carbons having identical group attached.

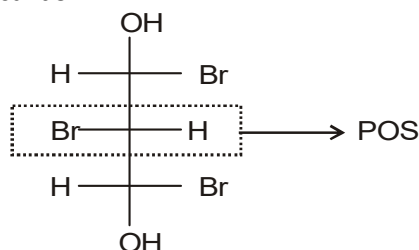
☞ If compound has Plane of symmetry then it will be certainly optically inactive and will be called meso form.

☞ After finding two identical carbons. We assign them as R or S. If first part is R and other is S then they will rotate the light in opposite direction but to equal extent the compound will be optically inactive (meso form).

$$\begin{aligned}
 \text{Total optical isomer} &= 2^{n-1} - 2^{\frac{n-1}{2}} + 2^{\frac{n-1}{2}} \\
 &= 2^{n-1}
 \end{aligned}$$

☞ When there is odd no. of identical carbon atom (i.e. symmetrical) then this compound will certainly contain pseudo chiral w.r.t. to which compound is symmetrical (i.e. POS).

☞ Other meso compound of the above compound will form by changing the place Br and H around Pseudo chiral carbon.

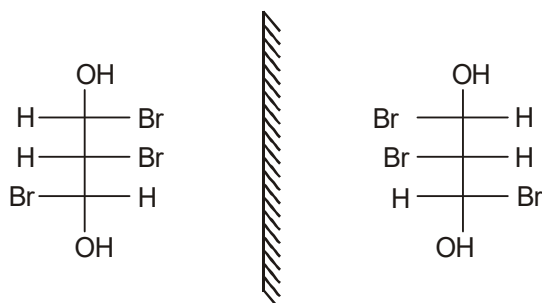




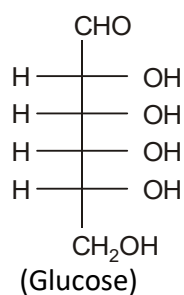
Total meso = 2

$$\text{optical} = 2^{n-1} - 2^{\frac{n-1}{2}} = 2^{3-1} - 2^{\frac{3-1}{2}}$$

$$= 2^2 - 2 = 4 - 2 = 2$$

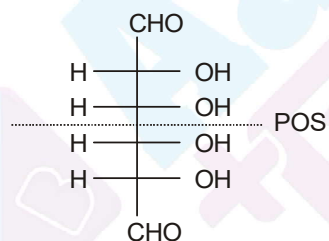


← Enantiomers →



Total no. of different chiral carbon = 4

Total optical isomer = $2^4 = 16$



Total no. of even chiral = 4

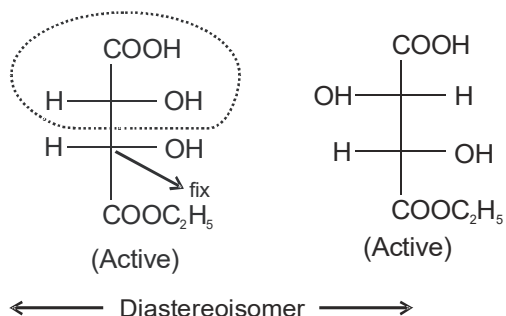
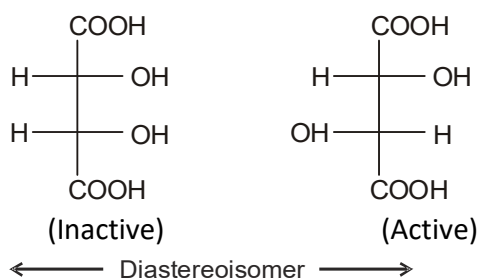
$$a = 2^{n-1} = 2^{4-1} = 2^3 = 8$$

$$m = 2^{\frac{n}{2}-1} = 2^{\frac{4}{2}-1} = 2^{2-1} = 2^1 = 2$$

Total isomer = $8 + 2 = 10$

Diastereoisomers

☞ For single chiral centre, there is no diastereoisomer. The stereoisomer which are not related as object and mirror image. They may be optically active or optically inactive.

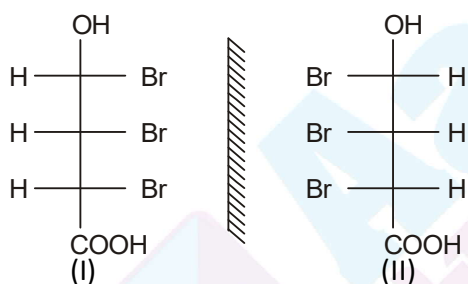


☞ Fix one chiral carbon

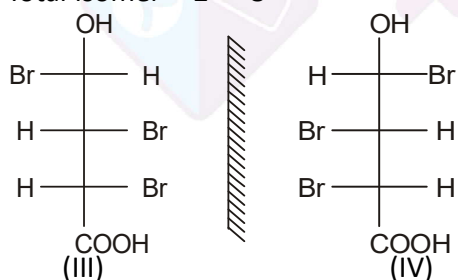
After one interchange

If (R, R) → (R, S)

For compound having 3 chiral carbon to get diastereoisomer, fix two chiral carbon and one interchange with left carbon or fix one chiral carbon and interchange with other two,



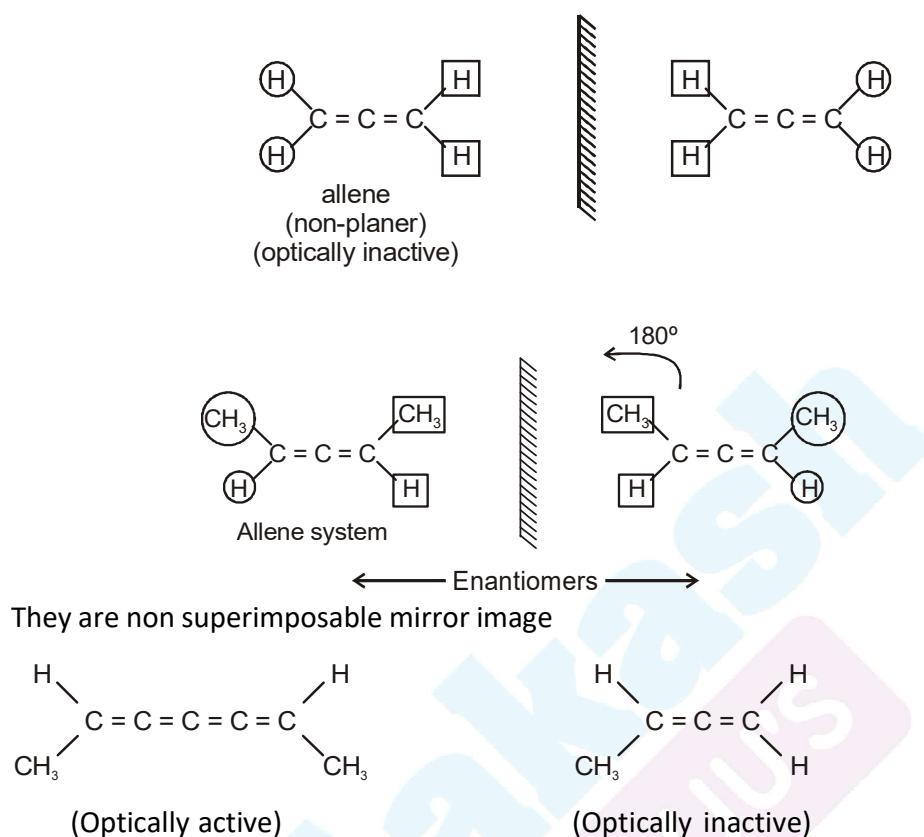
Total isomer = $2^3 = 8$



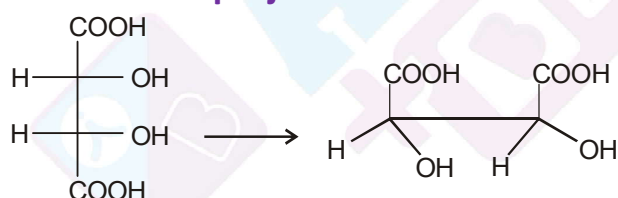
(I) and (III), I and (IV), (II) and (III), (II) and (IV) are diastereoisomers.



Allene system



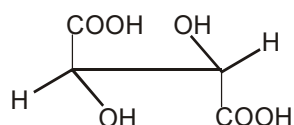
Conversion of fisher projection in saw horse structure



☞ First write first chiral carbon (as given in molecule).

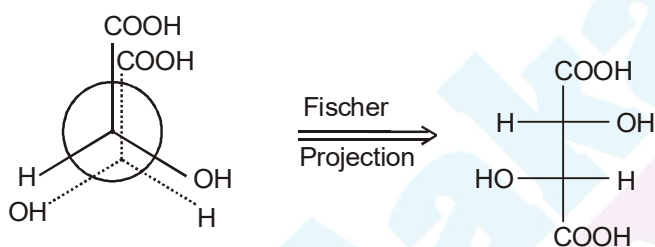
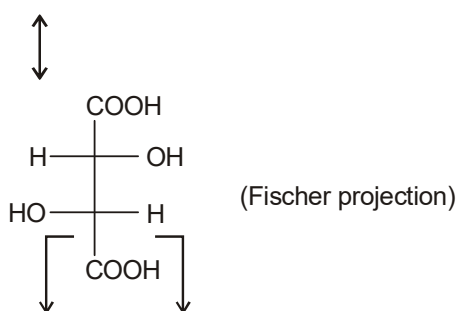
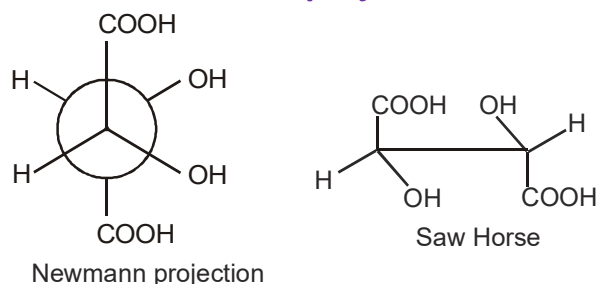
After it, change the position of second chiral carbon (if both group are on the same side) otherwise write as it is.

The above fischer projection can also written in sawhorse form as follows

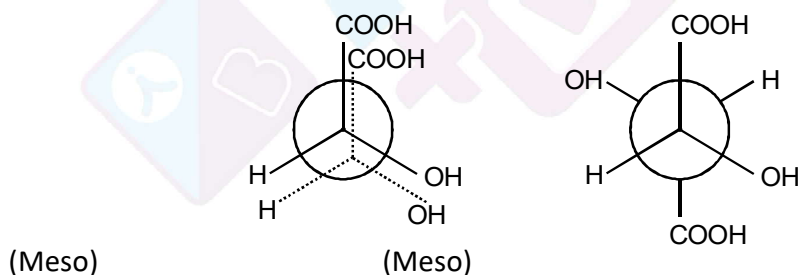




Conversion of newman projectino in to saw horse projection



☞ If all the identical groups are same side or in exactly opposite direction to each other in Newman projection then compound will be meso.



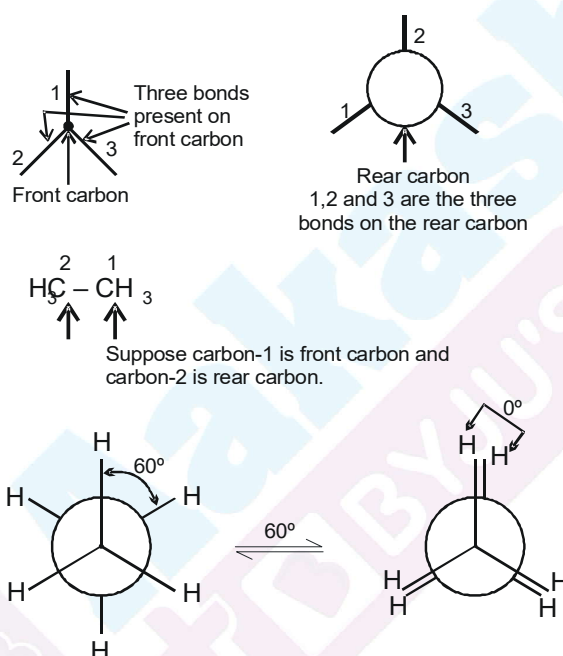
Conformation isomerism

Conformational Isomerism in Alkanes

Different spatial arrangements of the atoms that result from **restricted** rotation about a single bond are called conformations. Different conformations are also called conformational isomers.



When an ethane molecule rotates about its carbon-carbon single bond, two extreme conformations can result : the **staggered conformation** and the **eclipsed conformation**. An infinite number of conformations between these two extreme conformation is also possible. There are several ways to represent on paper the three dimensional conformation that, occur as a result of rotation about a single bond. **Wedge-and-dash** structures, **Saw horse** projections and **Newmann** projections are all commonly used methods. But here we will use only Newmann projections. In a Newmann projection you will look down the length of a particular carbon-carbon single bond. The carbon that is in the front, is represented by the point at which three bonds intersect and the carbon that is in the back is represented by a circle. The three lines emanating from each of the carbons represent the carbon's other three bonds.



Newmann projections of ethane

Staggered conformations

A conformation with a 60° dihedral angle is known as staggered conformation.

Eclipsed conformation

A conformation with a 0° dihedral angle is known as eclipsed conformation.

The electrons in a carbon-hydrogen bond will repel the electrons in another carbon-hydrogen bond if the bonds get too close to each other. The staggered conformation, therefore, is the most stable conformation because the carbon-hydrogen bond are as far away from each other as possible. The eclipsed conformation is the least stable conformation, because in no other conformation are the carbon-hydrogen bond closer to one another. In staggered conformation the distance between the hydrogen nuclei is 2.55 \AA . but, they are only 2.29 \AA

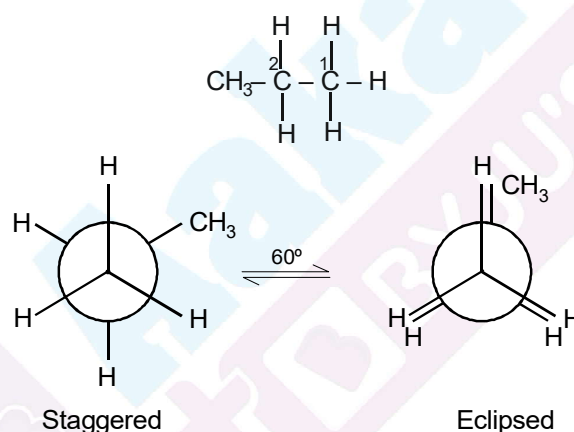


apart in the eclipsed conformation. The rotational barrier in ethane is 2.9 kcal/mol. This rotational barrier can be described in terms of the change in potential energy of the molecule as a function of the change in dihedral angle. The extra energy of the eclipsed conformation is called **torsional strain**. Torsional strain is the name given to the repulsion felt by bonding electrons of one substituent as they pass close the bonding electrons of another substituent. The energy barrier between staggered and eclipsed conformation in ethane molecule is 2.9 kcal/mol (12 kJ/mole). This barrier is more than RT (≈ 0.6 kcal/mol) at room temperature (energy for free rotation) and less than 16-20 kcal/mol (energy barrier for frozen rotation). Hence the rotation about carbon-carbon single bond is neither completely free nor frozen but only restricted.

Note

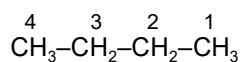
1. For free rotation, energy barrier is 0.6 kcal/mol.
2. For restricted rotation, energy barrier is in between > 0.06 and < 16 kcal/mol.
3. For frozen rotation, energy barrier is ≥ 16 kcal/mol.

Similarly propane has also two conformations.

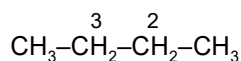


In this case, out of six substituents on two C's (carbon -1 and carbon-2) five, are hydrogens and one is CH_3 group.

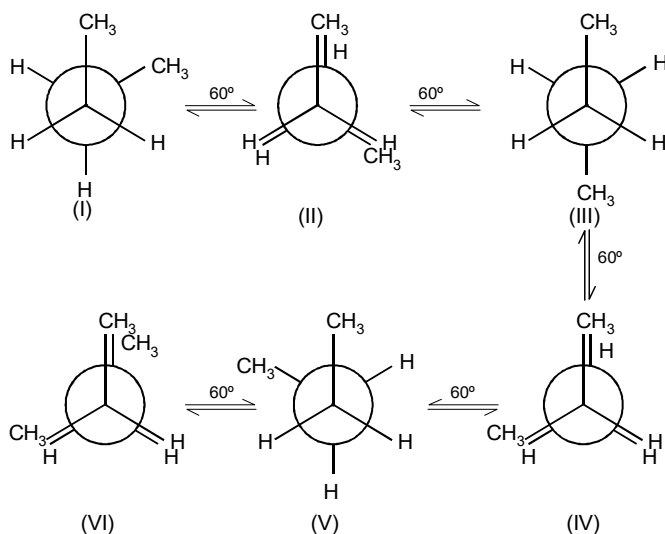
Butane has three carbon-carbon single bonds and the molecule can rotate about each of them.



If rotation will be about C - 2 and C -3 bond then conformation will be symmetrical.



For conformational analysis treat butane as the derivative of ethane. Out of six substituents four are hydrogens and two are methyl groups Different conformations of butane are obtained by rotation.



Butane has three staggered conformers (I, III and V) .

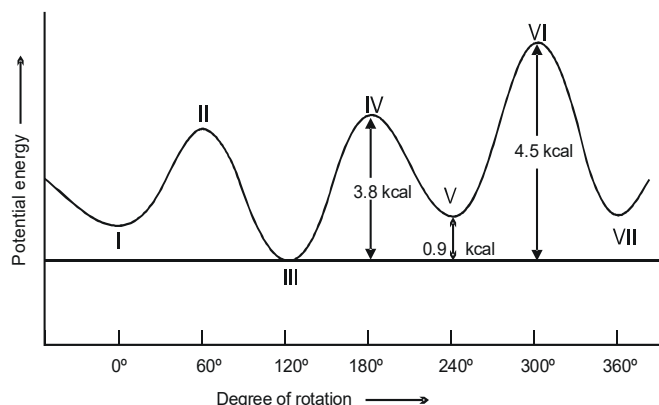
Conformer -(III), in which the two methyl groups are as far apart as possible, is more stable than the other two staggered conformers (I and V). The most stable of the staggered conformers is called the **anti conformer** (in anti conformation the angle between two methyl groups is 180°) and the other two staggered conformers are called gauche conformers. (anti in Greek for "opposite of" gauche in French for " left"). In gauche conformation the angle between two methyl groups is 60° .

In the anti conformer, the largest substituents (CH_3 and CH_3) are opposite to each other; in the gauche conformer, they are adjacent. Two gauche conformers have the same energy but each is 0.9 kcal/mol less stable than the anti conformer.

Anti and gauche conformers do not have the same energy because of the steric strain. **Steric strain** or **steric hindrance** is the strain put on a molecule when atoms or groups are large in size and due to this they are too close to each other, which causes repulsion between the electrons of atoms or groups. There is more steric strain in the gauche conformer than in the anti because the two methyl groups are closer together in the gauche conformer. Steric strain in gauche conformer is called gauche interaction.

The eclipsed conformer in which the two methyl groups are closest to each other (VI) is less stable than the other eclipsed conformers (II and IV). All these eclipsed conformers have both torsional and steric strain. Torsional strain is due to bond-bond repulsion and steric strain is due to the closeness of the eclipsing groups.

In general steric strain in the molecule is directly proportional to the size of the eclipsing groups. Eclipsed conformer (VI) is called the fully eclipsed conformer (angle between two methyl groups is zero) whereas (II) and (IV) are called eclipsed conformers. The energy diagram for rotation about the C-2–C-3 bond of butane is shown in the **Fig.**



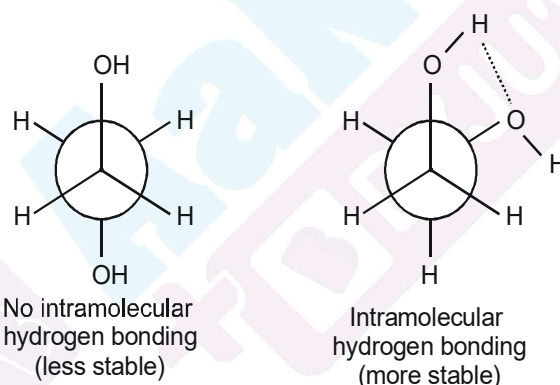
Thus the relative stabilities of the six conformers of n-butane in decreasing order is as follows:

Anti > gauche > eclipsed > fully eclipsed

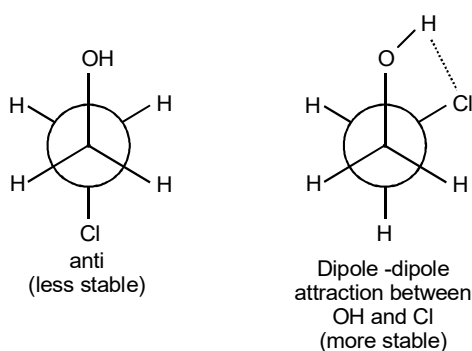
(III) (I) and (II) and (VI)

Thus molecules with carbon-carbon single bonds have many interconvertible conformers. Conformers cannot be separated because they rapidly interconvert.

Although anti conformation is more stable than the gauche conformation but in some cases gauche conformation is more stable than the anti because of the intramolecular hydrogen bonding which is geometrically possible only in the gauche conformation.

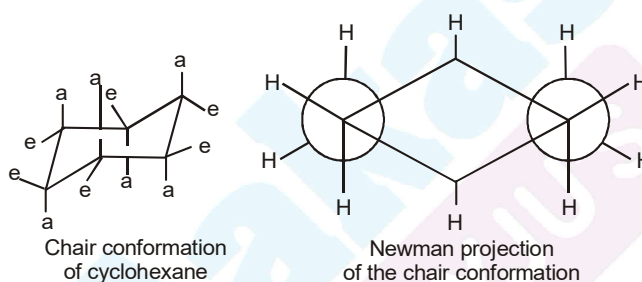


In Ethylene chlorohydrin also gauche conformation is more stable than the anti conformation due to the dipole-dipole attraction between OH and Cl which is geometrically possible only in the gauche conformation.

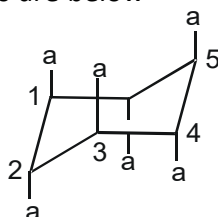


Confirmation of cyclohexane

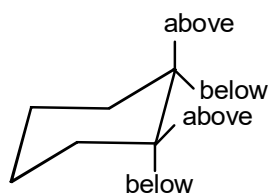
Despite Baeyer's prediction that five-membered cyclic compound would be the most stable, the six membered cyclic compound is the most stable. Six membered cyclic compound are most stable because they can exist in a conformation that is almost completely free of strain. This conformation is called the **chair conformation**. In a chair conformation of cyclohexane all bond angles are 111° which is very close to the 109.5° and all the adjacent carbon-hydrogen bonds are staggered.



- ⇒ Each carbon in chair conformation has an axial bond and an equatorial bond.
- ⇒ Axial bonds are perpendicular to the plane of the ring and equatorial bonds are in the plane of the ring.
- ⇒ If axial bond on carbon-1 is above the plane of the ring then axial bond on carbon-2 will be below the plane of the ring. Thus C - 1 , C - 3 and C - 5 axial bonds are above C - 1 , C - 4 and C - 6 axial bonds are below



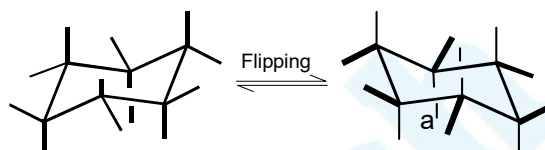
- ⇒ Thus C - 1 axial and C - 2 axial are trans to each other. Similarly C - 1 and C - 5 axials are cis to each other.
- ⇒ If axial bond on carbon - 1 will be above the plane then equatorial bond on this carbon will be below the plane.



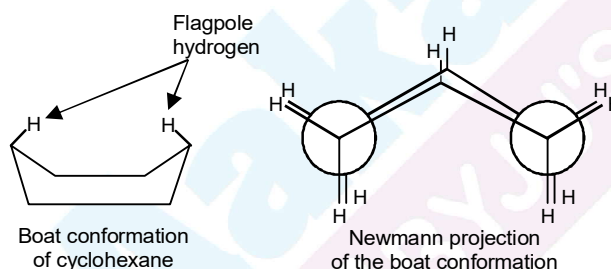
(i) Thus C - 1 equatorial and C -5 equatorial will be cis.

(ii) C - 1 axial and C-2 equatorial will be cis.

As a result of rotation about carbon-carbon single bonds cyclohexane rapidly interconverts between two stable chair conformations. This interconversion is known as ring-flip. When the two chair forms interconvert, axial bonds become equatorial and equatorial bonds become axial.



Cyclohexane can also exist in a boat conformation. Like the chair conformation, the boat conformation is free of angle strain. However, the conformation is less stable than the chair conformation by 11 Kcal/mole. Boat conformation is less stable because some of the carbon-hydrogen bonds in boat conformation are eclipsed.



The boat conformation is further destabilised by the close proximity of the flagpole hydrogens. These hydrogens are 1.8 Å apart but the vander Waal's radii is 2.4 Å. The flagpole hydrogens are also known as trans nuclear hydrogens.

When one hydrogen of cyclohexane is placed by a larger atom or group, crowding occurs. The most sever crowding is among atoms held by the three axial bonds on the same side of the molecule; the resulting repulsive interaction is called 1,3-diaxial interaction. This causes steric strain in the molecule.

Thus, monosubstituted cyclohexane will assume chair conformation in which the substituent occupies an equatorial position. Similarly in disubstituted cyclohexanes the chair conformation containing both the substituents in equatorial positions will be the preferred conformation. In general, the conformation with bulkier substituent in an equatorial position will be the preferred conformation. For examples:



GENERAL ORGANIC CHEMISTRY

NOMENCLATURE

SECTION A

Classification of carbon and hydrogen atoms, Types of alcohols and amines, Definition of chiral carbon, olefinic and acetylenic bonds, vinylic carbon, allylic carbon and benzylic carbon

1. Kekule's Principle

(a) Carbon has four valencies.

(b) Carbon has a property of catenation. Catenation is the binding of an element to itself through covalent bonds to form chain or ring molecules.

(c) A carbon atom can share 2, 4 or 6 electrons with other carbons & can form single, double or triple bond.

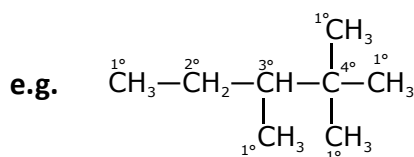
(d) For a carbon atom, it is not possible to make more than 3 bonds with an adjacent carbon atom because a carbon atom completes its octet from overlapping which has consists directional property.

2. Degree of Carbon

No. of carbon attached to carbon atom is the degree of that carbon.

There are four types : –

1. Primary carbon (1° carbon)
2. Secondary carbon (2° carbon)
3. Tertiary carbon (3° carbon)
4. Quaternary carbon (4° carbon)



3. Degree of Hydrogen

Degree of hydrogen is the degree of carbon on which that hydrogen is attached.

There are three types :



1. Primary hydrogen (1° hydrogen)
2. Secondary hydrogen (2° hydrogen)
3. Tertiary hydrogen (3° hydrogen)

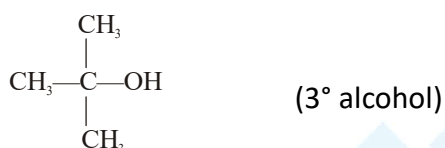
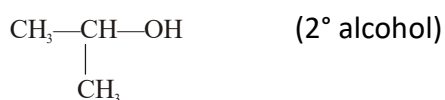
4. Degree of Alcohol

Degree of carbon on which $-OH$ group attached.

There are three types.

1. Primary alcohol (1° alcohol)
2. Secondary alcohol (2° alcohol)
3. Tertiary alcohol (3° alcohol)

e.g. CH_3-CH_2-OH (1° alcohol)



5. Degree of Amine

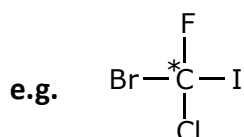
They are named according to the number of carbons attached to nitrogen. There are three types,

1. Primary Amine (1° Amine)
2. Secondary Amine (2° Amine)
3. Tertiary Amine (3° Amine)

e.g. $-NH_2$ 1° Amine
 $-NH-$ 2° -Amine
 $\begin{array}{c} -N- \\ | \end{array}$ 3° -Amine

6. Chiral carbon or asymmetric carbon atom

Chiral carbon or asymmetric carbon atom is a carbon atom that is attached to four different atoms or groups of atoms.





7. Olefinic and acetylenic bonds

A. Olefinic bond :

Alkenes are also called olefins because they form oily liquids on reaction with chlorine gas. An alkene consists of at least one double bond. This double bond is known as the olefinic bond.

e.g. $\text{CH}_3\text{CH}=\text{CH}_2$ Propene

B. Acetylenic bonds :

Acetylene, also called ethyne, the simplest and best-known member of the hydrocarbon series containing one or more pairs of carbon atoms linked by triple bonds, the triple bond is also called acetylenic bond.

e.g. $\text{CH}\equiv\text{CH}$ Ethyne

8. Vinylic carbon, allylic carbon and benzylic carbon

A. Vinylic Carbon :

Vinylic carbon is a carbon that is involved in a double bond with another carbon. It is sp^2 hybridized. Vinylic carbon makes a double bond with another carbon which is also sp^2 hybridized. Both carbons involved in this bond are vinylic carbons.

e.g. $\begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \text{---CH}=\text{CH}_2$ Vinyl

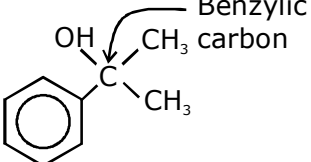
B. Allylic carbon :

Allylic carbon can be described as the carbon atom that is adjacent to the double bond. This carbon atom is the nearest to the double bond, but it is not a part of the double bond. The carbon atoms in the double bond are sp^2 hybridized. But the allylic carbon is sp^3 hybridized. It is bonded to the sp^2 hybridized carbon atom through a single bond.

e.g. $\begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \text{---CH}_2\text{---CH}=\text{CH}_2$ Allyl

C. Benzylic carbon :

A benzylic carbon is a saturated carbon that is directly attached to a benzene ring.

e.g. 

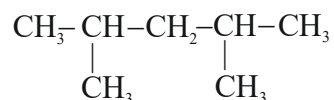


Example-1

How many 1° carbon atom will be present in a simplest hydrocarbon having two 3° & one 2° carbon atom?

- (A) 3 (B) 4
(C) 5 (D) 6

Sol. B



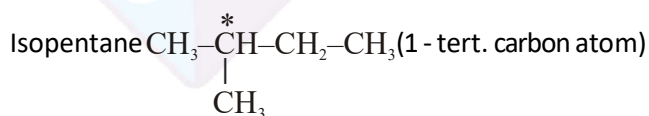
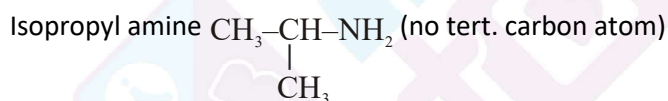
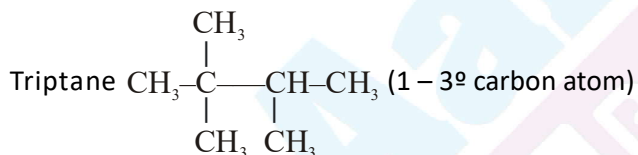
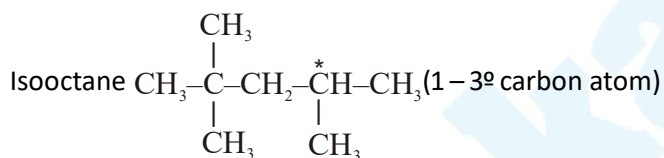
2, 4 - Dimethyl pentane is the compound having two 3° carbon & one 2° carbon atom & four 1° carbon atoms.

Example-2

In which of the following tert. carbon is absent -

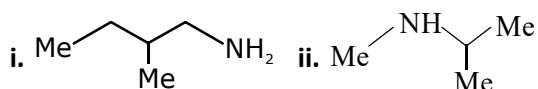
- (A) Isooctane (B) Triptane
(C) Isopropyl amine (D) Isopentane

Sol. C



Example-3

Indicate the following amine as 1°, 2° and 3°.



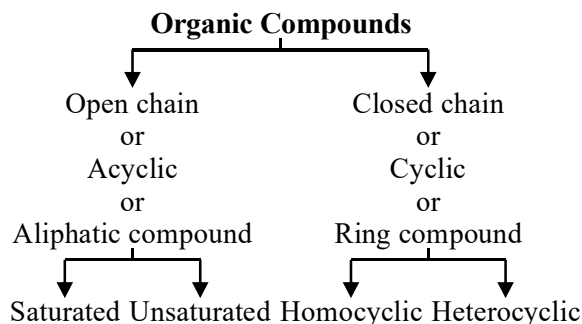
Ans. i → 1°, ii → 2°



SECTION B
CLASSIFICATION OF ORGANIC COMPOUNDS

On the basis of structure and , on the basis of homology

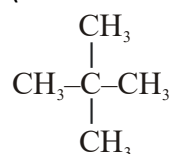
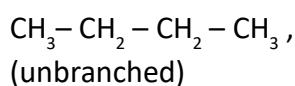
(A) Based on structure



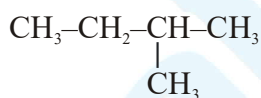
Aliphatic or Open chain compounds

Those compounds in which first & last carbon atoms are not connected with each other. Branched or unbranched chains are possible in these compounds.

For example :-



(branched)

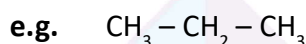


(branched)

There are two varieties in these compounds -

Saturated Hydrocarbons :-

(a) In such type, adjacent carbons are attached with single bonds.

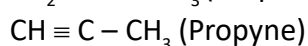
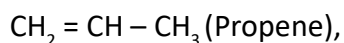


(b) General formula of these compounds is $\text{C}_n\text{H}_{2n+2}$

(c) These are also called as paraffins (Parum + Affinis i.e. little reactivity) because these are less reactive due to absence of π -bonds.

Unsaturated Hydrocarbons :-

(a) There will be a double bond or a triple bond between any two carbon atoms,



(b) General formula is C_nH_{2n} or $\text{C}_n\text{H}_{2n-2}$.

(c) Alkenes are also called as olefins because they react with halogens to form oily substances. (Oleum + fines i.e. Oil forming).

(d) Due to presence of π bonds these are more reactive.

**Closed chain compounds : –**

In these compounds first & last carbons are attached with each other.

e.g. Cyclopropane.

These are of two types –

Homocyclic compounds : –

These are the compounds in which the complete ring is formed by carbon atoms only.

These are also of two types -

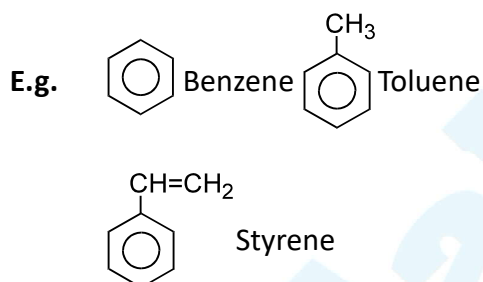
(a) Alicyclic compounds : –

These are the compounds having the properties like aliphatic compounds. These may be saturated or unsaturated like aliphatic compounds.

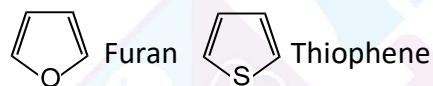
Cyclopropane, Cyclopropene, Cyclobutene

(b) Aromatic compounds : –

These compounds mostly consist of at least one benzene ring i.e. a six-membered carbocyclic ring having alternate single and double bonds. These compounds are fragrant and are hence, named as aromatic (greek word aroma means sweet smell).

**2.2.2 Heterocyclic Compounds : –**

These are cyclic compounds having ring or rings built up of more than one kind of atoms.

**(B) Based on homology**

If the difference of CH_2 or 14 molecular weight is present between successive members of a series of organic compounds then this is known as homologous series, members are known as Homologous and the overall concept is known Homology.

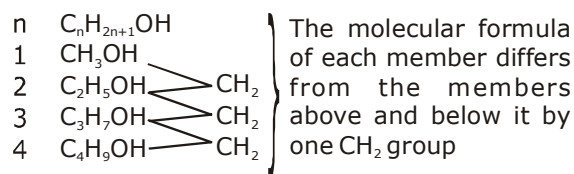
The general characteristics of a homologous series are :

- (i) General formula is same.
- (ii) General methods of preparation is same.
- (iii) Same chemical properties.
- (iv) Type of functional group must be same.
- (v) Physical properties are different.

e.g. The Homologous series of monohydric alcohols can be represented by the general formula $\text{C}_n\text{H}_{2n+1}\text{OH}$. The formula of various homologous can be written by giving the values



1, 2, 3, to n.



Example-4

Which of the following is not an aliphatic compound ?

- (A) Isopropane (B) Butane
(C) Hexane (D) None of these

Sol. D

All are aliphatic compound, because according to the definition all the hydrocarbons having straight or branched chain of carbon is aliphatic.

Example-5

Which of the following is the pair of homocyclic & heterocyclic compound ?

- (A) Cyclopropane and cyclohexane
(B) Cycloethane and oxyrane
(C) Pyridine and thiophene
(D) Cyclopentane and furan

Sol. D

Cyclopentane and furane is a pair of homocyclic & heterocyclic compound. In which cyclopentane is homocyclic and furane is heterocyclic.

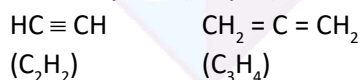
Example-6

The formula C_nH_{2n-2} shows -

- (A) Alkene & Alkadiyne (B) Alkyne & Alkadiyne
(C) Alkane & Alkadiene (D) Alkyne & Alkadiene

Ans. D

Sol. For Acetylene (Alkyne) & Allene (Alkadiene)



SECTION C

On the basis of group - Radicals of alkanes, Radicals of alkenes and alkynes, Radicals of aromatic hydrocarbon

(C) On the basis of group E

(a) Functional Group

- (1) It is responsible for chemical behaviour or properties of any organic compound.
(2) It is made up of single atom or group of atoms eg. $-O-$, $-OH$, $-COOH$ etc.



(b) Hydrocarbon Groups

If one hydrogen (or more hydrogen atoms in some cases) is taken out from a hydrocarbon, the group left is known as a hydrocarbon group. Hydrocarbons are of three major types, hydrocarbon groups also belong to three main classes, these are ;

- (1) Acyclic hydrocarbon groups
- (2) Alicyclic hydrocarbon groups
- (3) Aromatic benzenoid hydrocarbon groups

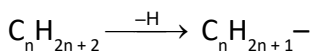
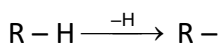
Acyclic Hydrocarbon Groups

Acyclic hydrocarbon groups are of three types :

- (i) Alkyl groups
- (ii) Alkenyl groups
- (iii) Alkynyl groups

(i) Alkyl groups :

These are univalent groups or radicals obtained by the removal of one hydrogen atom from a molecule of an alkane. The symbol 'R' is often used to represent an alkyl group. The general formula of an alkyl group is C_nH_{2n+1} .



Alkyl groups are of five types :

(a) Normal alkyl group :

This is formed by the removal of one primary hydrogen atom from the straight chain alkane. A normal alkyl group is written as n-alkyl group in common naming system and in its IUPAC nomenclature, the prefix n – is dropped.

Some examples are :

| R | Common Name | IUPAC Name |
|-----------------------------|--------------------|----------------|
| $CH_3-CH_2-CH_2-$ | n-Propyl (n-Pr) | Propyl (Pr) |
| $CH_3-CH_2-CH_2-CH_2-$ | n-Butyl (n-Bu) | Butyl (Bu) |
| $CH_3-CH_2-CH_2-CH_2-CH_2-$ | n-Pentyl | Pentyl |

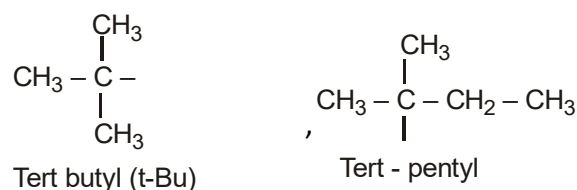
(b) Secondary alkyl group : This is formed by the removal of one hydrogen from the secondary carbon atom from alkane. It is denoted by sec – alkyl or S - alkyl group in both of the system of nomenclature.



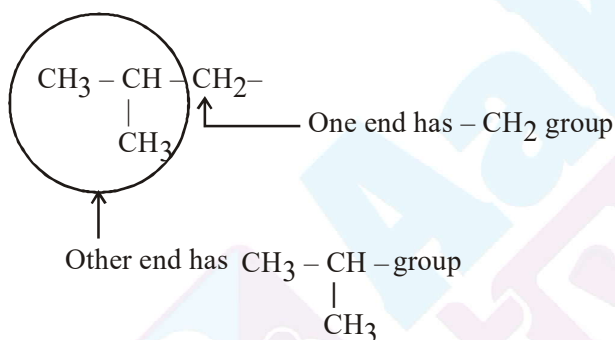
Some examples are given below :

| Structure | Common name | IUPAC name |
|--|-------------|----------------|
| $\begin{array}{c} \text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}_3 \\ \\ \text{(S-Bu)} \end{array}$ | sec-butyl | 1-Methylpropyl |

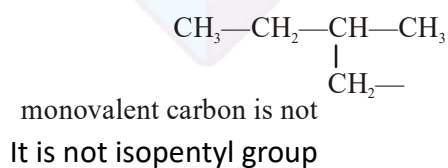
(c) Tertiary alkyl group : This group is formed by the removal of one hydrogen from the tertiary carbon of the corresponding alkane. It is denoted by *tert* or *t*-alkyl group in both system of nomenclature. Some example are :

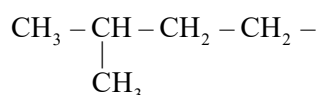


(d) Isoalkyl group : An alkyl group containing one terminal CH_2 - group and $\text{CH}_3 - \text{CH} -$ group on the other end with no other branching is said to be an *isoalkyl* group or *i*-alkyl group.

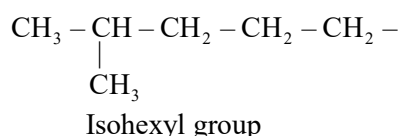


Hence, it is isoalkyl group, i.e., isobutyl group.

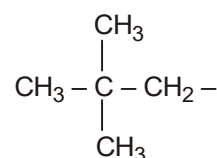
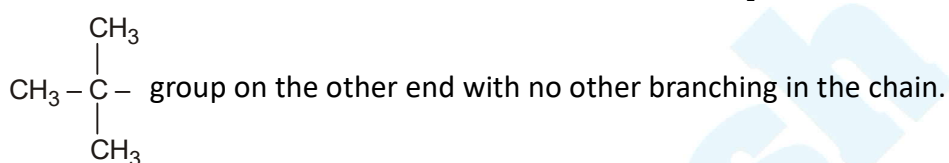




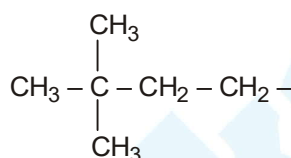
Isopentyl (or Isoamyl group)



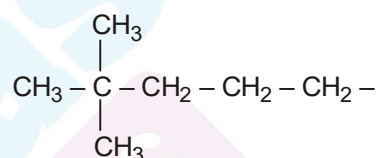
(e) Neoalkyl group : A neoalkyl group contains one $\text{CH}_2 -$ group on one end and one



Neopentyl group



Neohexyl group

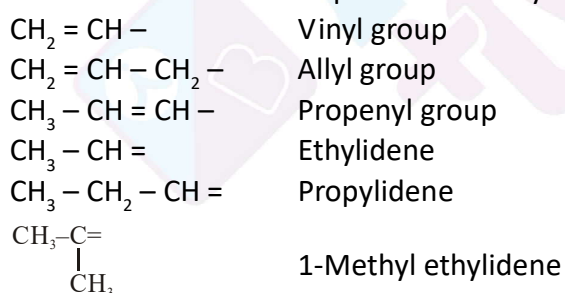


Neoheptyl group

Note : Methylene group : If two hydrogen atoms are removed from methane then the group obtained is methylene group, i.e., $-\text{CH}_2 -$

Alkenyl Group

Hydrocarbon group containing carbon-carbon double bond is called alkenyl group. Their common names are accepted in IUPAC system in most of the cases. Some examples are :



Alkynyl group

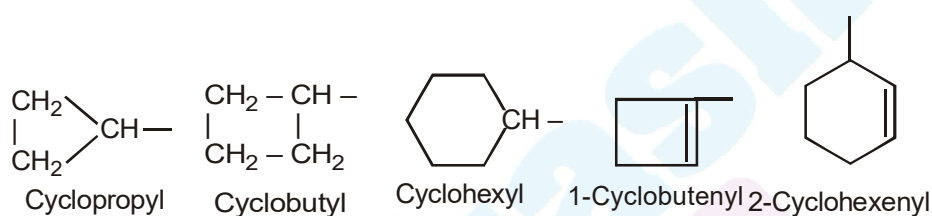
Hydrocarbon group containing carbon-carbon triple bond may be called an alkynyl group. Their common names are accepted in IUPAC system in most of the case. Some examples are :



| Structure | Common name | IUPAC name |
|---|-------------|------------|
| Alicyclic | Hydrocarbon | Groups |
| $\text{CH} \equiv \text{C} -$ | Ethynyl | Ethynyl |
| $\text{CH} \equiv \text{C} - \text{CH}_2 -$ | Propargyl | Propargyl |
| $\text{CH}_3 - \text{C} \equiv \text{C} -$ | Propynyl | Propynyl |

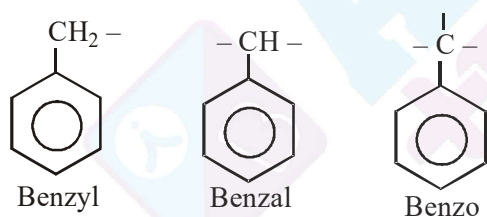
Alicyclic Hydrocarbon Groups

These are obtained when one hydrogen atom is removed from the ring carbon. These groups may be classified as :
cycloalkyl groups



Aromatic Benzenoid Hydrocarbon Groups

Aromatic hydrocarbon groups have one or more hydrogen atoms less than the present hydrocarbons. These are in general denoted by Ar- and are called aryl groups. The simplest aryl group is phenyl group (C_6H_5). This is denoted by Ph or ϕ .



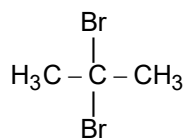
Example -7

$\text{C}_3\text{H}_6\text{Br}_2$ can show -

- (A) Two gem dibromide
- (B) Two vicinal dibromide
- (C) Two tert. dibromo alkane
- (D) Two sec. dibromo alkane

Ans. A

Sol. 1, 1 - Dibromo propane



2, 2 - Dibromo propane
(Two gem dibromides)

SECTION D

Common name system, Derived Name system

NOMENCLATURE

Mainly three systems are adopted for naming an organic compound –

* **Common Name or Trivial System**

Derived System

IUPAC system or Geneva System

5. **Common or trivial system**

Initially organic compounds are named on the basis of source from which they were obtained.

eg.

| S. No. | Organic Compound | Trivial Name | Source |
|--------|--|------------------------------|---|
| 1. | CH ₃ OH | Wood spirit or Methyl spirit | Obtained by destructive distillation of wood. |
| 2. | NH ₂ CONH ₂ | Urea | Obtained from urine |
| 3. | CH ₄ | Marsh gas (fire damp) | It was produced in marsh places. |
| 4. | CH ₃ COOH | Vinegar | Obtained from Acetum i.e. Vinegar |
| 5. | $\begin{array}{c} \text{COOH} \\ \\ \text{COOH} \end{array}$ | Oxalic acid | Obtained from oxalis plant. |
| 6. | HCOOH | Formic acid | Obtained from formicus [Red ant] |
| 7. | $\begin{array}{c} \text{CH}_3\text{-CH-COOH} \\ \\ \text{OH} \end{array}$ | Lactic acid | Obtained from milk |
| 8. | $\begin{array}{c} \text{CH}_2\text{-COOH} \\ \\ \text{CH(OH)COOH} \end{array}$ | Malic acid | Obtained from apple ⇒ malum |
| 9. | CH ₃ CH ₂ CH ₂ COOH | Butyric acid | Obtained from butter. |
| 10. | CH ₃ (CH ₂) ₄ COOH | Caproic acid | Obtained from goats. |



Some typical compounds in which common & trivial names are also differ.

| S. No. | Compound | Trivial Name | Common name |
|--------|---|--------------|-------------------|
| 1. | CH ₄ | Marsh gas | Methane |
| 2. | CH ₃ OH | Wood spirit | Methyl alcohol |
| 3. | CH ₃ COOH | Vinegar | Acetic acid |
| 4. | $\begin{array}{c} \text{CH}_3-\text{C}-\text{CH}_3 \\ \parallel \\ \text{O} \end{array}$ | Acetone | Dimethyl ketone |
| 5. | $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2=\text{CH}-\text{C}-\text{H} \end{array}$ | Acrolein | Acryl Aldehyde |
| 6. | $\begin{array}{c} \text{H}_3\text{C} \quad \text{O} \\ \quad \parallel \\ \text{CH}_3-\text{C}-\text{C}-\text{H} \\ \\ \text{CH}_3 \end{array}$ | Pivaldehyde | Neo valeraldehyde |

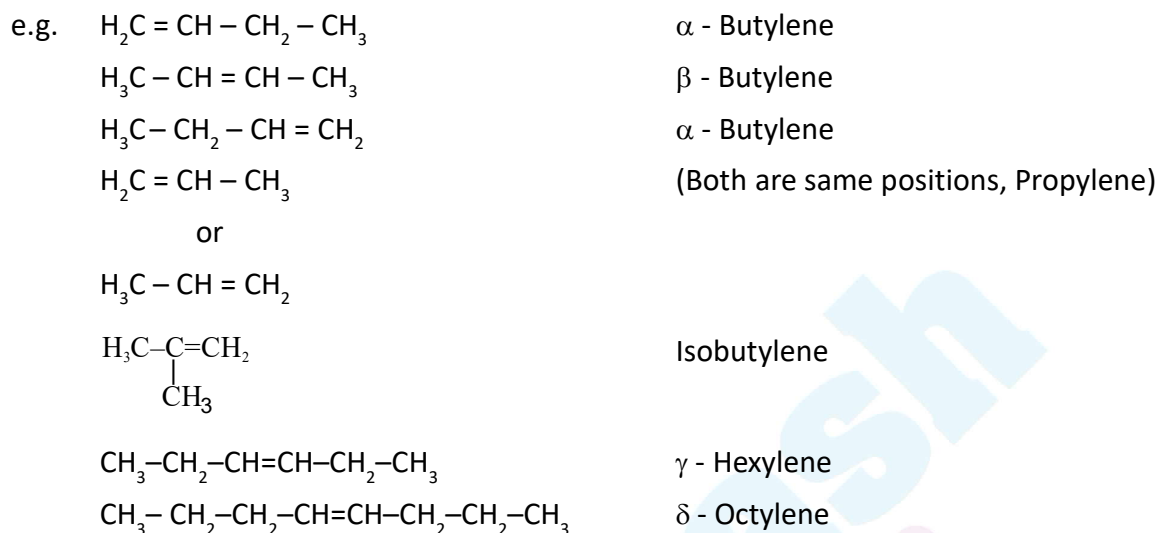
Common Names (R is termed as alkyl-)

| S. No. | Compound | Common Names |
|--------|---|----------------------------|
| 1. | R-X | Alkyl halide |
| 2. | R-OH | Alkyl alcohol |
| 3. | R-SH | Alkyl thioalcohol |
| 4. | R-NH ₂ | Alkyl amine |
| 5. | R-O-R | Dialkyl ether |
| 6. | R-S-R | Dialkyl thioether |
| 7. | $\begin{array}{c} \text{R}-\text{C}-\text{R} \\ \parallel \\ \text{O} \end{array}$ | Dialkyl ketone |
| 8. | R-NH-R | Dialkyl amine |
| 9. | $\begin{array}{c} \text{R}-\text{N}-\text{R} \\ \\ \text{R} \end{array}$ | Trialkyl amine |
| 10. | R-O-R' | Alkyl alkyl' ether |
| 11. | $\begin{array}{c} \text{R}-\text{C}-\text{R}' \\ \parallel \\ \text{O} \end{array}$ | Alkyl alkyl' ketone |
| 12. | R-S-R' | Alkyl alkyl' thio ether |
| 13. | R-NH-R' | Alkyl alkyl' amine |
| 14. | $\begin{array}{c} \text{R}-\text{N}-\text{R}' \\ \\ \text{R}'' \end{array}$ | Alkyl alkyl' alkyl'' amine |



Position of double bond : –

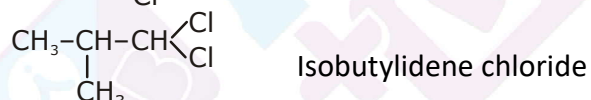
In an unsaturated hydrocarbon if the position of double bond is on 1st or last carbon then it's prefix will be α (alpha) if it is on 2nd carbon it is termed as β (Beta) & then γ (gamma) & δ (delta) and so on.



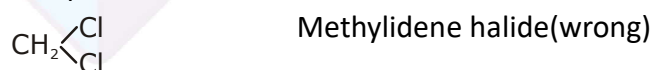
Common – Naming of dihalides : –

(a) When two same halogen atoms are attached to the same carbon such compounds are called **Gemdihalides**.

(b) Common names of such compounds are alkylidene halides



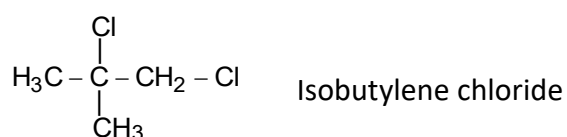
Exception :



Methylene chloride(right)

(c) When two same halogen atoms are attached to adjacent carbon, these are called as vicinal dihalides.

Common names of such compounds are alkylene halide.

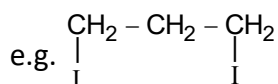




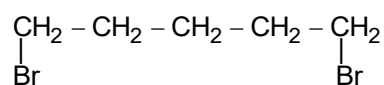
(d) When two same halogen atoms are attached at the two ends of a carbon chain its common naming will be polymethylene halide.

'poly' word indicates the number of $-\text{CH}_2-$ groups.

| | | | | | |
|-----------------|----|-----|-------|-------|------|
| $-\text{CH}_2-$ | 2 | 3 | 4 | 5 | 6 |
| Poly | di | tri | tetra | penta | hexa |



Trimethylene Iodide



Pentamethylene Bromide

Exception :

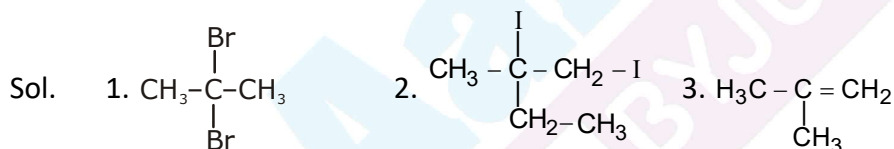
$\text{CH}_2 - \text{X}$ dimethylene halide (wrong)

|

$\text{CH}_2 - \text{X}$ ethylene halide (right)

e.g. Draw the structure of following organic compounds -

1. Isopropylidene Bromide
2. Active amylene Iodide
3. Isobutylene



Common - Naming of the functional group having carbon : -

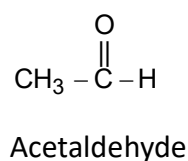
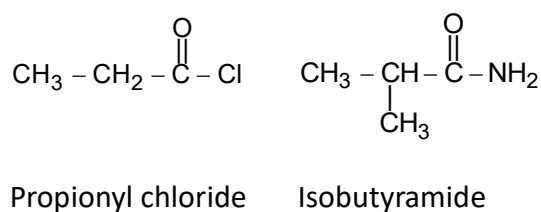
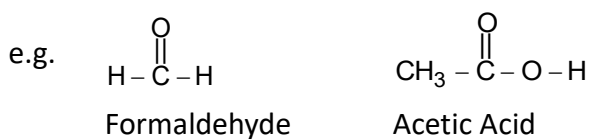
Chart - 1

| Functional group | Suffix | Functional group | Suffix |
|--|-------------|---|----------------|
| $\begin{array}{c} \text{O} \\ \\ -\text{C} - \text{H} \end{array}$ | -aldehyde | $\begin{array}{c} \text{O} \\ \\ -\text{C} - \text{OH} \end{array}$ | -oic Acid |
| $\begin{array}{c} \text{O} \\ \\ -\text{C} - \text{X} \end{array}$ | -oyl halide | $\begin{array}{c} \text{O} \\ \\ -\text{C} - \text{NH}_2 \end{array}$ | -amide |
| $-\text{C} \equiv \text{N}$ | -nitrile | $-\text{N} \equiv \text{C}$ | -isonitrile |
| $\begin{array}{c} \text{O} \\ \\ -\text{C} - \text{O} - \text{R} \end{array}$ | -ate | $\begin{array}{c} \text{O} \\ \\ -\text{C} - \text{O} \\ \\ \text{O} \\ \\ -\text{C} \\ \\ \text{O} \end{array}$ | -oic anhydride |

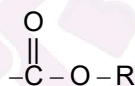


Prefix : –

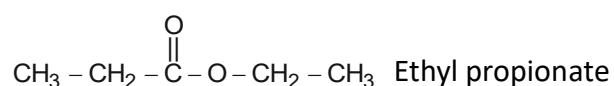
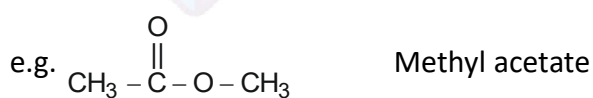
- 1 Carbon → Form-
 2 Carbon → Acet-
 3 Carbon → Propion-
 4 Carbon → Butyr-
 5 Carbon → Valer-
 3 C + (=) double bond → Acryl-
 4 C + double bond → Croton-

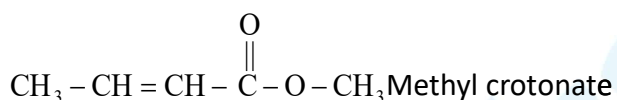
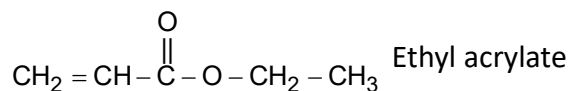
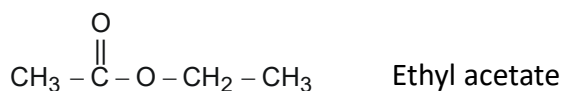


Nomenclature of Ester :-

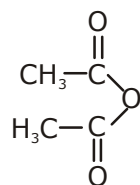


The group which is attached to the oxygen is written as alkyl & the remaining structure is named same as defined in chart-1.

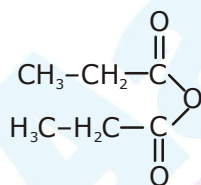




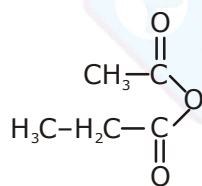
Nomenclature of Anhydride : –



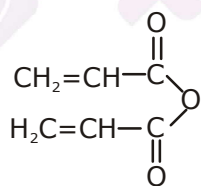
Acetic anhydride



Propionic anhydride



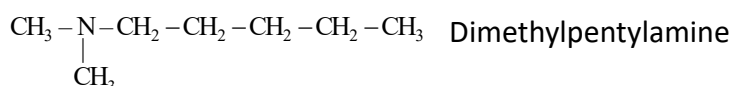
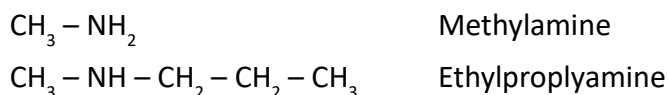
Acetic propionic anhydride



Acrylic anhydride

Nomenclature of Amine : –

The common name of amine is obtained by citing the name of the alkyl groups bonded to the nitrogen atom in alphabetical order followed by **amine**. The entire name is written in one word. For examples.



Example-8

Acrolein is -

- (A) An unsaturated aldehyde (B) A saturated aldehyde
 (C) A polymer (D) An alkene

Ans. A

Sol. $\text{CH}_2 = \text{CH} - \text{CHO}$ unsaturated aldehyde.

Example-9

The common name of the compound

$\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{NH}_2$ is -

- (A) Vinyl amine (B) Allyl amine
 (C) Divinyl amine (D) Diallylamine

Ans. B

Sol. $\text{CH}_2 = \text{CH} - \text{CH}_2$ - is allyl group.

Example-10

The common name of the compound $\text{CH}_2 = \text{CH} - \underset{\text{O}}{\underset{||}{\text{C}}} - \text{CH} = \text{CH}_2$ is -

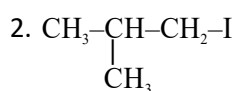
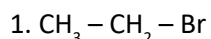
- (A) Divinyl ketone (B) Diallyl ketone
 (C) Both A and B (D) None

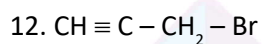
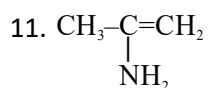
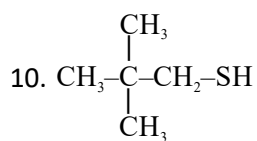
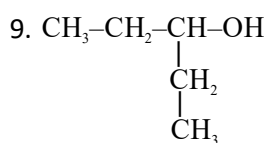
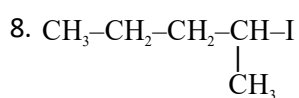
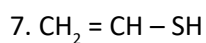
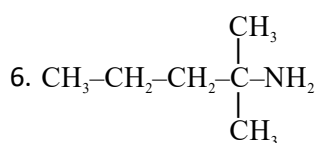
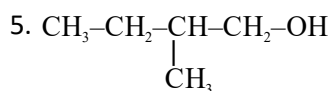
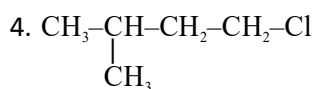
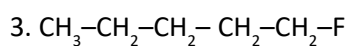
Ans. A

Sol. $\text{CH}_2 = \text{CH} -$ is called as vinyl group.

Example-11

Write the common names of the following -





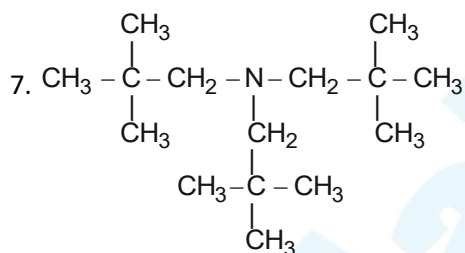
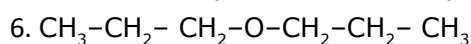
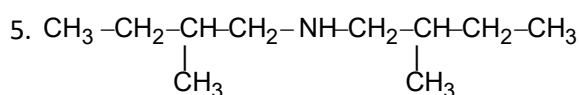
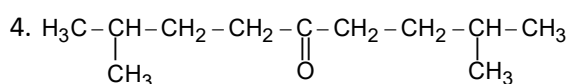
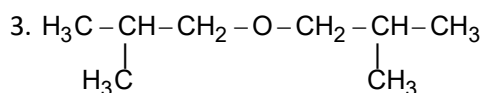
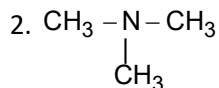
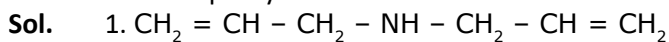
- Sol.**
1. Ethyl Bromide
 2. Isobutyl Iodide
 3. Amyl fluoride
 4. Isopentyl chloride
 5. Amyl alcohol
 6. Tertiary hexylamine
 7. Vinyl thioalcohol
 8. Secondary amyl Iodide
 9. Secondary amyl alcohol.
 10. Neopentyl thioalcohol
 11. Isopropenyl amine
 12. Propargyl Bromide



Example-12

Write down the structures of the following -

1. Diallylamine
2. Trimethylamine
3. Diisobutyl ether
4. Diisopentyl ketone
5. Di Active amyl amine
6. Di normal propyl ether
7. Trineopentyl amine



Example-13

Common name of the compound $\text{CH}_3 - \text{CH} = \text{CH} - \overset{\text{O}}{\parallel} \text{C} - \text{OH}$ is -

- (A) Crotonic acid
- (B) Acrylic acid
- (C) Allylic acid
- (D) None

Ans. A

Sol. 4C + (=) → croton
Suffix is 'ic' acid.

Example-14

Common name of the compound $\text{CH}_2 = \text{CH} - \overset{\text{O}}{\parallel} \text{C} - \text{H}$ is -

- (A) Croton aldehyde
- (B) Acryl aldehyde
- (C) Propion aldehyde
- (D) Butyr aldehyde

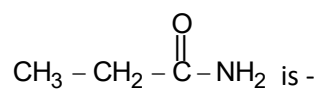
Ans. B

Sol. 3C + (=) → Acryl
Suffix is aldehyde.



Example-15

Common name of the compound



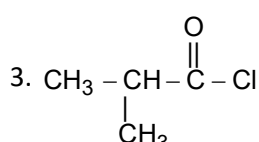
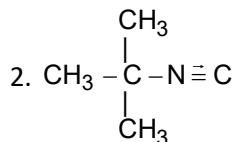
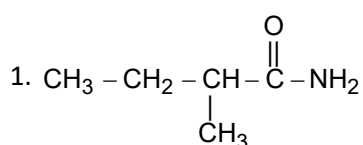
- (A) Acetamide (B) Propionamide
(C) Butyramide (D) Acetic amide

Ans. B

Sol. 3C → Propion
Suffix is amide.

Example-16

Write down the common names of the following :



- Sol.** 1. Secondary valeramide
2. Tertiary valero-isonitrile
3. Isobutyryl chloride

COMMON OR TRIVIAL NAMES

6. Derived system

According to this system name to any compound is given according to the parent name of the homologous series. This system is reserved for the following nine homologous series.



Chart - 2

| S. No. | Series Name of Homologous series | Derived Name | Structure of group |
|--------|----------------------------------|---------------|--|
| 1. | Alkane | Methane | $\begin{array}{c} \\ -C- \\ \end{array}$ |
| 2. | Alkene | Ethylene | $>C=C<$ |
| 3. | Alkyne | Acetylene | $-C \equiv C -$ |
| 4. | Alcohol | Carbinol | $\begin{array}{c} \\ -C-OH \\ \end{array}$ |
| 5. | Aldehyde | Acetaldehyde | $\begin{array}{c} \\ -C-CHO \\ \end{array}$ |
| 6. | Carboxylic acid | Acetic acid | $\begin{array}{c} \\ -C-COOH \\ \end{array}$ |
| 7. | Acid halide | Acetyl halide | $\begin{array}{c} \\ -C-COX \\ \end{array}$ |
| 8. | Amide | Acetamide | $\begin{array}{c} \\ -C-CONH_2 \\ \end{array}$ |
| 9. | Ketone | Acetone | $\begin{array}{c} & & \\ -C & -C & -C- \\ & & \\ & O & \end{array}$ |

Types of Ethylene:—
(Symmetrical & Unsymmetrical)

(a) Symmetrical : –

In the given two alkyl groups one group is attached to the one carbon of ethylene & next on the next carbon.

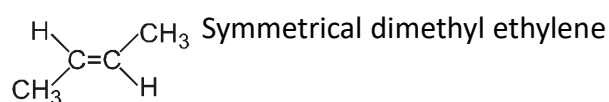
(b) Unsymmetrical : –

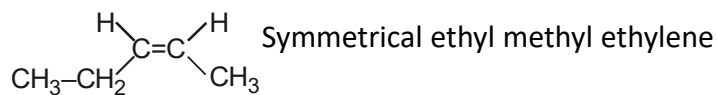
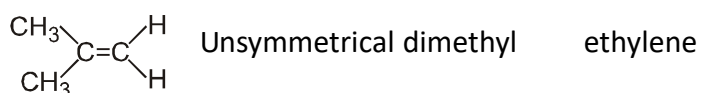
When both the given groups are attached on the same carbon.

Note : – Symmetrical & Unsymmetrical

terms are used only when two alkyl groups are given.

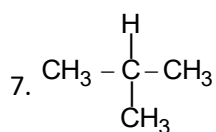
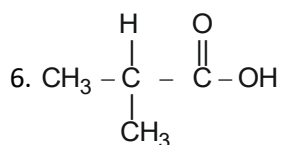
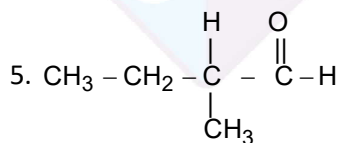
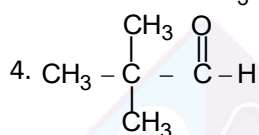
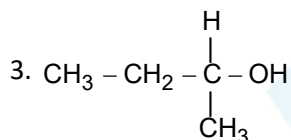
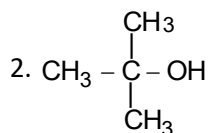
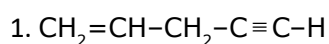
eg.

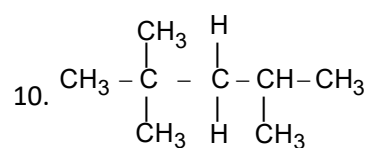
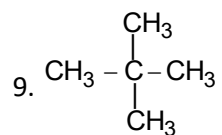
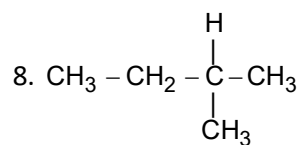




Example-17

Write down the derived names of the following-





- Sol.**
1. Allyl acetylene
 2. Tri methyl carbinol
 3. Ethyl methyl carbinol
 4. Tri methyl acetaldehyde
 5. Ethyl methyl acetaldehyde
 6. Dimethyl acetic acid
 7. Tri methyl methane
 8. Ethyl dimethyl methane
 9. Tetra methyl methane
 10. Tertiary butyl Isopropyl methane.



| Class of Compound | Structure | Common name |
|---|---|---------------------------|
| Alkanes | (i) CH ₄ | Methane |
| | (ii) CH ₃ - CH ₃ | Ethane |
| | (iii) CH ₃ - CH ₂ - CH ₃ | Propane |
| | (iv) $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{CH} - \text{CH}_3 \end{array}$ | Isobutane |
| | $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ | Neopentane |
| Alkenes | CH ₂ = CH ₂ | Ethylene |
| | CH ₃ - CH = CH ₂ | Propylene |
| Alkynes | CH ≡ CH | Acetylene |
| | CH ₃ - C ≡ CH | Methyl acetylene |
| | CH ₃ - C ≡ C - CH ₃ | Dimethyl acetylene |
| | CH ₃ - X | Methyl halide |
| Alkyl halides | $\begin{array}{c} \text{Br} \\ \\ \text{CH}_3 - \text{CH} - \text{CH}_3 \end{array}$ | Isopropyl bromide |
| | $\begin{array}{c} \text{Br} \\ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ | Tert-butyl bromide |
| | $\begin{array}{c} \text{Br} \\ \\ \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 \end{array}$ | Sec-butyl bromide |
| | CH ₃ - CHCl ₂ | Ethylidene chloride |
| | CH ₂ Cl - CH ₂ Cl | Ethylene dichloride |
| | Alcohol | CH ₃ - OH |
| CH ₃ - CH ₂ - OH | | Ethyl alcohol |
| CH ₃ - CH ₂ - CH ₂ - OH | | <i>n</i> - Propyl alcohol |
| $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2\text{OH} \\ \\ \text{CH}_3 \end{array}$ | | Isobutyl alcohol |
| HO - CH ₂ - CH ₂ OH | | Glycol |
| OHCH ₂ - CHOH - CH ₂ OH | | Glycerol |
| Ether | CH ₃ - O - CH ₃ | Dimethyl ether |
| | CH ₃ - CH ₂ - O - CH ₃ | Ethyl methyl ether |
| | CH ₃ - CH ₂ - O - CH ₂ - CH ₃ | Diethyl ether |

| Class of Compound | Structure | Common name |
|---|---|---|
| Aldehydes | CH ₃ -CH ₂ -CH ₂ -O-CH-CH ₃ CH ₃ | Isopropyl propyl ether |
| | HCHO | Formaldehyde |
| | CH ₃ - CHO | Acetaldehyde |
| | CH ₃ - CH ₂ - CH ₂ - CHO | Butyraldehyde |
| Ketones | $\begin{array}{c} \text{O} \\ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \end{array}$ | Acetone |
| | $\begin{array}{c} \text{O} \\ \\ \text{CH}_3 - \text{CH}_2 - \text{C} - \text{CH}_3 \end{array}$ | Ethyl methyl ketone |
| | $\begin{array}{c} \text{O} \\ \\ \text{CH}_3 - \text{CH}_2 - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \end{array}$ | Ethyl propyl ketone |
| Carboxylic acids | HCOOH | Formic acid |
| | CH ₃ - COOH | Acetic acid |
| | CH ₃ - CH ₂ - CH ₂ - COOH | Butyric acid |
| | $\begin{array}{c} \text{COOH} \\ \\ \text{COOH} \end{array}$ | Oxalic acid |
| | $\begin{array}{c} \text{COOH} \\ / \\ \text{CH}_2 \\ \backslash \\ \text{COOH} \end{array}$ | Malonic acid |
| | $\begin{array}{c} \text{CH}_2 - \text{COOH} \\ \\ \text{CH}_2 - \text{COOH} \end{array}$ | Succinic acid |
| Esters | $\begin{array}{c} \text{CH}_2 - \text{COOH} \\ / \\ \text{CH}_2 \\ \backslash \\ \text{CH}_2 - \text{COOH} \end{array}$ | Glutaric acid |
| | HCOOCH ₃ | Methyl formate |
| | CH ₃ COOC ₂ H ₅ | Ethyl acetate |
| | CH ₃ -CH ₂ -CH ₂ -COOC ₂ H ₅ | Ethyl butyrate |
| | Anhydrides | $\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{CH}_3 - \text{C} - \text{O} - \text{C} - \text{CH}_3 \end{array}$ |
| $\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{CH}_3 - \text{CH}_2 - \text{C} - \text{O} - \text{C} - \text{CH}_2 - \text{CH}_3 \end{array}$ | | Propionic anhydride |
| Acid chlorides | $\begin{array}{c} \text{O} \\ \\ \text{CH}_3 - \text{C} - \text{Cl} \end{array}$ | Acetyl chloride |
| Cyanides | CH ₃ - CN | Methyl cyanide |
| | CH ₃ - CH ₂ - CN | Ethyl cyanide |



SECTION - E :

Any given organic structure has only one IUPAC name and any given IUPAC name represents only one molecular structure.

The IUPAC name of any organic compound essentially consists of three parts, i.e.,

(1) Root word (2) Suffix and (3) Prefix

Root Word

It is the basic unit of the name. It denotes the number of carbon atoms present in the parent chain of the molecule. Chain containing one to four carbon atoms are known by special root words (based upon the common names of alkanes) while chains from C₅ onwards are known by Greek number roots. Thus :

| Chain length | Word root | Chain length | Word root |
|-----------------|-----------|-----------------|-----------|
| C ₁ | Meth | C ₁₁ | Undec |
| C ₂ | Eth | C ₁₂ | Dodec |
| C ₃ | Prop | C ₁₃ | Tridec |
| C ₅ | Pent | C ₁₄ | Tetradec |
| C ₆ | Hex | C ₂₀ | Eicos |
| C ₇ | Hept | C ₃₀ | Triacont |
| C ₈ | Oct | C ₄₀ | Tetracont |
| C ₉ | Non | C ₅₀ | Pentacont |
| C ₁₀ | Dec | C ₆₀ | Hexacont |

Suffix

There are two types of suffixes, i.e., Primary suffix and Secondary suffix.

(a) Primary suffix : A primary suffix is always added to the root word to indicate whether carbon chain is saturated or unsaturated. The primary suffix for the various saturated and unsaturated carbon chains and groups are given below :

| Nature of carbon chain | Primary suffix | Chain length |
|------------------------|----------------|--------------|
| Saturated, C – C | –ane | Alkane |
| Unsaturated, C = C | –ene | Alkene |
| Unsaturated, C ≡ C | –yne | Alkyne |

| Nature of group | Primary suffix | Generic name |
|----------------------------|----------------|--------------|
| Alkane - one hydrogen atom | –yl | Alkyl |
| Alkene - one hydrogen atom | –enyl | Alkenyl |
| Alkyne - one hydrogen atom | –ynl | Alkynyl |



If the parent, carbon-chain contains two, three, four or more double or triple bonds, numerical prefixes such as di (for two), tri (for three), tetra (for four) etc. are added to the primary suffix. For example :

| | <i>Type of carbon chain</i> | <i>Primary suffix</i> | <i>Generic name</i> |
|-------|-----------------------------|-----------------------|---------------------|
| (i) | Having two double bonds | diene | Alkadiene |
| (ii) | Having three double bonds | triene | Alkatriene |
| (iii) | Having n double bonds | polyene | Alkapolyene |
| (iv) | Having two triple bonds | diyne | Alkadiyne |
| (v) | Having three triple bonds | triyne | Alkatriyne |

(b)Secondary suffix : Suffix added after the primary suffix to indicate the particular functional group (groups) present in the carbon chain is known as secondary suffix. Secondary suffix of some important functional groups are given below.

| <i>Class of organic compounds</i> | <i>Functional group</i> | <i>Secondary suffix</i> |
|-----------------------------------|-------------------------|-------------------------|
| Alcohols | – OH | –ol |
| Aldehydes | – CHO | –al |
| Ketones | – CO – | –one |
| Carboxylic acids | – COOH | –oic acid |
| Acid chlorides | – COCl | –oyl chloride |
| Esters | – COOR | Alkyl... oate |
| Nitrile | – CN | nitrile |
| Amide | – CONH ₂ | –amide |

It may be noted that while adding the secondary suffix to the primary suffix, the terminal 'e' of the primary suffix (i.e., ane, ene, yne) is dropped if the secondary suffix begins with **a, e, i, o, u, & y** but is retained if the secondary suffix begins with a **consonant except y**.

| Structure | Root Word | Primary suffix | Secondary suffix | IUPAC name |
|---|------------------|-----------------------|-------------------------|-------------------|
| CH ₃ – CH ₂ – OH | Eth | ane | ol | Ethanol |
| CH ₃ – CH ₂ – CH ₂ – CHO | But | ane | al | Butanal |
| $\text{CH}_2 = \text{CH} - \overset{\text{O}}{\parallel}{\text{C}} - \text{CH}_3$ | But | ene | one | Butenone |
| CH ₃ – (CH ₂) ₄ – COOH | Hex | ane | oic | Hexanoic acid |



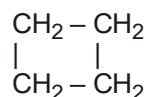
Prefix

Prefixes are used to indicate

(i) the cyclic nature of compound and

(ii) the nature of the substituents present on the parent chain. Thus, prefixes are of two types :

(a) Primary prefix : The primary prefix cyclo is added before the root word to indicate the cyclic nature of the compound. Thus for



Cyclo + but + ane
 Primary prefix Word-root Primary suffix
 ↓
 Cyclobutane

In open chain compound no prefix (primary) is added.

(b) Secondary prefix : In IUPAC system of nomenclature, certain functional groups are not considered as functional groups but instead are treated as substituents. These are called secondary prefix and are added immediately before the root word (or the primary prefix in case of alicyclic compounds) in **alphabetical** order to denote the side chains or substituent groups. The secondary prefixes for some groups which are always treated as substituent groups are given below :

| Substituent group | Secondary prefix |
|---|--------------------|
| -F | Fluoro |
| -Cl | Chloro |
| -Br | Bromo |
| -I | Iodo |
| -NO ₂ | Nitro |
| -NO | Nitroso |
| $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ \end{array}$ | 1-Methyl ethyl |
| -OR | Alkoxy |
| $\begin{array}{c} \oplus \\ -\text{N} \equiv \text{N} \end{array}$ | Diazo |
| -NH ₂ | Amino |
| -CH ₃ | Methyl |
| -C ₂ H ₅ | Ethyl |
| CH ₃ - CH ₂ - CH ₂ - | Propyl |
| $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \\ \\ \text{CH}_3 \end{array}$ | 1,1-Dimethyl Ethyl |



The order of IUPAC naming given below :

Secondary prefix + Primary prefix + word root + Primary suffix + Secondary suffix.

Secondary prefix – Primary prefix - Generic name

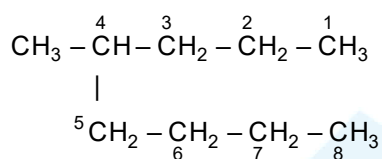
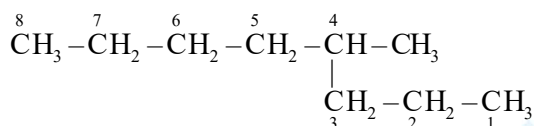
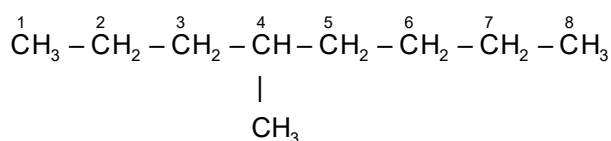
IUPAC Nomenclature of Branched-chain

Alkanes

Branched-chain alkanes are named according to the following rules :

1. Longest chain rule :

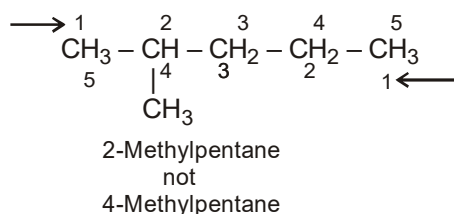
Locate the longest continuous chain of carbon atoms. This chain determines the parent name of the alkane. Notice that the longest continuous chain is chosen regardless of how the molecule is written.

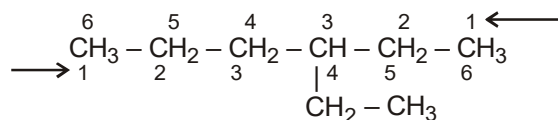


2. Lowest Locant Rule or Lowest Sum Rule :

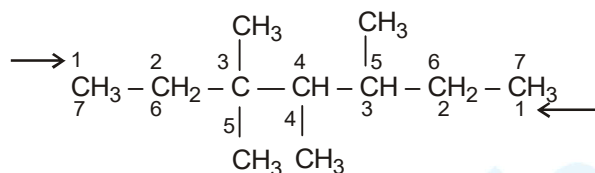
The carbon atoms of the longest continuous chain, i.e., parent chain are numbered by arabic numerals 1, 2, 3, 4 from one end of the chain to the other in such a manner that carbon atom carrying first substituent gets the lowest number. The number that locates the position of the substituent is known as **locant**.

However, if there are two or more substituents, the numbering of parent chain is done in such a way that the sum of locants is the lowest. This is called the **lowest sum rule**.





3-Ethylhexane
not
4-Ethylhexane



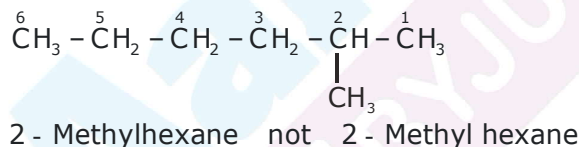
3,3,4,5-Tetramethylheptane

Position of the substituents should be 3, 3, 4 and 5 because
position should not be 3, 4, 5 and 5 because

$$3 + 4 + 5 + 5 = 17$$

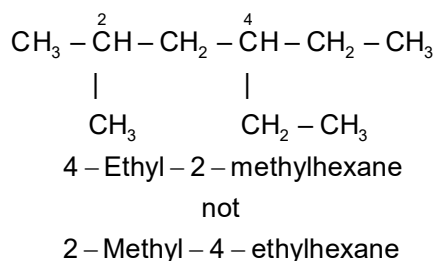
3. Name of the branched chain alkane :

The substituent name and the parent alkane are joined in one word and there is a hyphen between the number and the substituent name.



4. Alphabetical order of the side chains :

When two or more substituents are present, give each substituent a number corresponding to its position on the longest chain. The substituent groups be listed alphabetically.

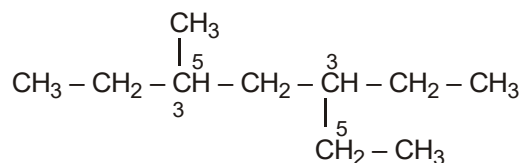


5. Numbering of different alkyl groups at equivalent positions :

If two different alkyl groups are present at equivalent positions the numbering of the parent chain is done in such a way that alkyl group which comes first in the alphabetical



order gets the lower number. For example :



3-Ethyl-5-methylheptane

not

5-Ethyl-3-methylheptane

Note :

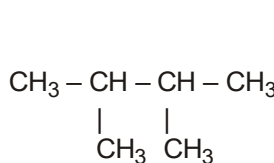
In some books it is mentioned that if different alkyl groups are present as substituents on the identical positions then numbering must be done so as to give the smallest alkyl group the minimum number but it is not the case.

6. Naming of some alkyl groups at different positions :

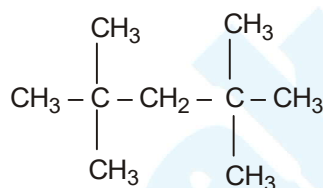
When two or more substituents are identical, indicate this by the use of prefixes di, tri, tetra and so on. Then make certain that each and every substituent has a number. Commas are used to separate numbers from each other.

Note :

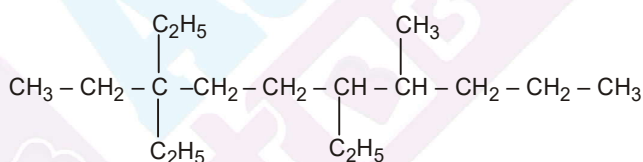
The prefixes di, tri, tetra, sec, tert are ignored in alphabetising substituent groups. The prefixes iso, neo and cyclo are not ignored, For example :



2,3-Dimethylbutane

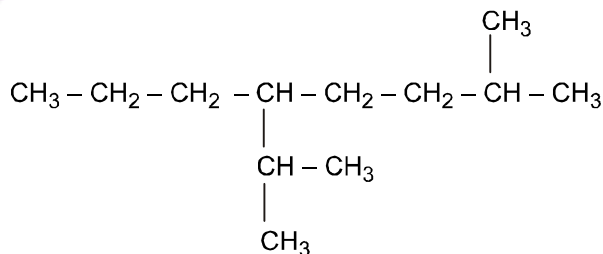


2,2,4,4-Tetramethylpentane



3,3,6-Triethyl-7-methyldecane

not 7-Methyl-3, 3,6-triethyldecane



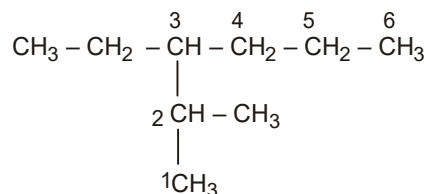
5-Isopropyl-2-methyloctane

not 2-Methyl-5-isopropyloctane

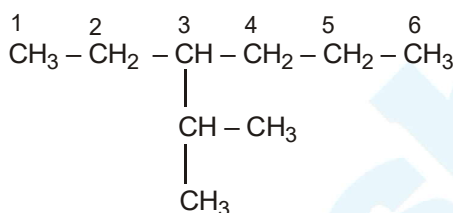


7. Rule for larger number of substituents :

If a compound has two or more chains of the same length, the parent hydrocarbon is the chain with the greater number of substituents.



3-Ethyl-2-methylhexane
(two substituents) \Rightarrow correct name



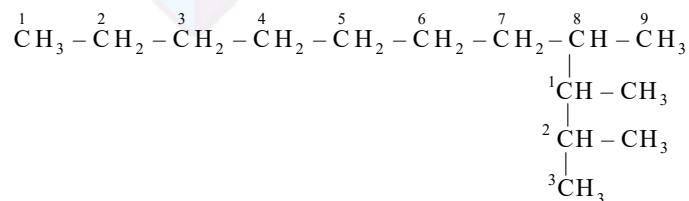
3-Isopropylhexane
(one substituents) \Rightarrow wrong name

The order of IUPAC naming given below :

8. Numbering the complex substituent :

Name such as isopropyl, *sec* butyl and *tert* butyl are acceptable substituent names in the IUPAC system of nomenclature but systematic substituent name are preferable.

Systematic substituent name are obtained by numbering the substituent starting at the carbon that is attached to the parent hydrocarbon. This means that the carbon that is attached to the parent hydrocarbon is always the number-1 carbon of the substituent. In a compound such as 5-(1,2-Dimethylpropyl) nonane, the complex substituent is in parentheses; the numbers inside the parentheses indicate the position on the substituent, whereas the number outside the parentheses indicates a position on the parent hydrocarbon.



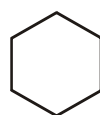
5-(1,2-Dimethyl propyl) nonane

Nomenclature of Cycloalkanes

1. Cycloalkanes are named by adding primary prefix before parent name (i.e., alkane). For example :

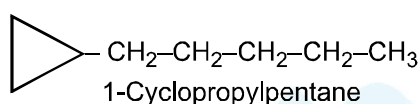
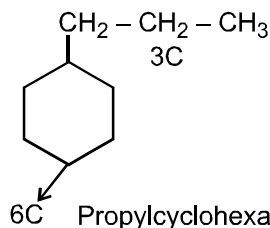


Cyclopropane

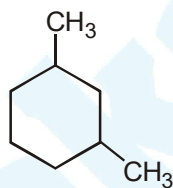


Cyclohexane

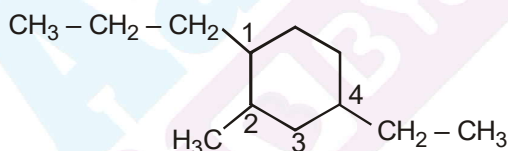
2. In the case of alkyl substituted cycloalkanes, the ring is the parent hydrocarbon unless the substituent has more carbon than the ring. In that case, the substituent is the parent hydrocarbon and the ring is named as a substituent.



3. If there is more than one substituent on the ring, the substituents are represented in alphabetical order. One of the substituents is given the number 1 position and the ring is numbered from that position in a direction (either clockwise or anticlockwise) that gives a second substituents the lowest possible number.



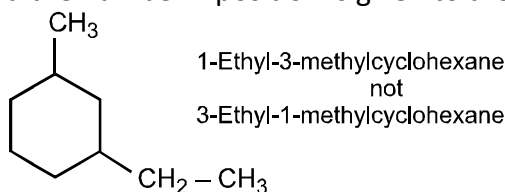
1,3-Dimethylcyclohexane



4-Ethyl-2-methyl-1-propylcyclohexane
not
1-Ethyl-3-methyl-4-propylcyclohexane

because $4 + 2 + 1 = 7$
 $1 + 3 + 4 = 8$

- (4) If the ring has only two substituents and they are different, the substituents are cited in alphabetical order and the number 1 position is given to the first cited substituent.





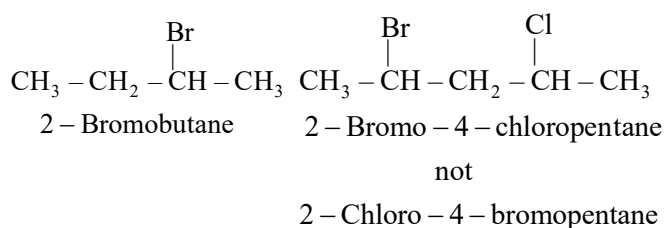
Nomenclature of Substituted alkanes (Having Two Functional groups)

or

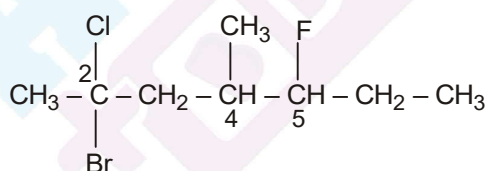
Nomenclature of Alkanes Having Secondary Prefix

Alkyl Halides :

(i) They are named as substituted alkanes, i.e., Haloalkanes. Some examples are :



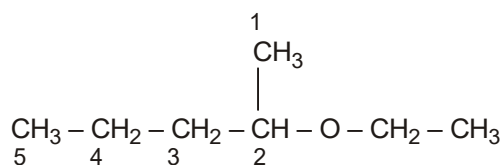
(ii) When the parent chain has both a halo and an alkyl group, number the chain from the end nearer to the first substituent, regardless of whether it is halo or alkyl group. If two substituents has equal number from the end of the chain, then number the chain from the end nearer to the substituent that has alphabetical precedence.



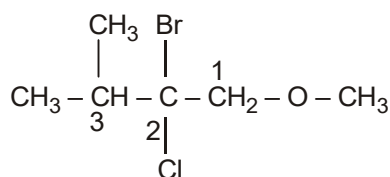
2-Bromo-2-chloro-5-fluoro-4-methylheptane

Nomenclature of Ethers :

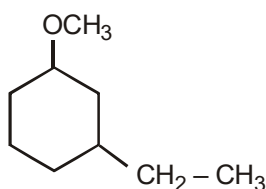
In the IUPAC system ethers are named as alkoxy alkanes. The larger alkyl group is chosen as the parent alkane.



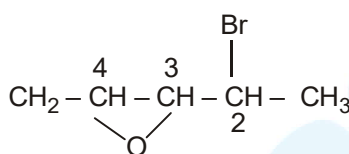
2-Ethoxypentane



2-Bromo-2-chloro-1-methoxy-3-methylbutane



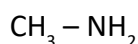
3-Ethyl-1-methoxycyclohexane



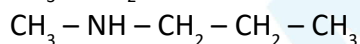
2-Bromo-3,4-epoxypentane

Nomenclature of Amines :

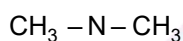
(a) Common Name : The common name of amine is obtained by citing the name of the alkyl groups bonded to the nitrogen atom in alphabetical order followed by **amine**. The entire name is written in one word. For examples.



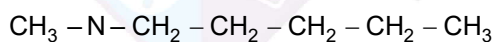
Methylamine



Methylpropylamine



Trimethylamine



Dimethylpentylamine



(b) IUPAC Name :

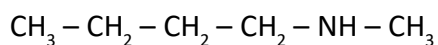
(i) The generic name of amines is alkanamine. The 'e' at the end of the alkane name for the longest continuous carbon chain in the amine is replaced by amine.

(ii) Position of nitrogen is denoted by least possible number in the longest possible carbon chain.

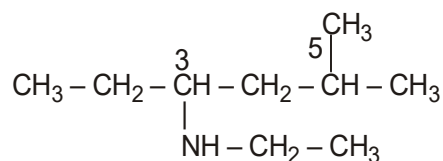
(iii) The name of any other alkyl groups bonded to nitrogen (in secondary and tertiary amines) is preceded by an N to indicate that group is bonded to a nitrogen rather than to a carbon.



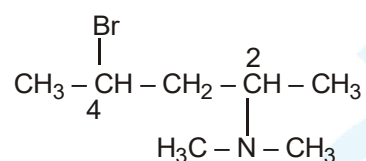
(iv) All substituents, whether they are attached to nitrogen or to the parent chain or listed in alphabetical order.



N-Methyl-1-butanamine or N-Methyl butan-1-amine



N-Ethyl-5-methyl-3-hexanamine



4-Bromo-N, N-dimethyl-2-pentanamine

Nomenclature of Alkenes

The following rules are used for naming alkene :

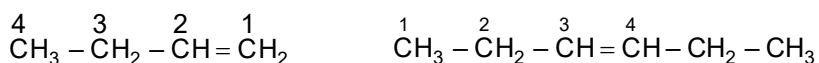
1. Determine the parent name by selecting the longest chain that contains the double bond.

General parent names are :

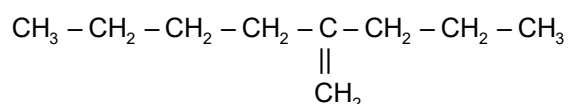
| | | |
|--------------|---|--------------------|
| Alkene | : | One double bond |
| Alkadiene | : | Two double bonds |
| Alkatriene | : | Three double bonds |
| Alkatetraene | : | Four double bonds |

2. The longest continuous chain containing the functional group **double bond** is numbered in a direction that gives the functional group the lowest possible number.

Designate the position of double bond by using the number of the first carbon atom of the double bond. For example, 1-butene signifies that double bond is between first and second carbon; 3-hexene signifies that double bond is present between carbon-3 and carbon-4



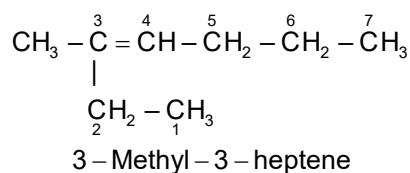
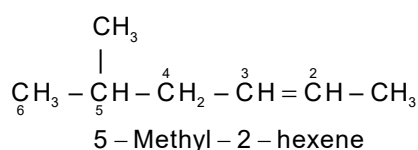
3. The parent chain must contain the functional group (multiple bond) regardless of whether it also denotes the longest continuous chain of carbon or not. For example :



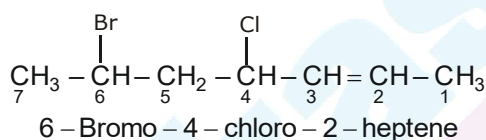
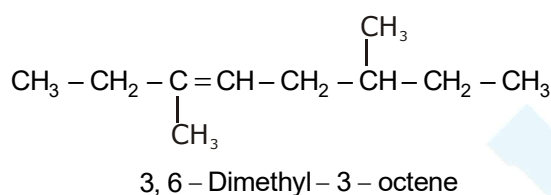
The longest continuous chain has eight carbons but the longest continuous chain containing double bond has six carbons, so the parent name of the compound is hexene.



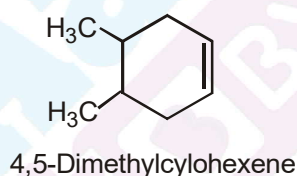
4. If the chain has the substituents, it is still numbered in the direction that gives the functional group/double bond the lowest possible number. For example :



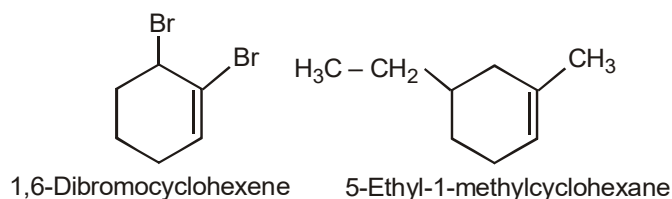
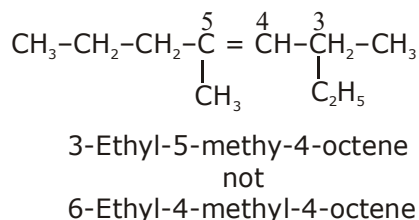
5. If a chain has more than one substituent the substituents are cited in alphabetical order as in case of alkenes.



6. In cycloalkenes, a number is not needed to denote the position of the functional group since the ring is always numbered so that the double bond is between carbon-1 and carbon-2.

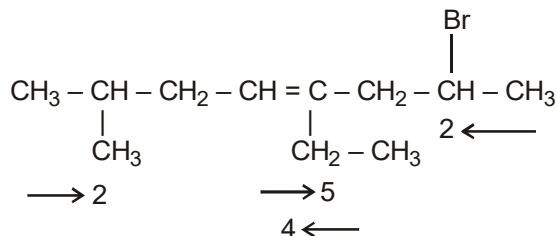


7. If the same number for the double bond is obtained in both directions, the correct name is the one that contains the lowest substituent number. (not sum of the lowest substituents)





8. If both directions lead to the same number for the functional group (double bond) and the same low numbers for one or more substituents, then these substituents are ignored and the direction is chosen that given the lowest number to one of the remaining substituents.



2-Bromo-4-ethyl-7-methyl-4-octene

not

7-Bromo-5-ethyl-2-methyl-4-octene

because $4 < 5$

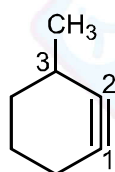
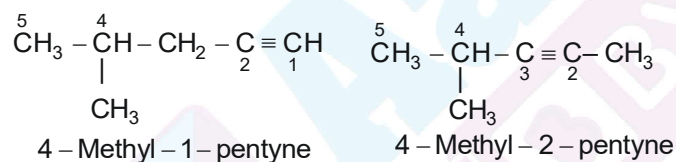
Nomenclature of Alkynes

(i) Alkynes are named in the same way as the alkanes.

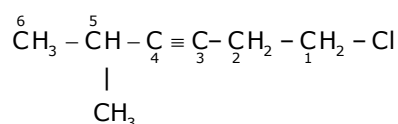
(ii) The general parent names are :

| | | |
|--------------|---|--------------------|
| Alkyne | : | One triple bond |
| Alkadiyne | : | Two triple bonds |
| Alkatriyne | : | Three triple bonds |
| Alkatetrayne | : | Four triple bonds |

The IUPAC names of some alkynes are given below :



3-Methyl cyclo hex-1-yne

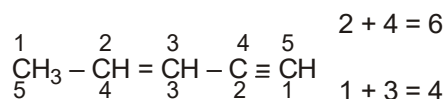


1 - Chloro - 5 - methyl - 3 - hexyne



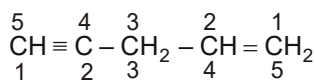
Nomenclature of Hydrocarbons Having Double As Well As triple Bonds :

- When double and triple bonds are present, the hydrocarbon is named as **alkenyne** \equiv **alk + en + yne**
- The numbering of the parent should always be done from that end which has lowest sum for the multiple bonds. For example.

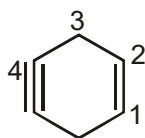


Pent-3-en-1-yne

- If, however, there is a choice in numbering, the double bond is always given preference over the triple bond.



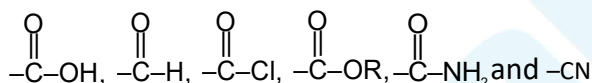
Pent-1-en-4-yne



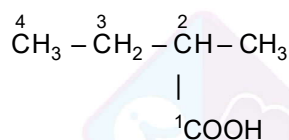
Cyclohex-1-en-4-yne

4. When a chain compound has terminal functional group

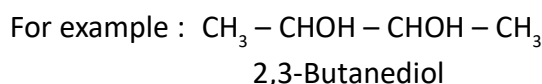
Chain terminating functional groups are those groups in which carbon of the functional group is monovalent. Examples are



When a chain terminating functional group is present, it is always given number - 1 and number one is usually omitted from the final name of the compound.



- (4) When compound contains two or more like groups, the numerical prefixes di, tri etc. are used and the terminal 'e' from the primary suffix is retained while writing the IUPAC name.



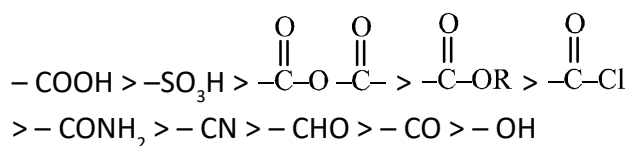
SECTION - C :

Nomenclature of Polyfunctional Compounds

- Principal functional group** : When an organic compound contains two or more different functional group, one of the functional group is selected as the principal functional group while all other groups (secondary functional group) are treated as substituents.



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



Prefix name of different functional groups are as follows :

| Group | Secondary prefix Name | Secondary Surfix |
|--|-----------------------|------------------|
| -COOH | Carboxy | Oic acid |
| -SO ₃ H | Sulpho | Sulphonic acid |
| -COOR | Alkoxy carbonyl | Alkyl oate |
| -COCl | Chloro formyl | oyl chloride |
| -CONH ₂ | Carbamoyl | amide |
| -CN | Cyano | nitrile |
| -NC | Isocyano | isonitrile |
| -CHO | Formyl or aldo | al |
| -CO- | Keto or oxo | one |
| -OH | Hydroxy | ol |
| -SH | Mercapto | thiol |
| -NH ₂ | Amino | Amine |
| -OR | Alkoxy | |
| $ \begin{array}{c} \quad \\ -\text{C}-\text{C} \\ \diagdown \quad / \\ \quad \quad \text{O} \end{array} $ | Epoxy | |
| -N=N- | Azo | |
| -NO ₂ | Nitro | |
| -NO | Nitroso | |
| -X | Halo | |

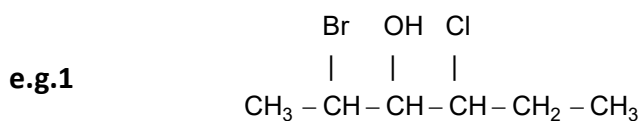
- 2. Selection of Principal chain :** The principal chain is selected in such a way that it includes the maximum number of functional groups (as substituents) including the principal group.
- 3. Numbering of Principal chain :** The principal chain present in polyfunctional compound is numbered in such a way that principal functional group gets the lowest number followed by multiple bonds and the substituents, i.e.,

Principal functional group > double bond > triple bond > substituents

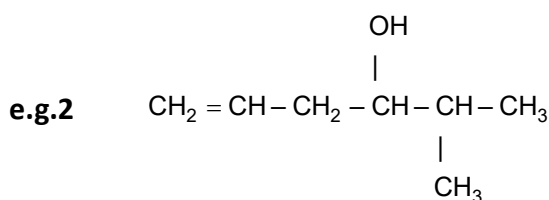
- 4. Alphabetical order :** Substituents, side chains and secondary functional groups are arranged in alphabetical order. To illustrate these rules, let us consider the examples of different class of organic compounds.



IUPAC Name of Alcohols



- (i) The longest chain has six carbons : hex.
- (ii) Compound is saturated Hexane.
- (iii) The alcohol function is designated as ol, hexanol.
- (iv) Number the chain to give the – OH the lowest possible number, 3-hexanol.
- (v) Name all the substituents with prefixes. The complete name is 2-Bromo-4-chloro-2-hexanol.



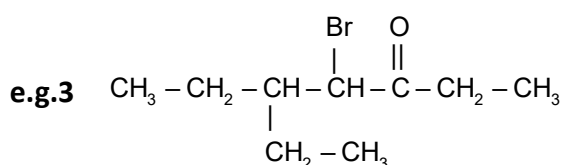
- (i) The longest chain has six carbons : hex.
- (ii) There is presence of double bond, hexene
- (iii) The principal functional group is – OH ; hexenol.
- (iv) Number the chain to give the – OH group the lowest possible number. Incorporate these numbers in the primary and secondary suffix, 5-Hexen-3-ol. The first number-5-refers the position of double bond and the second number - 3 locates the – OH group.
- (v) Name all other substituents with prefixes.
The complete name is 2-Methyl-5-hexen-3-ol. or 2-methyl-hex-5-en-3-ol

IUPAC Nomenclature of Aldehydes and ketones

(A) Ketones : General name of ketones are as follows :

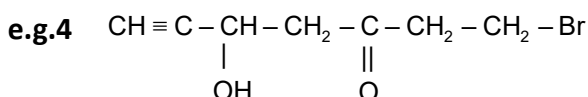
- Alkanone : one keto group
 Alkanedione : two keto groups
 Alkanetrione : three keto groups

Thus 'e' of the hydrocarbon is replaced by – **one** when compound has only one CO group.



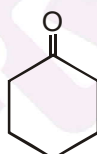
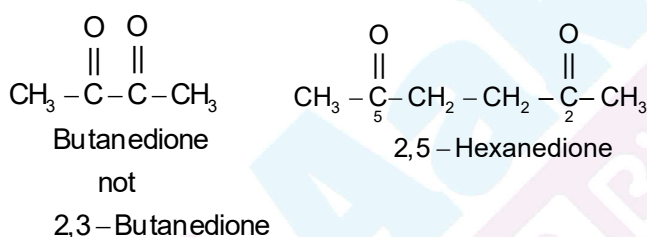


- (i) There are seven carbons having keto groups : heptanone.
- (ii) Number the chain to give the position of keto group the lowest possible number : 3-heptanone.
- (iii) Give name and position of other substituents with respect to keto groups. Thus, the complete name is :
4-Bromo-5-ethyl-3-heptanone



- (i) Seven carbon chain : hept
- (ii) One carbon-carbon triple bond : heptyne
- (iii) Principal functional group is keto : heptynone.
- (iv) Position of keto should be represented by lowest possible in number : 3 - heptynone
- (v) Position of other groups and substituents are determined with respect to keto group. The complete name is : 1 - Bromo - 5 - hydroxy - 6 - heptyn - 3 - one

Position of functional group can only be designated if positional isomersim is possible is that given structure.



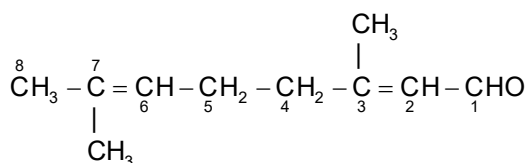
Cycloalkanone



Cyclohexanone

(B) Aldehydes :

1. The general name is : Alkanal, Alkenal or Alkynal i.e., 'e' of the hydrocarbon is replaced by **al**.
2. The position of the aldehydic group does not have to be designated since it is always at the end of the parent hydrocarbon and therefore, is always at the number 1 position.





(i) Compound is derivative of alkadiene having functional group – CHO. Thus, the general name is alkadienal.

(ii) Principal chain has 8C's hence alkadienal is octadienal.

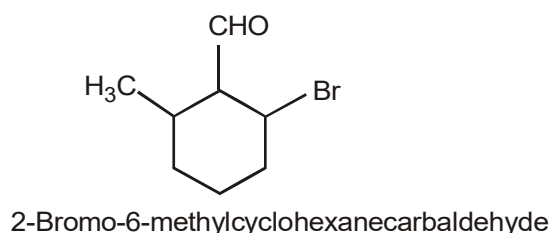
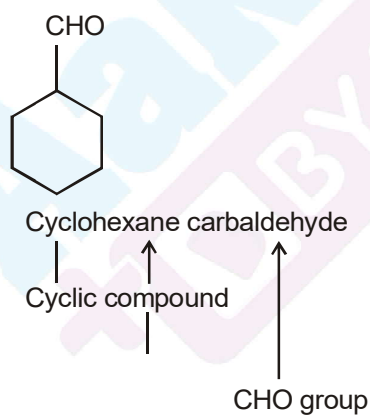
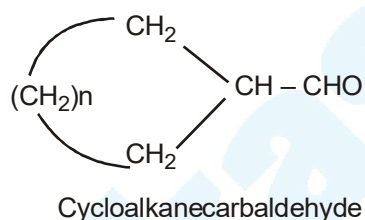
(iii) Position of – CHO is always 1 and position of other functional groups and substituents are determined with respect to the position of – CHO

The complete name is 3, 7 – Dimethyl-2,6-octadienal.

or 3,7-Dimethylocta-2,6-dienal

Note :

If the aldehyde group is attached to a ring, the aldehyde is named by adding carbaldehyde to the name of the cyclic compound

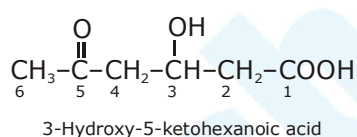
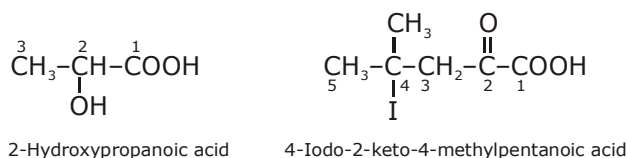




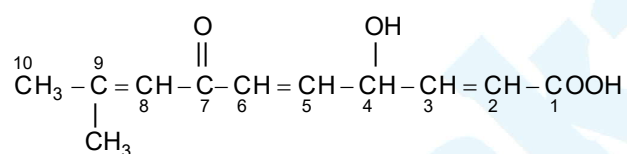
IUPAC Nomenclature of Carboxylic Acids

(i) Replace 'e' of the hydrocarbon by **oic acid**.

(ii) For naming a substituted carboxylic acid, the longest possible chain containing carboxylic group is numbered from 1 to n beginning with the carboxylic carbon.



Example :



(i) Ten carbon in the longest chain : dec

(ii) Three double bonds : decatriene

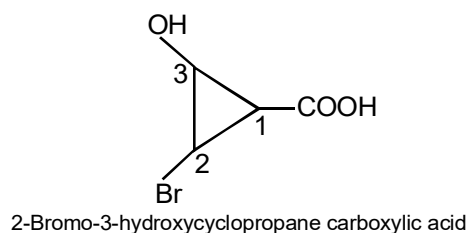
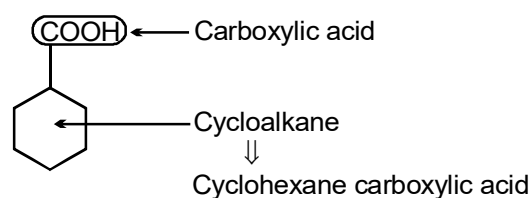
(iii) Functional group is carboxylic : decatrienoic acid

(iv) Three double bond are present at 2, 5 and 8 : 2,5,8-decatrienoic acid.

(v) The other groups are named with prefixes. The complete name is 4-Hydroxy-7-keto-9-methyl-deca-2,5,8-Trien-oic acid.

Note :

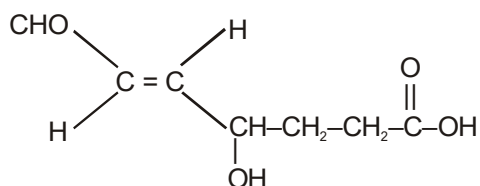
Carboxylic acid in which carboxylic group is attached to a cyclic compound can be named as Cycloalkanecarboxylic acid or Cycloalkenecarboxylic acid or Cycloalkynecarboxylic acid





Problem 7.

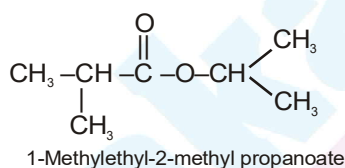
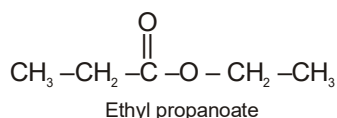
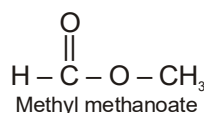
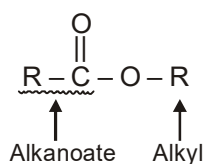
Provide a IUPAC name for the given compound :



Nomenclature of Esters

Esters are named in the following way :

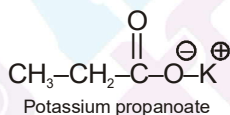
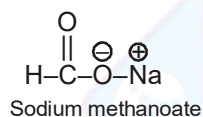
- (i) The first word of the name is the stem name of the alkyl group attached to oxygen.
- (ii) The second word of the name is the name of the parent acid with the suffix –ic acid replaced by –ate.
- (iii) This nomenclature applies for both common and IUPAC name of esters.



Note-1 :

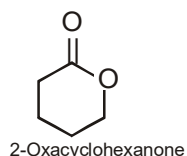
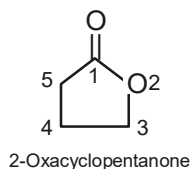
Salts of carboxylic acids are same as follows :

The cation is named first followed by the name of the acid again with ic acid is replaced by ate.



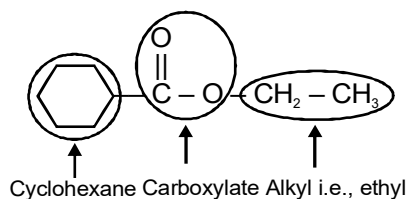
Note -2 :

Cyclic esters are called lactones. The IUPAC system names these compound as oxacycloalkanone.

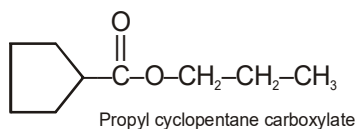


Note -3 :

Esters in which carbonyl group of ester is attached to a cyclic system can be named as : Alkyl cycloalkane carboxylate

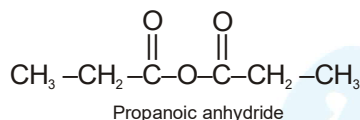
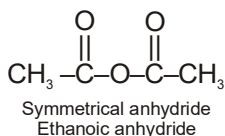


Thus the IUPAC name is ethyl cyclohexane carboxylate

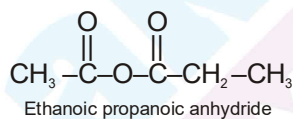


IUPAC Nomenclature of Anhydrides

- (i) Symmetrical anhydrides are named by using the acid name and replacing **acid** with **anhydride**.

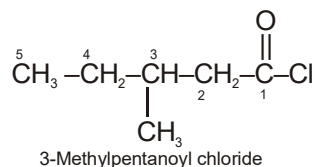
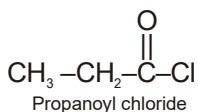
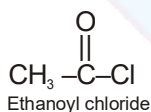


- (ii) Mixed anhydrides are named by starting the names of both acids in alphabetical order followed by **“anhydride”**.



Nomenclature of Acid Chloride :

Acid chloride is named by using the acid name and replacing **ic acid** with **yl chloride**, i.e.,
 Alkanoic acid → Alkanoyl chloride
 Alkenoic acid → Alkenoyl chloride
 Alkynoic acid → Alkynoyl chloride

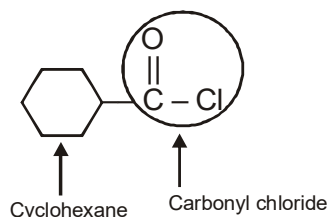


IUPAC name of acid chloride in which carbonyl group of acid is attached with cyclic ring :

Cycloalkane carbonyl chloride

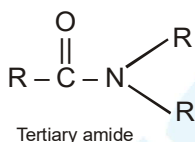
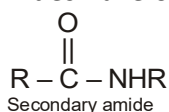
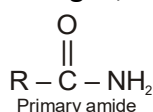


For example,

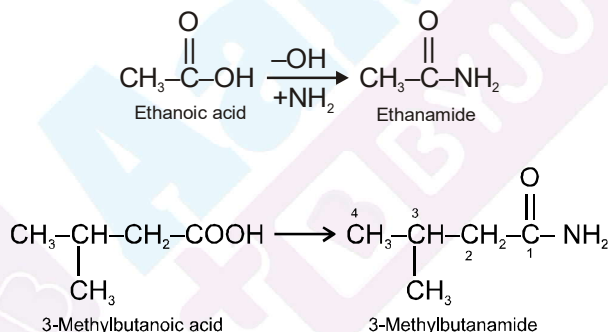


Nomenclature of Amides

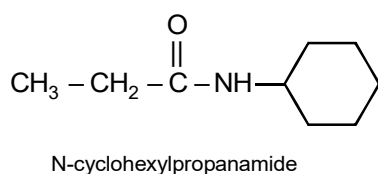
Amides are classified as primary, secondary or tertiary, depending on the number of alkyl group bonded to the nitrogen atom. Primary amides have no alkyl groups bonded to nitrogen, secondary amides have one and tertiary amide have two.

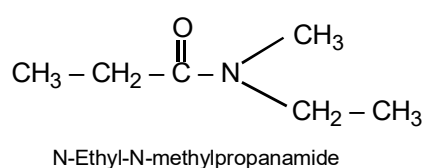
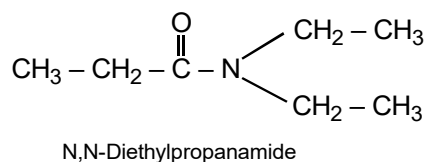
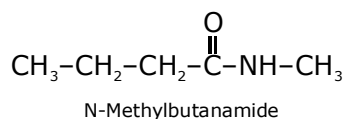


(A) Primary Amides : Primary amides are named by using the acid name, replacing **oic acid** with **amide**. Thus the general name is Alkanamide, Alkenamide and Alkynamide.



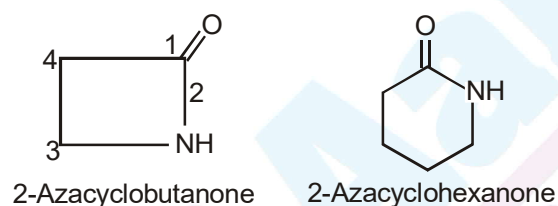
(B) Secondary and Tertiary amides : In these two amide, the name of the substituents are indicated first, followed by the name of the amide. The name of each substituent is preceded by a capital N to indicate that the substituent is bonded to a nitrogen. Substituent present on nitrogen are arranged alphabetically.





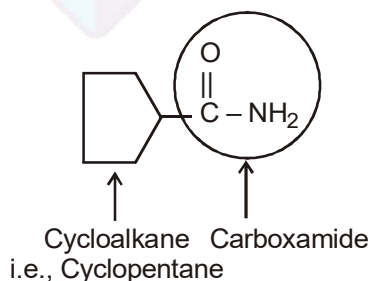
Note - 1 :

Cyclic amides are called **lactams**. The IUPAC system name these compounds as Azacycloalkanone



Note - 2 :

Acid amide in which carbonyl group is attached to the cyclic system can be named as Cycloalkane carboxamide

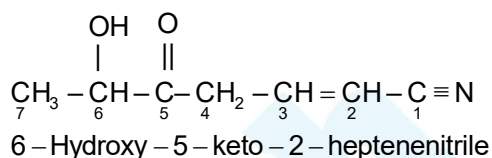
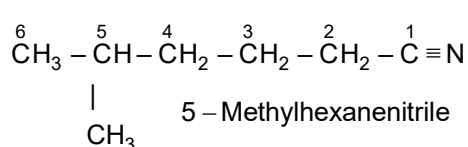
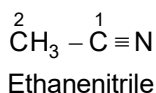


Thus the name is Cyclopentane carboxamide.

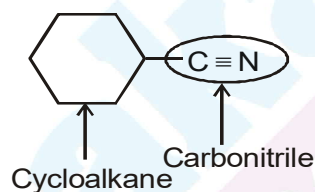


Nomenclature of Cyanides

Nitriles are compounds that contain a $-C \equiv N$ functional group. They are considered to be the carboxylic acid derivatives because they react with water to form carboxylic acids like acid chlorides, esters and amides. In IUPAC nomenclature nitriles are named by adding nitrile to the hydrocarbon name, i.e., Alkanenitrile, Alkenenitrile, Alkynenitrile.



IUPAC Nomenclature of cyanide in which carbon of cyano group is attached with cyclic ring : The name of such compounds are cycloalkane carbonitrile
For example,

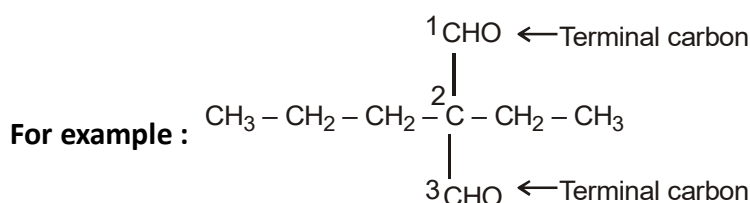


The name is thus Cyclohexane carbonitrile

Nomenclature of Compounds Having two or More Like Chain Terminating Principal Functional Groups, (Such as $-\text{CHO}$, $-\text{COOH}$, $-\text{COCl}$, $-\text{COOR}$, $-\text{CONH}_2$, and $-\text{CN}$)

IUPAC Nomenclature

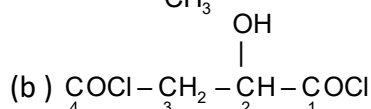
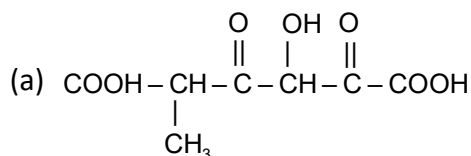
- If compound has only two such functional groups then carbon of one group will be one terminal carbon and carbon of the other functional group be other terminal carbon of the principal chain.



- Three carbon chain : Prop.
- Two same principal functional group : Alkanedial, i.e., Propanedial.

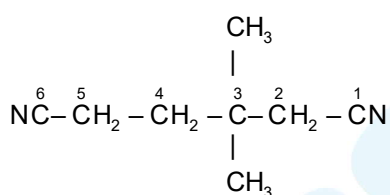


(iii) Two substituents at carbon-2 of the principal chain i.e., ethyl and propyl.
The name of the compound is : 2-Ethyl-2-propylpropanedial



(a) 3-Hydroxy-2,4-diketo-5-methylhexanedioic acid

(b) 2-Hydroxybutanedioyl chloride



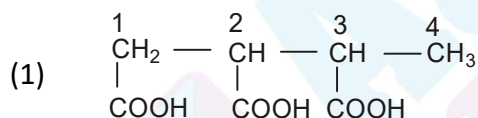
3,3-Dimethylhexanedinitrile

2. If compound has more than two like groups then two functional groups are treated as principal functional groups.

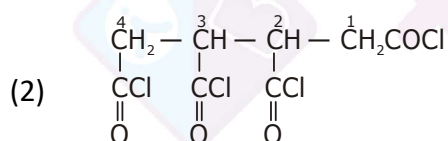
(i) Carbon of the functional group/groups is not included in the longest possible chains.

(ii) All functional groups having highest priority should be treated as principal functional groups.

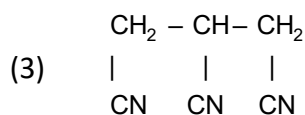
(iii) Compound is always treated as derivative of hydrocarbon.



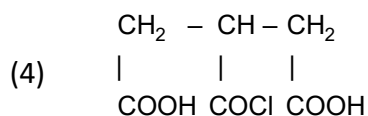
the name is 1,2,3-Butanetricarboxylic acid or Butane-1,2,3-tricarboxylic acid



Butane -1, 2, 3, 4- tetracarbonyl chloride



1,2,3 - Propanetricarbonitrile

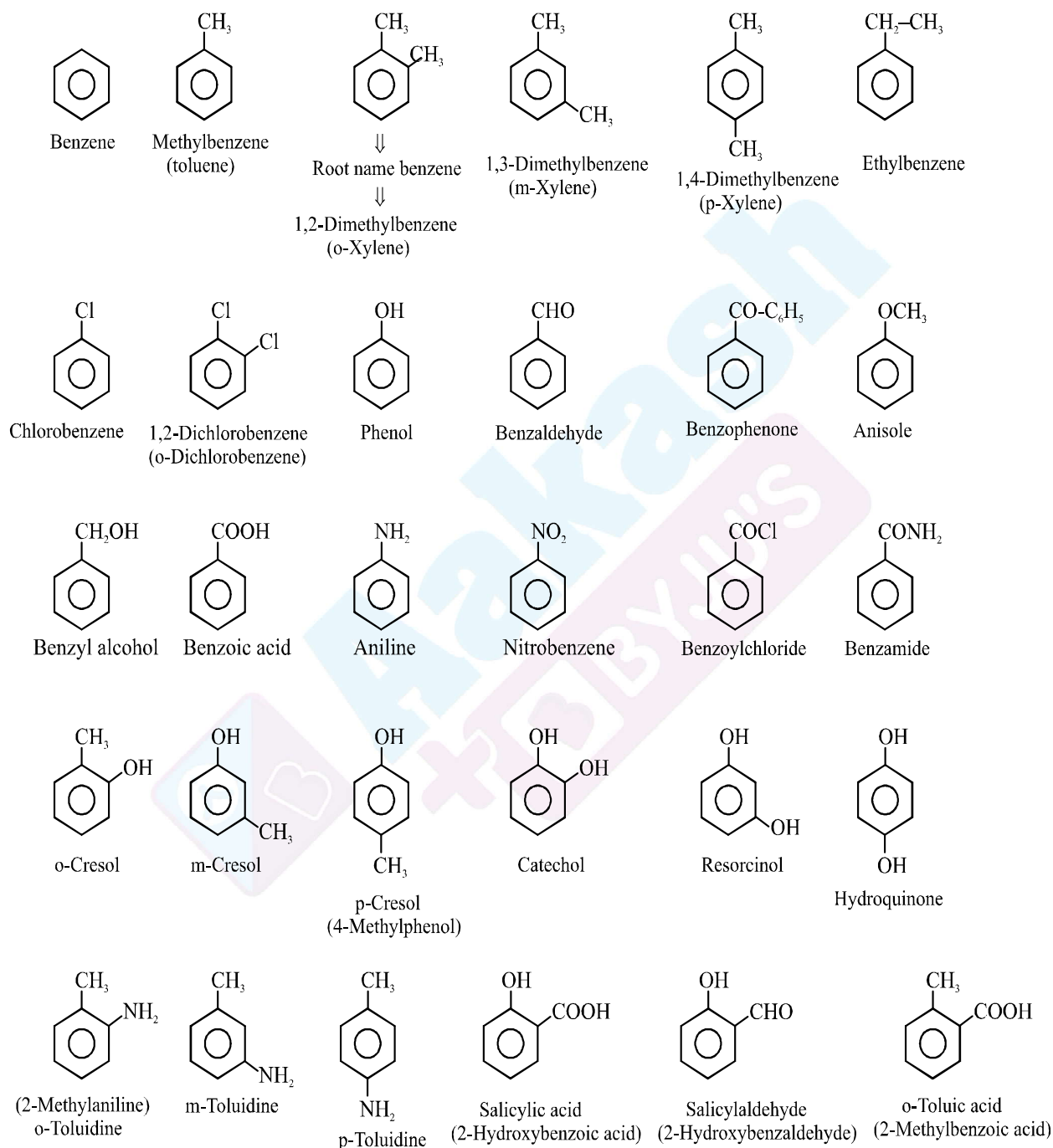


3-Chloroformyl pentane-1,5-dioic acid



Nomenclature of Aromatic Compounds

The common names of most of the aromatic compounds are accepted as their IUPAC names. The derivatives of these compounds have their roots derived from the names of these compounds.





GENERAL ORGANIC CHEMISTRY

Purification of Organic Compounds

The methods to be employed depend on the physical state of the compound.

Crystallisation : This method is based on the differences in the solubility of the organic compound and its impurities in a solvent.

- (a) **Preparation of the solution** : Organic substance is powdered and is dissolved in a suitable solvent by heating. The amount of solvent should be just sufficient to dissolve the whole of the solid on heating.

Choice of Solvent. The choice of solvent is very important in the crystallisation process. The main conditions of the solvent are:

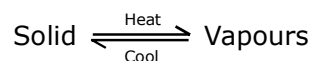
- (i) The organic substance should dissolve in the solvent upon heating and it should get separated on cooling.
- (ii) The solvent should not dissolve the impurities.
- (iii) The solvent should not react chemically with the substance.

For example, suppose we want to purify sugar containing an impurity of common salt. This can be done by treating the mixture with ethanol around 350 K. The sugar will dissolve whereas common salt remains insoluble.

- (b) **Filtration of the solution.** The hot saturated solution is filtered preferably through a fluted filter paper placed in a glass funnel. The use of the fluted filter paper makes the filtration rapid. The jacket of the hot water funnel is heated from outside and this keeps the solution hot in the glass funnel. This will prevent the formation of crystals during filtration.
- (c) **Crystallisation.** The hot filtration is allowed to cool slowly and undisturbed in a beaker or in a crystallising dish. After some time the crystals of the pure compound are formed.
- (d) **Separation of the crystals.** The crystals formed are separated from the mother liquor by filtration. The filtration is normally done by use of Buckner funnel and a suction pump. This enables the filtration under reduced pressure and is therefore, quite fast.
- (e) **Drying of crystals.** The crystals are dried by pressing between the folds of filter paper and then placed in a stream of air oven for some time. The crystals are finally dried over sulphuric acid or calcium chloride in a desiccator.



Sublimation : Certain organic solids directly change from solid to vapour state on heating. This process is called sublimation. The vapours on cooling change back to the solid form



The sublimation process is used for the separation of those solids which sublime on heating from non-volatile solids. The process is generally used for the purification of camphor, naphthalene, anthracene, benzoic acid, etc. containing non-volatile impurities.

Distillation : This method is used for the purification of liquids which boil without decomposition and contain non-volatile impurities. The simple distillation involves its boiling point so that it is converted into vapours. On cooling the vapours, pure liquid is obtained. The distillate contains pure liquid while the impurities are left behind in the distillation flask **e.g.** Ether from ethyl alcohol.

Fractional Distillation : This process is used to separate a mixture of two or more miscible liquids which have boiling points close to each other. The fractionating column is a long tube provided with obstructions to the passage of the vapours moving upwards and liquid moving downwards. This method may be used to separate a mixture of acetone (b.p. 330 K) and methyl alcohol (b.p. 338 K).

Distillation under Reduced pressure (Vaccum Distillation) : Certain liquids have a tendency to decompose at a temperature below their boiling points. Such liquids cannot be purified by ordinary distillation. Therefore vacuum distillation is used for liquids which decompose at a temperature below their normal boiling points.

Ex. glycerol boils with decomposition at 563 K.

Steam distillation : The process of steam distillation is used for the separation and purification of liquid which is appreciably volatile in steam, from non-volatile components of a mixture. Thus, the process of steam distillations is used to purify the substances which

- (i) are volatile in steam but are not miscible with water
- (ii) possess sufficiently high vapour pressure at the boiling point temperature of water (100°C)
- (iii) contain non-volatile impurities.



The process of steam distillation can be applied for the separation of a mixture of o-nitrophenol and p-nitrophenol. In this process, water vapours carry along with them vapours of o-nitrophenol which is more volatile and they get condensed in the receiver ; p-nitrophenol with higher b.p. remains in the distillation flask. The method can also be used for the purification of impure sample of aniline.

The proportion of water and liquid in the mixture that distills over is given by the relation

$$\frac{\omega_1}{\omega_2} = \frac{p_1 \times 18}{p_2 \times M}$$

where ω_1 and ω_2 stand for the masses of water and the organic liquid that distills over; p_1 and p_2 represent the vapour pressures of water and the liquid at the distillation temperature and M is molecular mass of the liquid (molecular mass of water being 18).

Ex. o-, m-, p-chlorotoluenes, o-, p-nitrobenzene

Chromatography : This method is based on the differences in the rates at which the components of a mixture are adsorbed on a suitable adsorbent. There are many forms of chromatography such as column chromatography, paper chromatography, thin layer chromatography (TLC), gas chromatography, etc. The simplest method is column chromatography.

Applications of chromatographic method. This method has been used

- (i) To separate ortho and para nitro-anilines.
- (ii) To separate blue and red dyes.
- (iii) To separate and purify plant pigments and other natural products.

Types of chromatography :

Based on the principle involved chromatography is classified into different categories. Two of these are.

- (a) Adsorption chromatography, and (b) Partition chromatography

(a) Adsorption chromatography :

Adsorption chromatography is based on the fact that different compounds are adsorbed on an adsorbent to different degrees. Commonly used adsorbents are silica gel and alumina, When a mobile phase is allowed to move over a stationary phase (adsorbent), the compo-

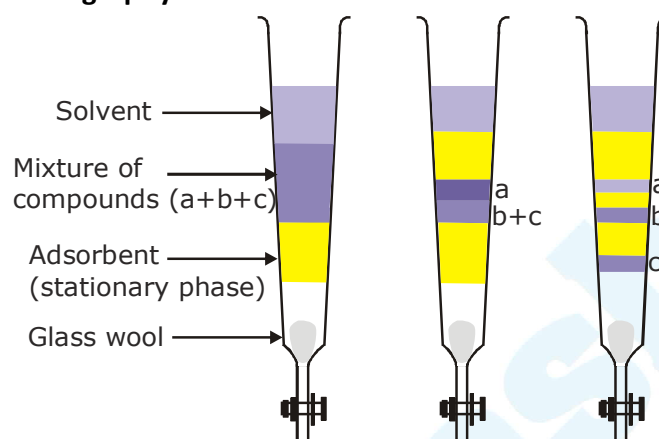


nents of the mixture move by varying distances over the stationary phase. Following are two main types of chromatographic techniques based on the principle of differential adsorption.

(i) Column chromatography, and

(ii) Thin layer chromatography.

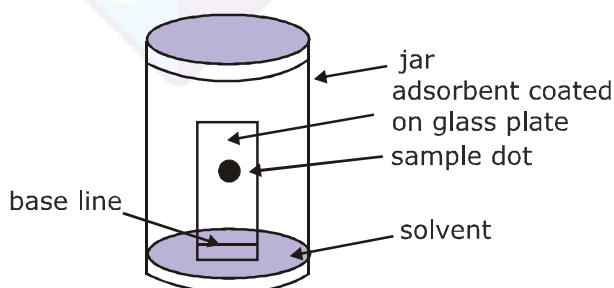
Column chromatography:



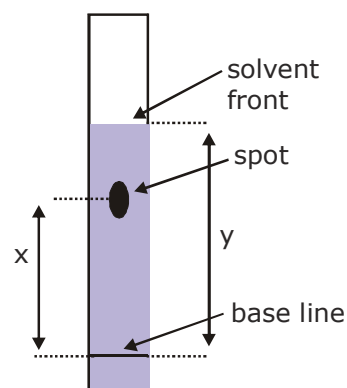
Column chromatography. Different stages of separation of components of a mixture

Column chromatography involves separation of a mixture over a column of adsorbent (stationary phase) packed in a glass tube. The column is fitted with a stopcock at its lower end. The mixture adsorbed on adsorbent is placed on the top of the adsorbent column packed in a glass tube. An appropriate eluant which is a liquid or a mixture of liquids is allowed to flow down the column slowly. Depending upon the degree to which the compounds are adsorbed, complete separation takes place. The most readily adsorbed substances are retained near the top and others come down to various distances in the column

Thin layer chromatography :



Thin layer chromatography Chromatogram being developed



Developed chromatogram



Thin layer chromatography (TLC) is another type of adsorption chromatography, which involves separation of substances of a mixture over a thin layer of an adsorbent coated on glass plate. A thin layer (about 0.2 mm thick) of an adsorbent (silica gel or alumina) is spread over a glass plate of suitable size. The plate is known as thin layer chromatography plate or chromatoplate. The solution of the mixture to be separated is applied as a small spot about 2 cm above one end of TLC plate. The glass plate is then placed in a closed jar containing the eluant. As the eluant rises up the plate, the components of the mixture move up along with the eluant to different distances depending on their degree of adsorption and separation takes place. The relative adsorption of each component of the mixture is expressed in terms of its **retardation factor** i.e. R_f value.

$$R_f = \frac{\text{Distance moved by the substance from base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$$

The spots of coloured compounds are visible on TLC plate due to their original colour. The spots of colourless compounds which are invisible to the eye but fluoresce, can be detected by putting the plate under ultraviolet light. Another detection technique is to place the plate in a covered jar containing a few crystals of iodine spots of compounds, which adsorb iodine will show up as brown spots. Sometimes an appropriate reagent may also be sprayed on the plate. For example, Amino acids may be detected by spraying the plate with ninhydrin solution

(b) Partition Chromatography :



Paper chromatography (chromatography paper in two different shapes)

Partition chromatography is based on continuous differential partitioning of components of mixture between stationary and mobile phases. Paper chromatography is a type of partition chromatography. In paper chromatography, a special quality paper known as chromatography paper is used. Chromatography paper contains water trapped in it, which acts as the stationary phase.



A strip of chromatography paper spotted at the base with the solution of the mixture is suspended in a suitable solvent or a mixture of solvents. This solvent rises up the paper by capillary action and flows over the spot. The paper selectively retains different components according to their differing partition in the two phases. The paper strip so developed is known as a chromatogram. The spots of the separated coloured compounds are visible at different heights from the position of initial spot on the chromatogram. The spots of the separated colourless compounds may be observed either under ultraviolet light or by the use of an appropriate spray reagent as discussed under thin layer chromatography.





HYDROCARBON

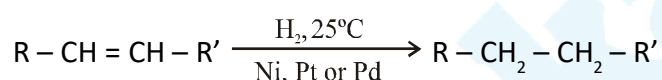
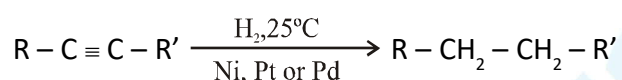
ALKANE

Introduction :

Alkanes are the saturated non-polar hydrocarbon having general formula $C_n H_{2n+2}$.
Hydrocarbon – Those organic compounds which contain only carbon and hydrogen atoms are known as hydrocarbons.

Preparation of alkane :

(I) By catalytic reduction of alkenes and alkynes



Hydrogenation → Addition of H_2 to unsaturated bond.

Hydrogenation is of two kind

(a) Heterogeneous and (b) Homogeneous

(a) Heterogeneous → It is two phase hydrogenation, the catalyst is finely divided metal like Ni, Pt or Pd and a solution of alkene.

(b) Homogeneous → It is one phase hydrogenation where both catalyst and alkenes are in solution phase. In this, hydrogenation catalyst are organic complex of transition metal like Rh or Ir.

Hydrogenation is exothermic, qualitative and during the hydrogenation, total heat evolved to hydrogenate one mole of unsaturated compound is called heat of hydrogenation. Heat of hydrogenation is the measurement of stability of isomeric alkenes.

$$\text{Stability of alkene} \propto \frac{1}{\text{Heat of hydrogenation}}$$

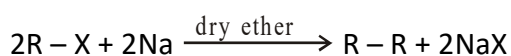
(II) From alkyl halide

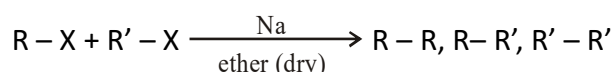
(A) From organometallic compound →

compound having $C - M$ bond.

(M → metal)

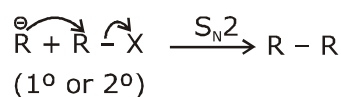
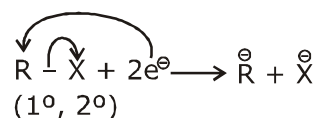
(i) By Wurtz reaction



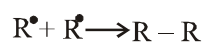
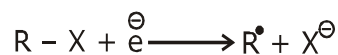
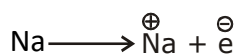


Mechanism \longrightarrow Two mechanisms are suggested

(a) Ionic mechanism



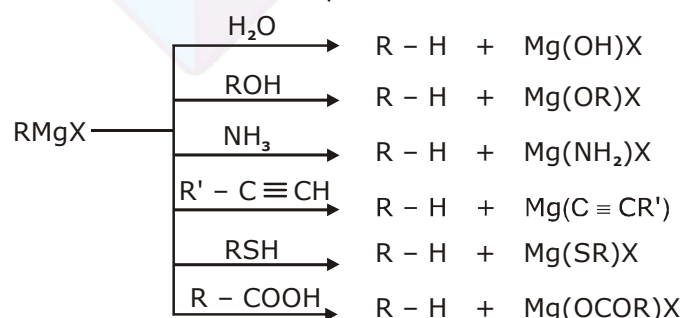
(b) Free radical mechanism



Note :

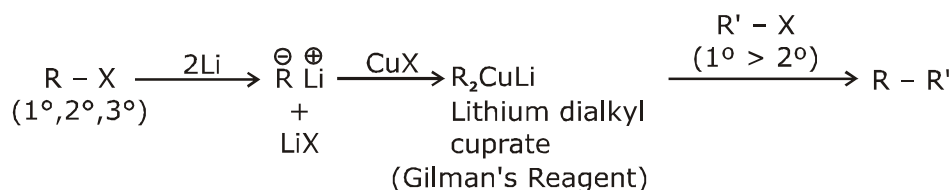
The alkyl halide should be 1° or 2°, with 3° R-X. S_N2 and free radical coupling is not possible due to steric hinderance, so in that case elimination or disproportionation is possible.

In the ionic mechanism, alkyl sodium ($\overset{\ominus}{R}Na^{\oplus}$) gives $\overset{\ominus}{R}$ which is strong base as well as nucleophile so it gives S_N2 reaction with R-X. So, ether should be dry otherwise, if moisture is present then $\overset{\ominus}{R}$ forms R-H instead of R-R with H₂O.



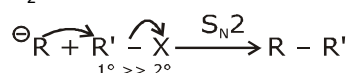


(iii) By Corey house alkane synthesis:



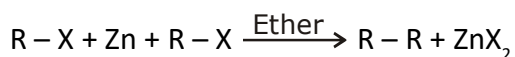
Mechanism :

R_2CuLi is the source of $\ominus R$

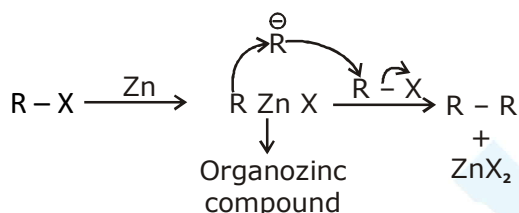


R_2CuLi do not react with $-NO_2$, $-CN$, $>C=O$ etc.

(iv) By Frankland reagent:

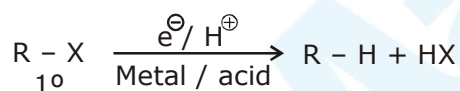


Mechanism



(B) By reduction of alkyl halides

(i) With metal-acid :

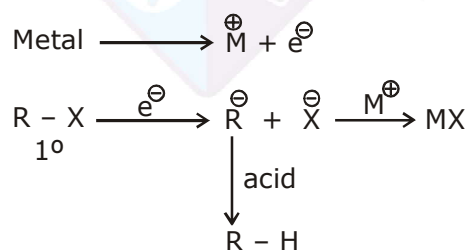


Reducing agent

Zn / acid, Zn - Cu / H_2O or Zn - Cu + acid

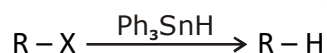
Zn - Cu / C_2H_5OH , Na - Hg / acid, Al - Hg / H_2O etc.

Mechanism :



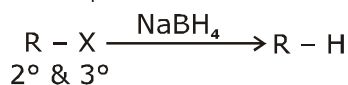
(ii) With metal hydrides :

(a) Triphenyltin Hydride (Ph_3SnH) : It reduces 1° , 2° & 3° $R-X$



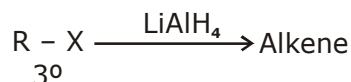


(b) NaBH_4



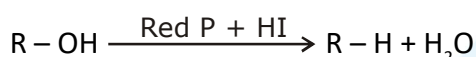
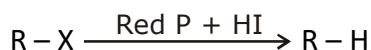
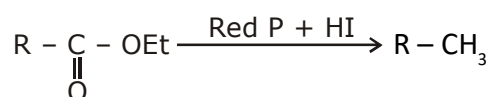
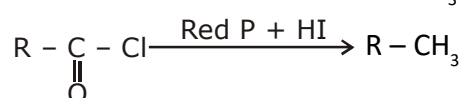
(c) $\text{R} - \text{X} \xrightarrow{\text{LiAlH}_4} \text{R} - \text{H}$

$1^\circ \text{ \& } 2^\circ$



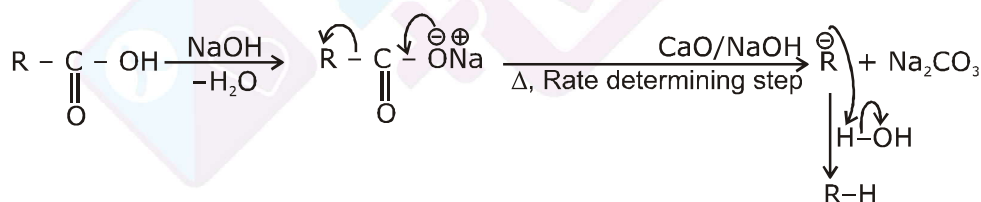
(III) By red P & HI

Red P & HI is strong reducing agent.

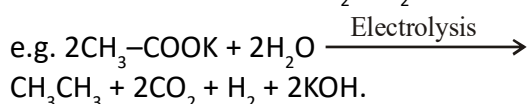
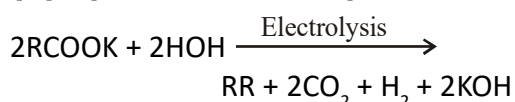


(IV) By soda lime

Fatty acids are good source of hydrocarbons. Heating of sodium salt of carboxylic acid ($\text{R} - \text{COONa}$) with soda lime ($\text{NaOH} - \text{CaO}$) gives hydrocarbon, which is known as decarboxylation (e.g. replacement of $-\text{COOH}$ group by $-\text{H}$) Decarboxylation also takes place on heating only, when compound is geminal dicarboxylic acid or there has keto group or double bond on β carbon.



(V) By Kolbe's electrolysis

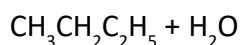
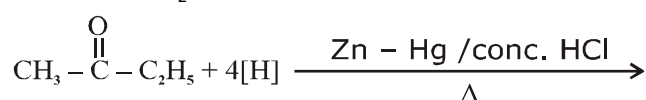
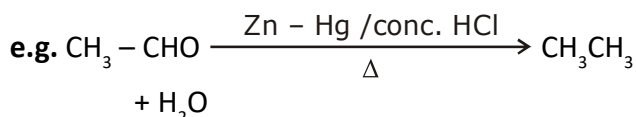
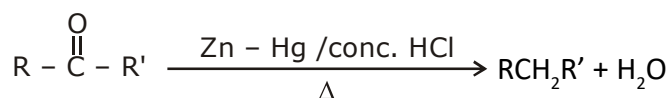
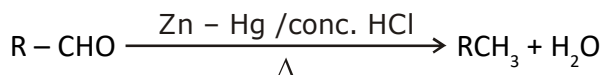




If n is the number of carbon atoms in the salt of carboxylic acid, the alkane formed has $2(n - 1)$ carbon atoms.

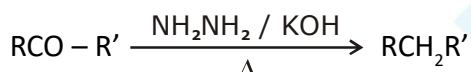
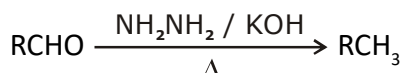
(VI) Reduction of aldehydes, ketones

(a) By Clemmensen's reduction with Zn - Hg / conc. HCl



Clemmensen reduction is not used for compound which have acid sensitive groups.

(b) By Wolff-Kishner reduction with NH_2NH_2 / KOH



Wolff-Kishner reduction is not used for compounds which have base sensitive groups.

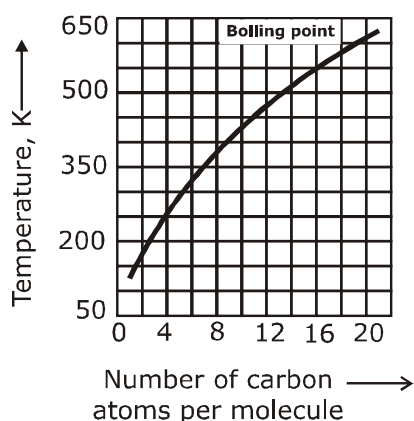
Physical Properties of Alkanes :

(I) Physical State :

The first four members (C_1 to C_4) are gases : the next thirteen members, (C_5 to C_{17}) are liquids while the higher members are waxy solids.

(II) Boiling Points :

The boiling points of n-alkanes increases regularly with the increase in the number of carbon atoms.

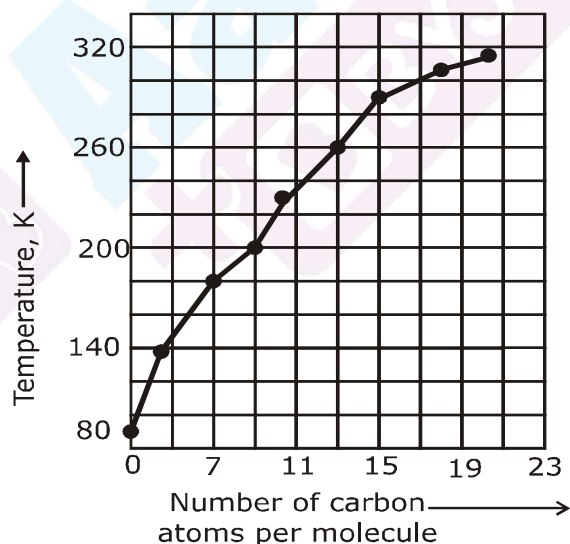


Among the isomeric alkanes, the branched chain isomers have relatively low boiling points as compared to their corresponding straight chain isomers. Greater the branching of the chain, lower is the boiling point. This is due to the fact that branching of the chain makes the molecules more compact and brings it close to a sphere, so the magnitude of van der waals forces decreases.

(III) Melting Points :

It is evident that the increase in melting point is relatively more in moving from an alkane having odd number of carbon atoms to the higher alkane with even no. of 'C' while it is relatively less in moving from an alkane with even number of carbon atoms to the higher alkane.

Explanation : The alkanes with even no. of 'C' atoms are more closely packed.



(IV) Solubility :

In keeping with the popular rule "like dissolves like". hydrocarbons are insoluble in polar solvent like water because they are predominantly non-polar in nature.

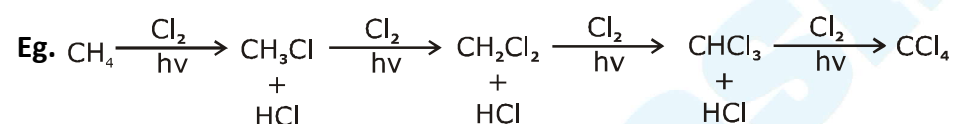
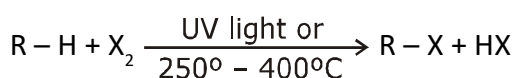
**(V) Density :**

The densities of alkanes increase with increasing molecular weight but become constant at about 0.8 g cm^{-3} . This means that all alkanes are lighter than water so they float over water.

Chemical Reactions of Alkanes :

Characteristic reaction of alkanes are free radical substitution reaction, these reaction are generally chain reactions which are completed in three steps mainly.

- (i) Chain initiation,
- (ii) Chain propagation,
- (iii) Chain termination,

Examples of free radical substitution reaction :

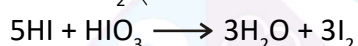
When equimolar amount of methane and Cl_2 are taken, a mixture of four possible products are formed, but if we take excess of CH_4 then yield of CH_3Cl will be the major product.

Reactivity of X_2 : $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

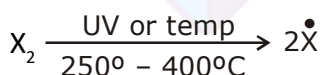
Reactivity of H : $3^\circ \text{H} > 2^\circ \text{H} > 1^\circ \text{H}$

With F_2 alkanes react so vigorously that, even in the dark and at room temperature, reactants are diluted with an inert gas.

Iodination is a reversible reaction, so HI formed as a by-product is a strong reducing agent and reduces alkyl iodide back to alkane. Hence iodination can be carried out only in presence of strong oxidizing agent like HIO_3 , HNO_3 or HgO

**Mechanism of halogenation of CH_4 :**

- (i) Chain initiation \rightarrow It is an endothermic step.



- (ii) Chain propagation \rightarrow



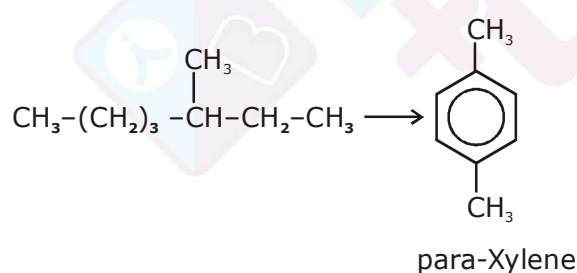
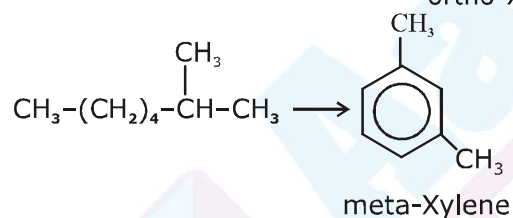
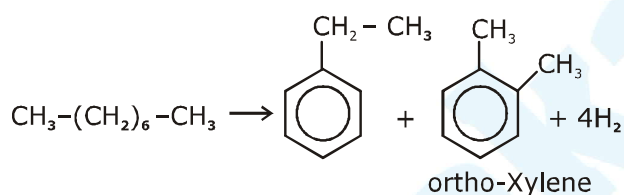
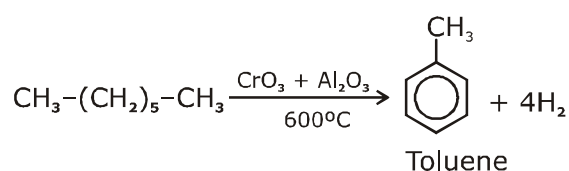


(iii) Chain termination → It is always exothermic

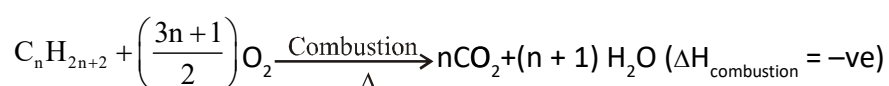


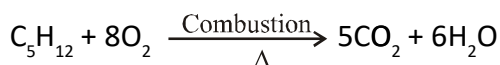
Each photon of light cleaves one chlorine molecule to form two chlorine radicals, each chlorine atom starts a chain and on an average each chain contains 5000 repetitions of the chain propagating cycle so about 10,000 molecules of CH_3Cl are formed by one photon of light.

Aromatization :



Combustion : (i.e. complete oxidation)



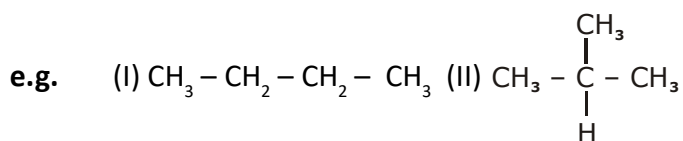


Heat of combustion : Amount of heat i.e. liberated when 1 mole of hydrocarbon is completely burnt into CO₂ & H₂O.

Heat of combustion as a measure of stability of alkane :

Combustion is used as a measurement of stability.

More branched alkanes are more stable and have lower heat of combustion.



Stability : II > I

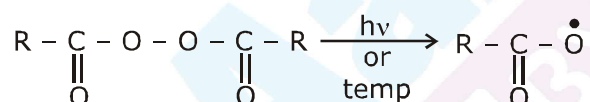
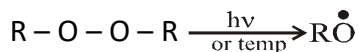
$\Delta H_{\text{comb.}}$: I > II

More branched alkane has more no. of primary C - H bonds. (therefore it has more bond energy).

Homologues : Higher homologues have higher heat of combustion.

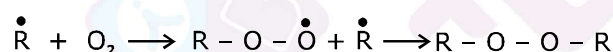
Isomers : Branched isomers have lower heat of combustion.

(i) Initiators → They initiate the chain reaction, initiators are R₂O₂, peresters, etc.



(ii) Inhibitors → A substance that slow down or stop the reaction are known as inhibitors.

For example - O₂ is a good inhibitor.

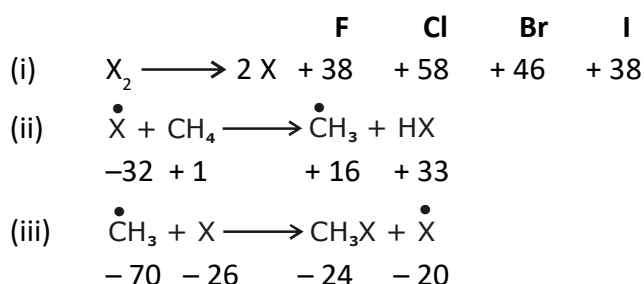


All reactive alkyl free radicals are consumed so reaction will stop for a period of time.

Relative reactivity of halogen towards, methane :

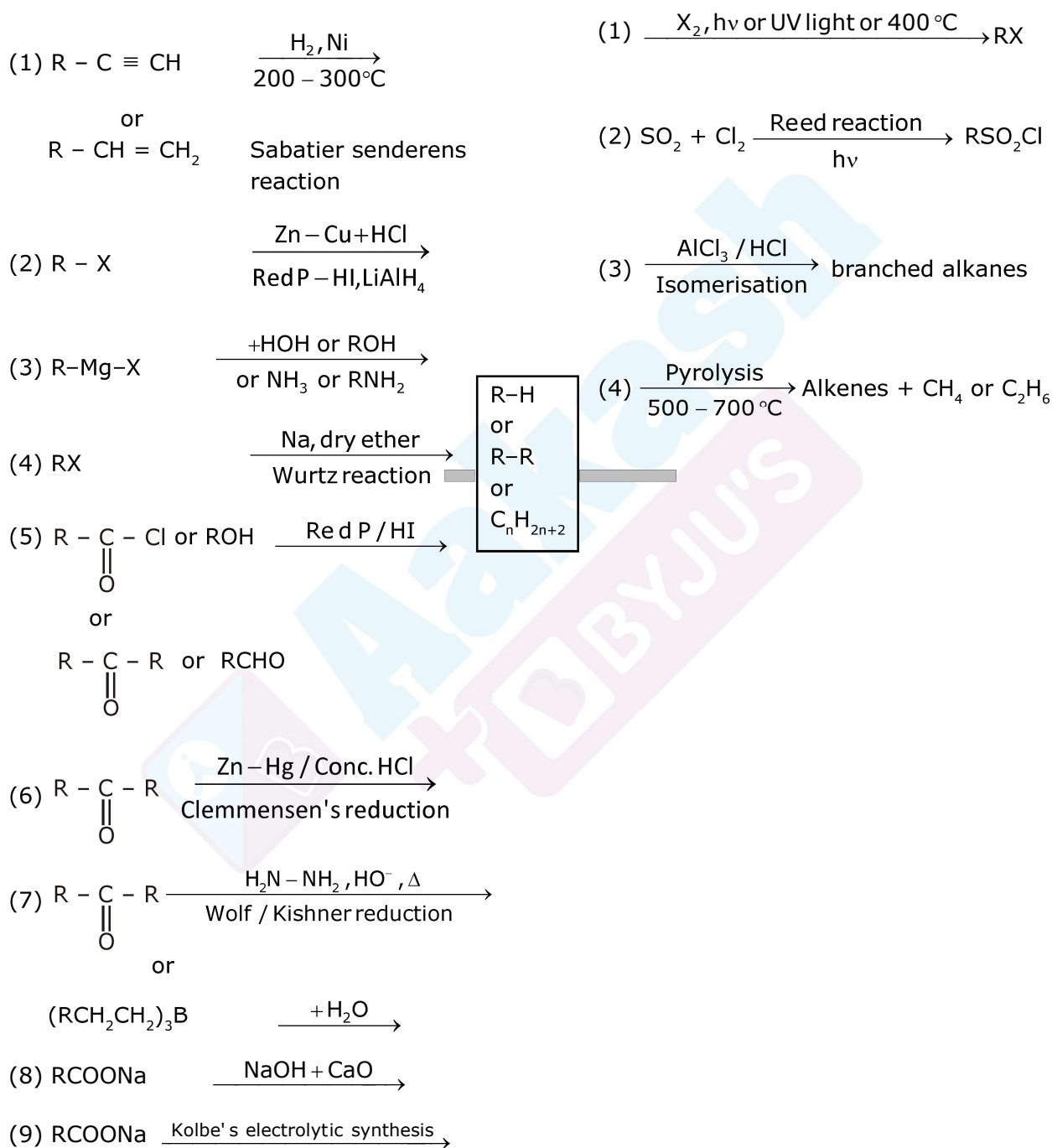
Order of reactivity is F₂ > Cl₂ > Br₂ > I₂ which can be explained by the value of ΔH (Energy change)

Steps of halogenation, value of ΔH for each step. (kcal/mol)





REACTION CHART FOR ALKANES





HYDROCARBON (ALKENE)

ALKENE

Introduction :

Alkenes are hydrocarbons with carbon-carbon double bonds. Alkenes are sometimes called olefins, a term derived from olefinic gas, meaning "oil forming gas". Alkenes are among the most important industrial compound and many alkenes are also found in plants and animals. Ethylene is the largest – volume industrial organic compound, used to make polyethylene and a variety of other industrial and consumer chemicals.

Structure and bonding in Alkenes

- (1) Alkenes are unsaturated hydrocarbons having at least one double bond.
- (2) They are represented by general formula (G.F.) C_nH_{2n} (one double bond).
- (3) In ethene C = C bond length is 1.34 Å.
- (4) Its bond energy is 146 kcal mol⁻¹.
- (5) The hybridization of (C = C) alkenic carbon is sp².
- (6) The πe^- cloud is present above and below the plane of σ -bonded skeleton.
- (7) They are also known as olefins since ethene, the first member of the homologous series forms an oily liquid substance when treated with halogens.
- (8) Compounds may exist as conjugated polyenes or as cumulated polyenes or as isolated polyenes.

Note :

That angle between double bond - single bond will be greater than angle between single bond - single bond since repulsion due to p electrons (double bond - single bond repulsion > single bond-single bond repulsion according to VSEPR theory).



Physical properties of Alkenes / Hydrocarbons

Table : III

| | Physical properties | Homologous series | Isomers |
|----|---------------------|--|---|
| 1. | Physical state | C ₁ - C ₃ gases C ₄ - C ₂₀ liquids >C ₂₀ : solids | |
| 2. | Dipole moment (μ) | | cis > trans |
| 3. | Polarity | | cis > trans (for C _{ab} =C _{ab} type of alkenes) |
| 4. | Melting point | increases with M.W. | trans > cis (due to more packing capacity) |
| 5. | Boiling point | increases with M.W. | cis > trans # branching decreases B.P. $\begin{array}{c} \text{C} \\ \\ \text{C} - \text{C} = \text{C} < \text{C} - \text{C} = \text{C} - \text{C} \end{array}$ polarity increases, boiling point increases |
| 6. | Solubility | practically insoluble in water but fairly soluble in nonpolar solvents like benzene petroleum ether, etc. | cis > trans polarity increases, solubility in polar solvents increases. |
| 7. | Stability | | trans > cis (cis isomers has more vander Waal repulsion) |

Laboratory test of alkene

Table : IV

| Functional Group | Reagent | Observation | Reaction | Remarks |
|--|---|---|---|-----------------|
| $\begin{array}{c} \diagup \\ \text{C} = \text{C} \\ \diagdown \end{array}$ | (1) Bayer's Reagent alk. dil. cold KMnO ₄ | Pink colour disappears | $\text{CH}_2 = \text{CH}_2 + \text{H}_2\text{O} + \text{O} \xrightarrow{\text{alk. KMnO}_4} \begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$ | Dihydroxylation |
| | (2) Br ₂ / H ₂ O | Bromine water colour decolourises | $\text{Br}_2 + \text{CH}_2 = \text{CH}_2 \longrightarrow \begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \quad \\ \text{Br} \quad \text{Br} \\ \text{White ppt} \end{array}$ | Dibromination |
| | (3) O ₃ (ozone) | $\begin{array}{c} \diagdown \\ \text{C} = \text{O} \\ \diagup \end{array}$ Compounds | $\text{H}_2\text{C} = \text{CH}_2 + \text{O}_3 \xrightarrow{\text{Zn} / \text{H}_2\text{O}} 2\text{HCHO}$ | Ozonolysis |



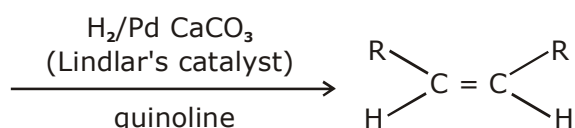
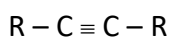
Preparation of Alkenes

(I) BY PARTIAL REDUCTION OF ALKYNES

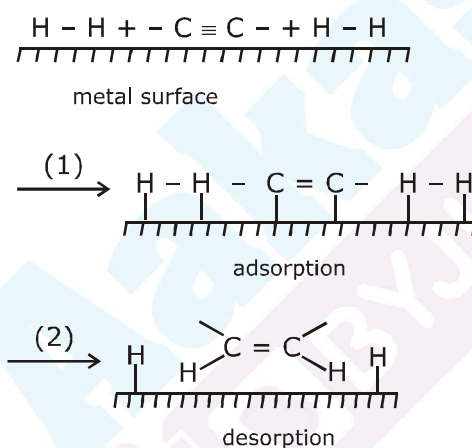
(a) By catalytic hydrogenation of alkynes in presence of poisoned catalyst A syn addition of hydrogen : Synthesis of cis-alkenes : This is performed by :

(i) **Lindlar's catalyst** : Metallic palladium deposited on calcium carbonate with lead acetate and quinoline.

General Reaction



Mechanism of hydrogenation :

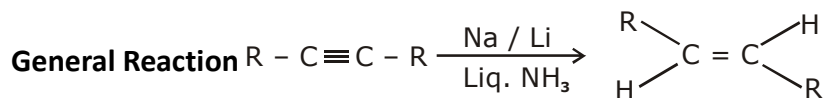


Steps : The reactant alkyne molecules and hydrogen molecules get adsorbed at the surface of metal catalyst. It is chemical adsorption (chemisorption).

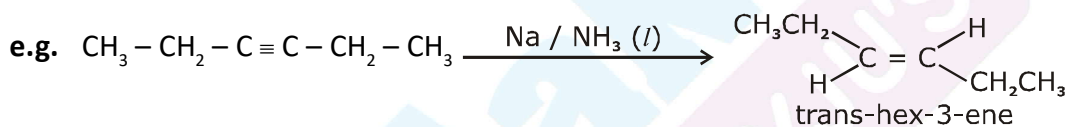
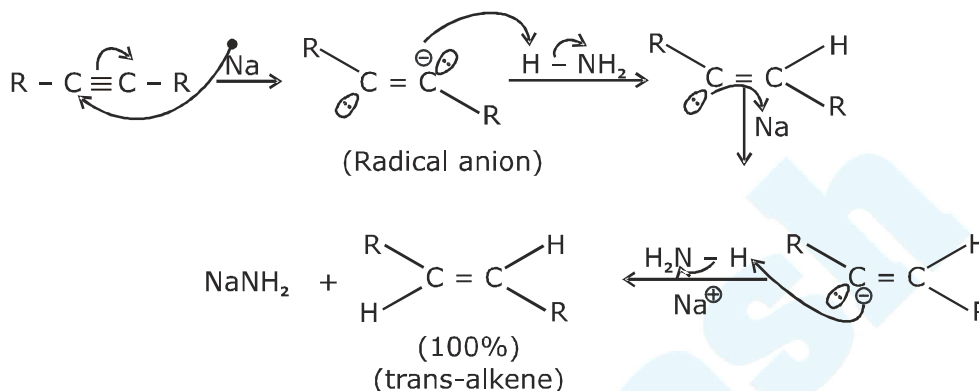
In this state, the reactants lie very close to each other and so the hydrogen atoms start forming bond with carbon. Two hydrogen atoms are added to two triply bonded carbon atom from the same side of π bond and a **cis or syn addition product** is formed. The product alkene now escapes away from the surface of the catalyst. Quinoline occupies the metal surface inhibiting further reduction to alkanes. **Quinoline** therefore is called **catalyst poison** and **palladium** is called **deactivated catalyst** or **poisoned catalyst**.



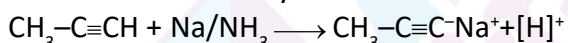
(b) Birch reduction : (Anti addition of hydrogen : synthesis of trans-alkenes)



Mechanism : Reagents $\text{Na}(\text{or Li, K}) + \text{liq NH}_3 \longrightarrow \text{Na}^{\oplus} + e^{\ominus}(\text{solvated electron})$



Note : This process of reduction is not eligible when terminal alkynes are taken ($R - C \equiv CH$) because terminal alkynes form sodium salt with Na metal.

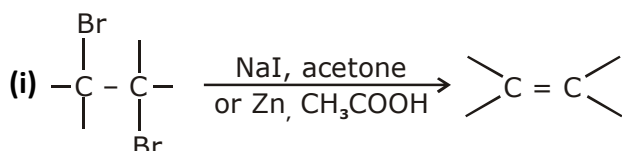


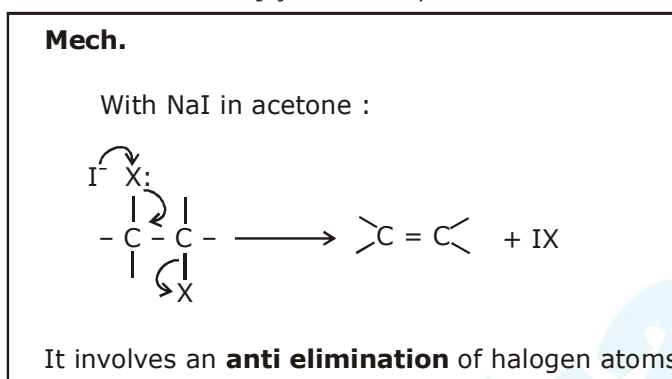
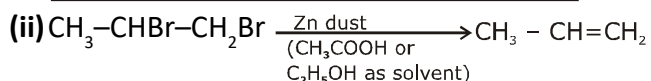
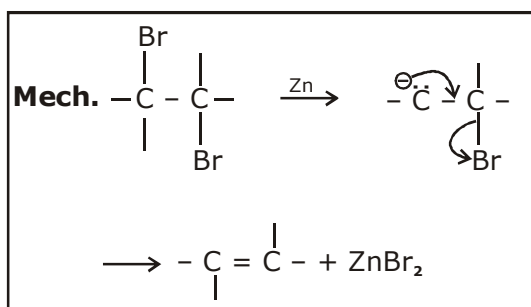
(II) BY DEHALOGENATION OF VICINAL DIHALIDES

There are two types of dihalides namely gem (or geminal) dihalides in which the two halogen atoms are attached to the same carbon atom and vicinal dihalides in which the two halogen atoms are attached to the adjacent carbon atoms.

Dehalogenation of vicinal dihalides can be affected either by NaI in acetone or zinc in presence of acetic acid or ethanol.

General Reaction :





Remarks :

(1) Both are E2 elimination.

(2) Both are stereospecific anti elimination.

(III) DEHYDROHALOGENATION OF ALKYL HALIDES

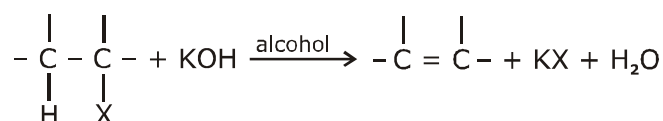
Dehydrohalogenation is the elimination of a hydrogen and a halogen from an alkyl halide to form an alkene.

Dehydrohalogenation can take place by E1 and E2 mechanism.

(i) Hot alcoholic solution of KOH EtO⁻ / EtOH (ii) NaNH₂ (iii) t-BuO⁻K⁺ in t-BuOH

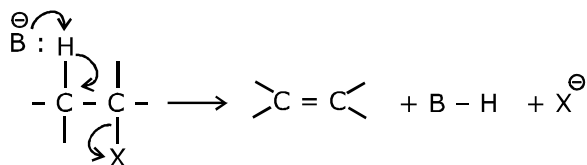
(i) Dehydrohalogenation by the E₂ mechanism : Second-order elimination is a reliable synthetic reaction, especially if the alkyl halide is a poor S_N2 substrate. E2 dehydrohalogenation takes place in one step, in which a strong base abstracts a proton from one carbon atoms and halogen as the leaving group leaves the adjacent carbon.

General reaction :

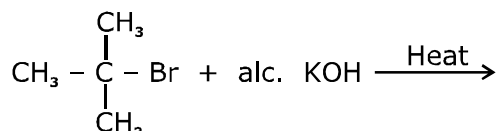




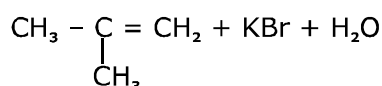
Mechanism :



Undergo elimination of hydrogen halide (HX) leading to the formation of alkenes.

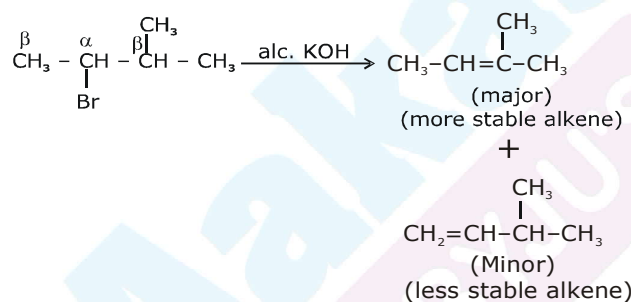


e.g.

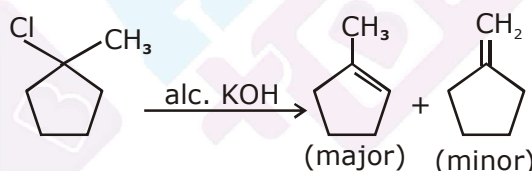


Here β - H is eliminated by base hence called **β elimination** following **Saytzeff rule**.

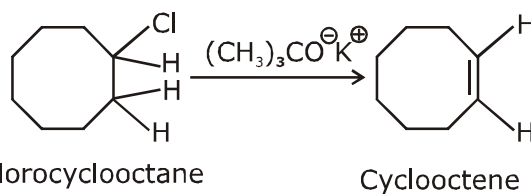
i.e, (Highly substituted alkene is major product). It also involves an anti elimination of HX.



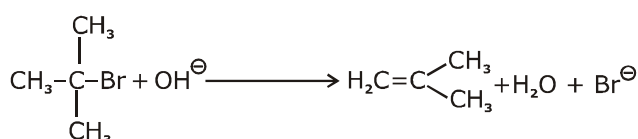
e.g.



e.g.



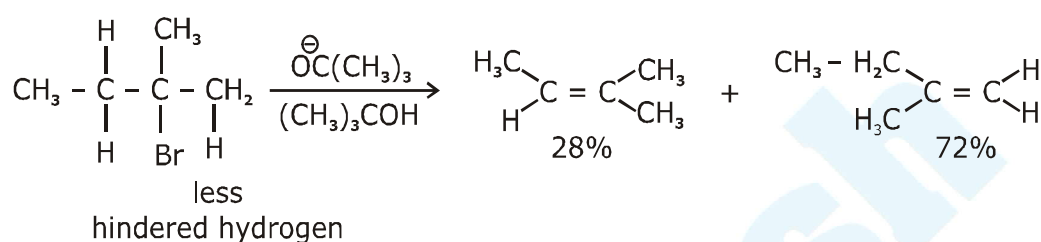
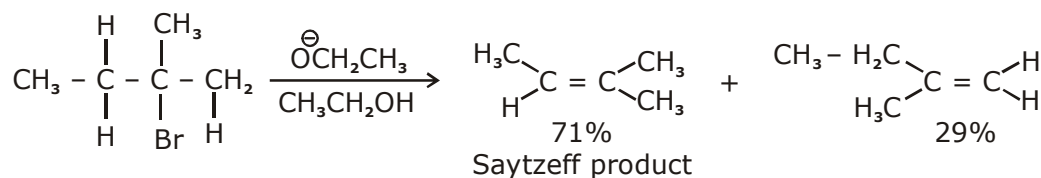
e.g.



(ii) Formation of the Hoffmann product:

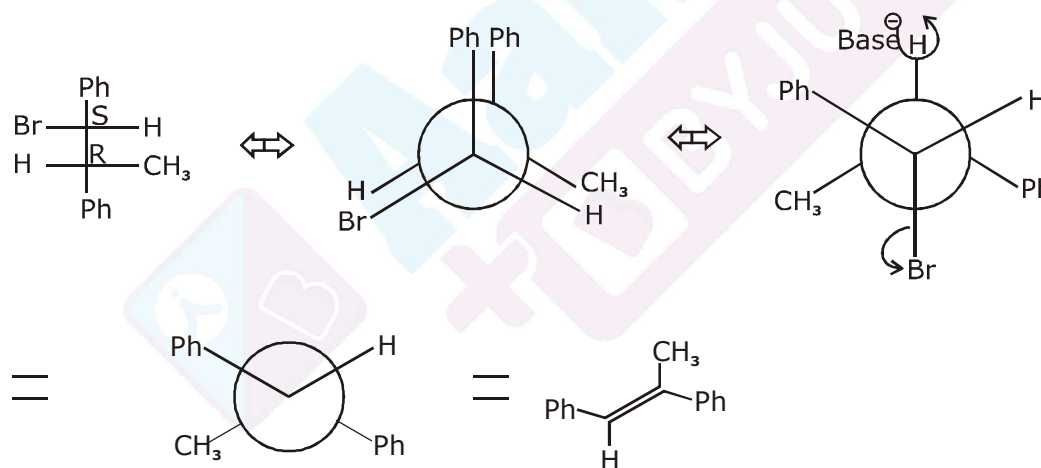


Bulky bases can also accomplish dehydrohalogenation that do not follow the Saytzeff rule. Due to steric hindrance, a bulky base abstracts a less hindered proton, often the one that leads to formation of the least highly substituted product, called the Hoffmann product.



Stereospecific E₂ reactions :

The E₂ elimination is stereospecific because it normally goes through an anti and coplanar transition state. The products are alkene, and different diastereomers of starting materials commonly give different diastereomers of alkenes.



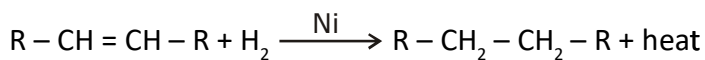
Chemical Reactions of Alkenes

(I) CATALYTIC HYDROGENATION OF ALKENES : (HETEROGENEOUS HYDROGENATION)

Hydrogenation : The function of catalyst

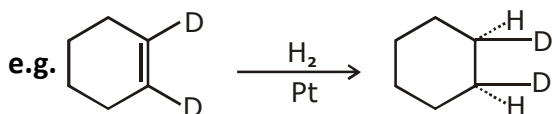
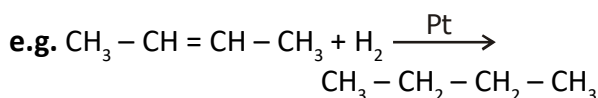


Hydrogenation of an alkene is an exothermic reaction ($\Delta H^\ominus = -120 \text{ kJ mol}^{-1}$)



As a consequence, both hydrogen atoms usually add from the same side of the molecule. This mode of addition is called **syn** addition.

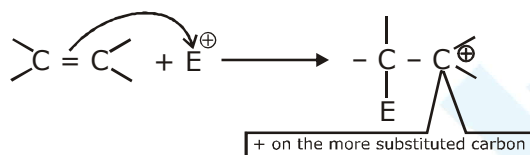
Hydrogenation of an alkene is formally a reduction, with H_2 adding across the double bond to give an alkane. The process usually requires a catalyst containing Pt, Pd or Ni.



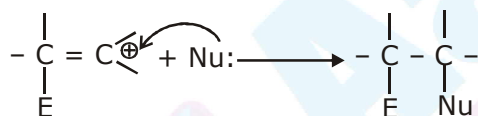
(II) ELECTROPHILIC ADDITION REACTIONS

Mechanism

Step 1 : Attack of the electrophile on π bond forms a carbocation.

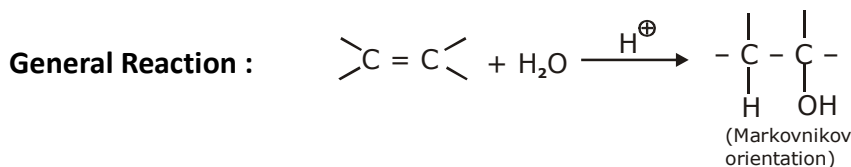


Step 2 : Attack by a nucleophile gives the product of addition.



(i) Acid-Catalyzed Hydration of Alkenes :

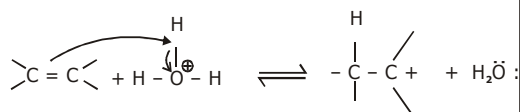
Alkenes add water in the presence of an acid catalyst to yield alcohols. The addition takes place with Markovnikov's rule. The reaction is reversible, and the mechanism for the acid-catalyzed hydration of an alkene is simply the reverse of that for the dehydration of an alcohol. The carbocation intermediate may rearrange if a more stable carbocation is possible by hydride or alkyl migration. Thus, a mixture of isomeric alcohol products may result.



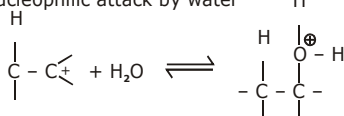


Mech.

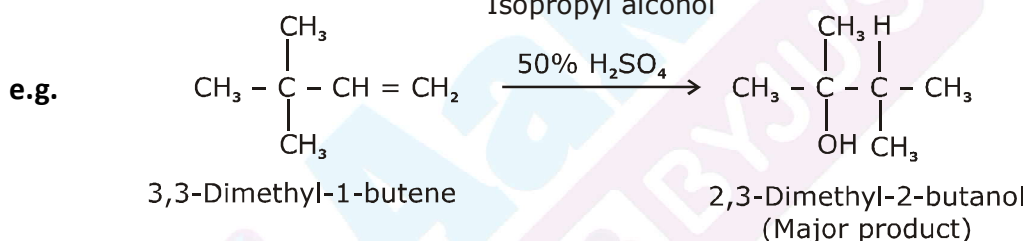
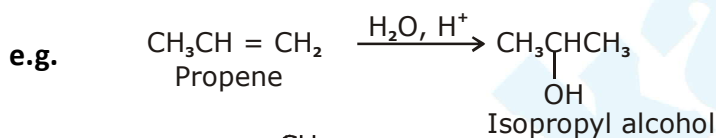
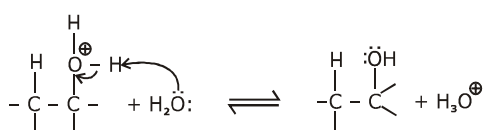
Step 1 : Protonation of the double bond forms a carbocation



Step 2 : Nucleophilic attack by water



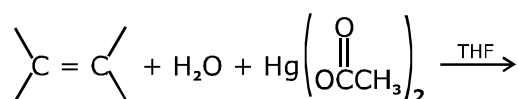
Step 3 : Deprotonation of the alcohol



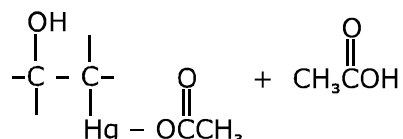
(ii) (a) Oxymercuration - Demercuration :

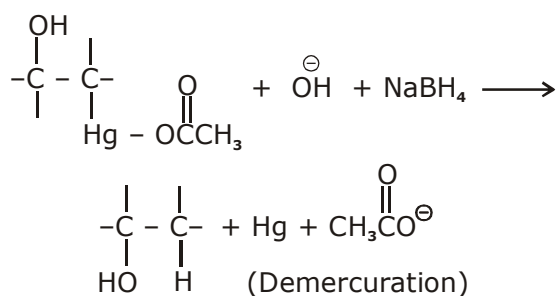
Alkenes react with mercuric acetate in a mixture of water and tetrahydrofuran (THF) to produce (hydroxyalkyl) mercury compounds. These can be reduced to alcohols with sodium borohydride and water.

Oxymercuration

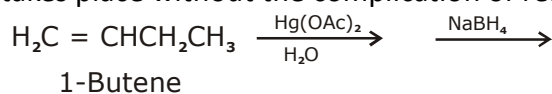


General Reaction :

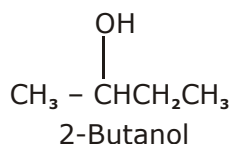




In the oxymercuration step, water and mercuric acetate add to the double bond; in the demercuration step, sodium borohydride reduces the acetoxymercury group and replaces it with hydrogen. Then net addition of H –and –OH takes place with Markovnikov's rule and generally takes place without the complication of rearrangements.

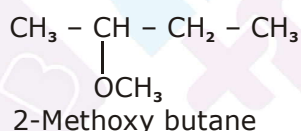
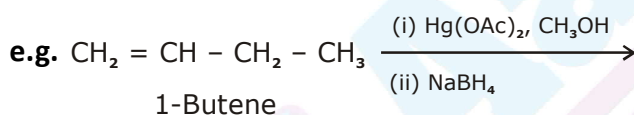
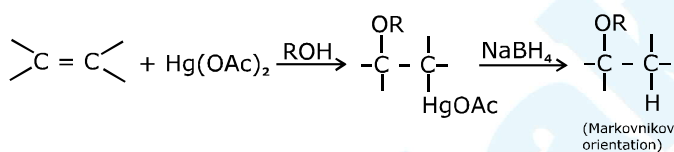


e.g.



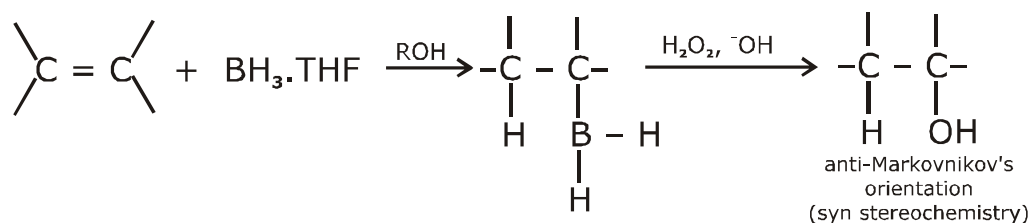
(b) Alkoxymercuration - Demercuration :

General reaction :

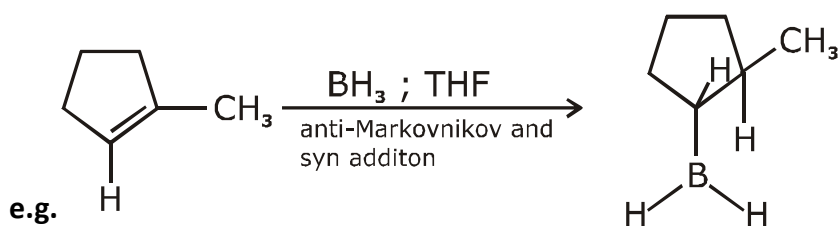


(iii) Hydroboration-Oxidation (SYN ADDITION)

General Reaction

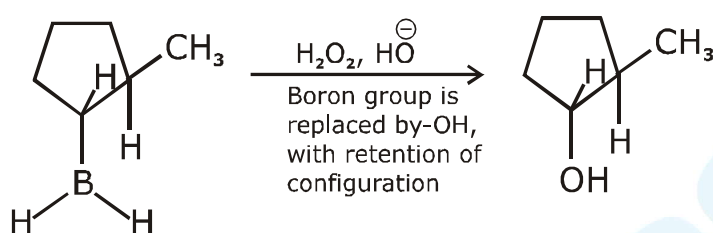


An alkene reacts with BH_3 in THF or diborane to produce an alkylborane. Oxidation and hydrolysis of the alkylborane with hydrogen peroxide and base yields an alcohol.



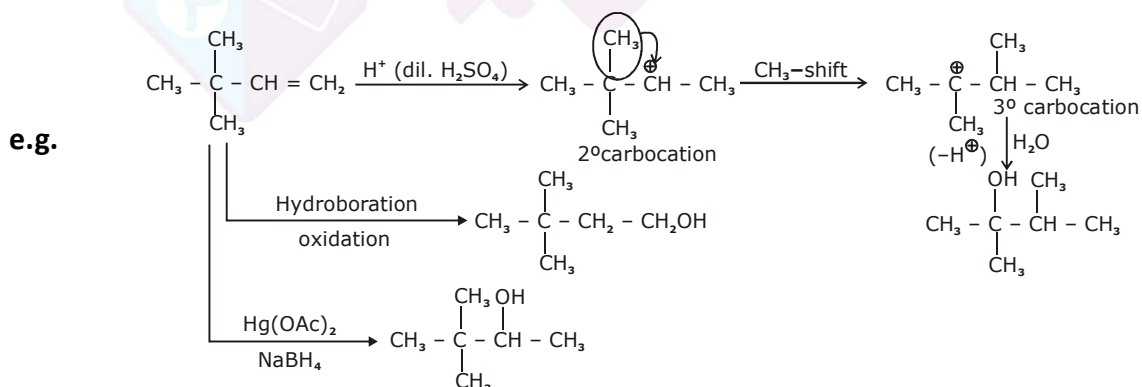
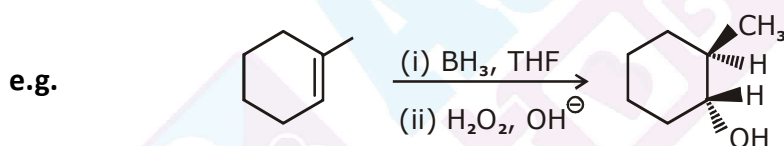
+ other enantiomer + dialkyl- and trialkylborane

Oxidation



+ other enantiomer

In the first step, boron and hydrogen undergo syn addition with the alkene. In the second step, treatment with hydrogen peroxide and base replaces the boron with -OH with retention of configuration. The net addition of -H and -OH occurs with anti Markovnikov's rule and syn stereoselectivity. Hydroboration-oxidation therefore, serves as a useful regiochemical complement to oxymercuration-demercuration.



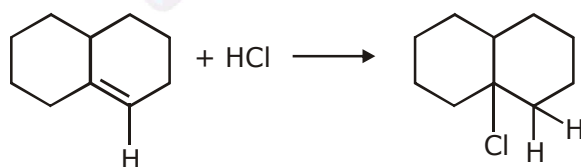
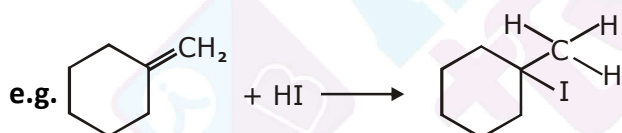
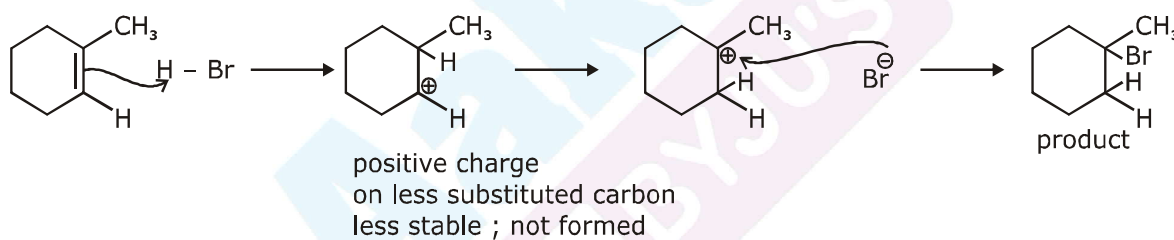
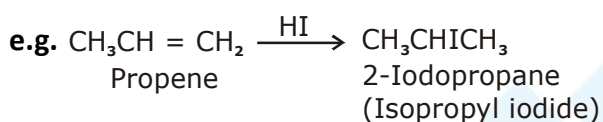
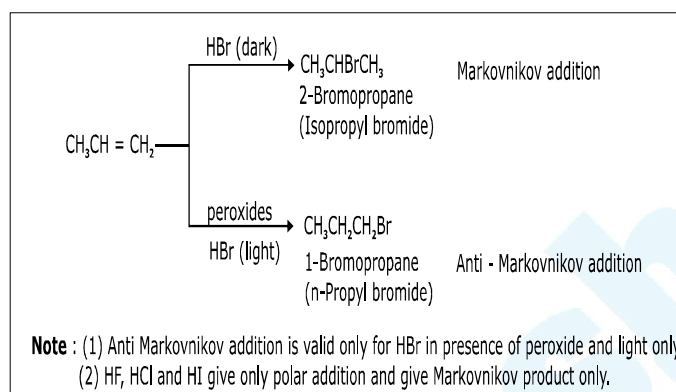
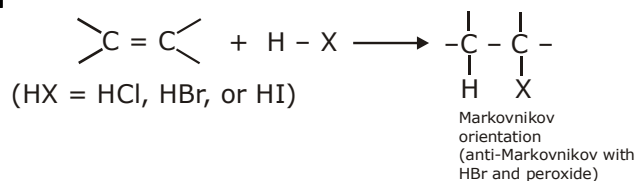
(i) Hydration with dil. H_2SO_4 proceeds via carbocation rearrangement.

(ii) Hydration with $\text{Hg}(\text{OAc})_2$, H_2O , followed by NaBH_4 proceeds via Markovnikov's rule.

(iii) Hydration with $(\text{BH}_3)_2$ followed by $\text{H}_2\text{O}_2 / \text{OH}^-$ proceeds via Anti Markovnikov's rule.



(iv) Addition of Hydrogen Halides: General Reaction

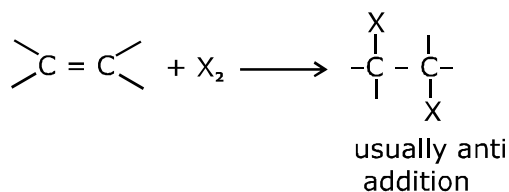


(v) Addition of Halogen :

Halogen add to alkenes to form vicinal dihalides.



General Reaction



(X₂ = Cl₂, Br₂)

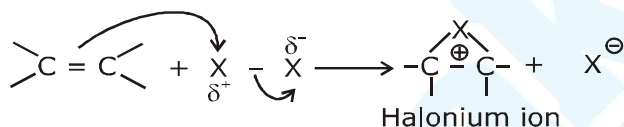
The electron rich double bond induces a dipole in an approaching halogen molecule making one halogen electron deficient and another electron rich.

Note :

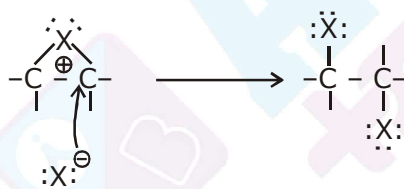
- (i) F₂ is not added because F⁺ is never generated. Moreover reaction is explosive giving CO₂ & H₂O
- (ii) I₂ is not added because reaction is reversible with equilibrium in backward direction.
- (iii) Reaction with bromine is basis for test of alkenes.
- (iv) Halogen addition is stereospecific anti addition.
- (v) Halogens can also be added in presence of sunlight and give free radical addition.
(Reactivity of halogen addition in sunlight is F₂ (explosive) > Cl₂ > Br₂ > I₂)

Mechanism

Step-1 Formation of a halonium ion

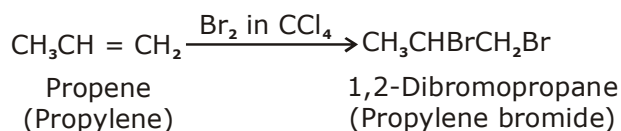


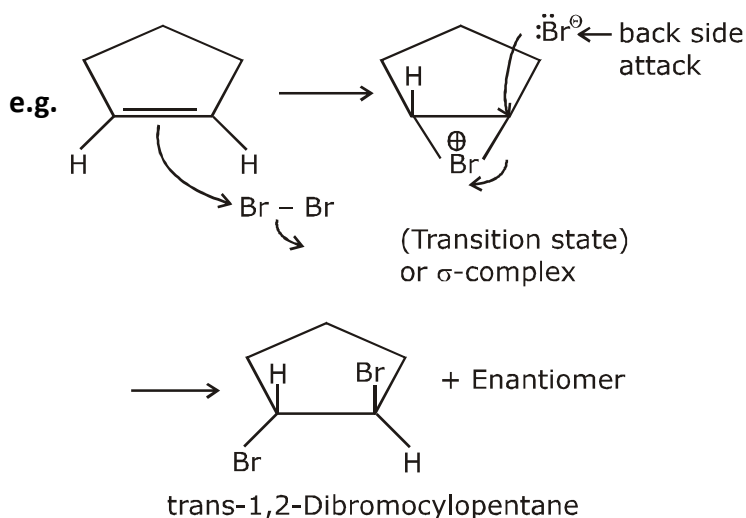
Step-2 Opening of the halonium ion



X[⊖] attacks from the back side of halonium ion.

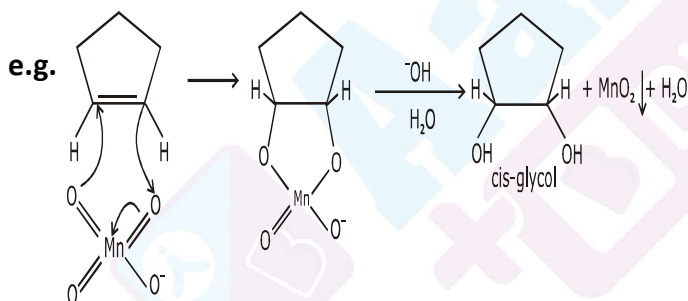
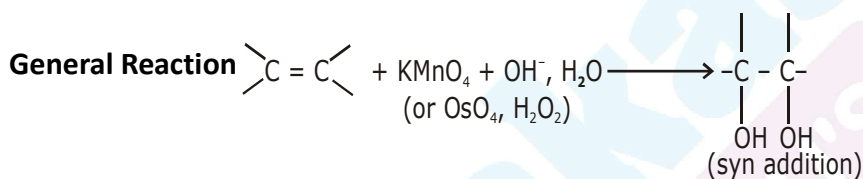
e.g.



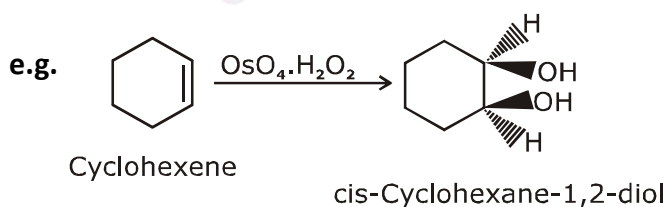


(vi) Hydroxylation of Alkenes:

(a) Syn Hydroxylation : (Reaction with Beayer's reagent, (cold dilute alkaline KMnO_4 solution). Both OH groups are added from same face of alkene. This addition is example of syn addition.

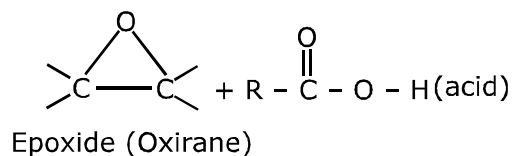
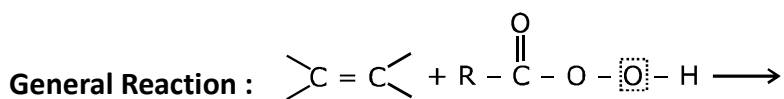


The same function of syn addition of 2 - OH groups is performed by $\text{OsO}_4 / \text{H}_2\text{O}_2$

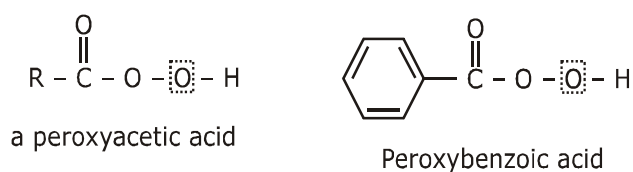


(III) EPOXIDATION OF ALKENES :

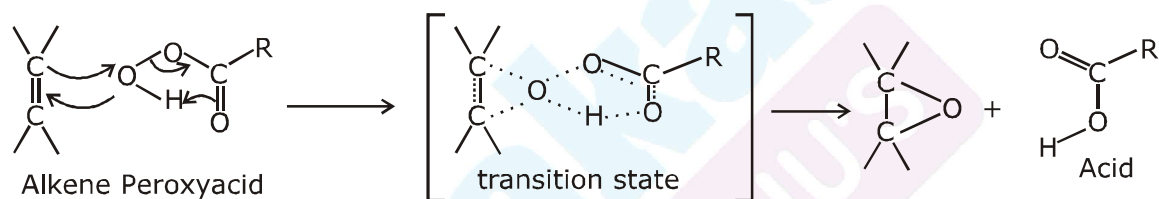
An alkene is converted to an epoxide by a peroxyacid, a carboxylic acid that has an extra oxygen atom in a $-\text{O}-\text{O}-$ (peroxy) linkage.



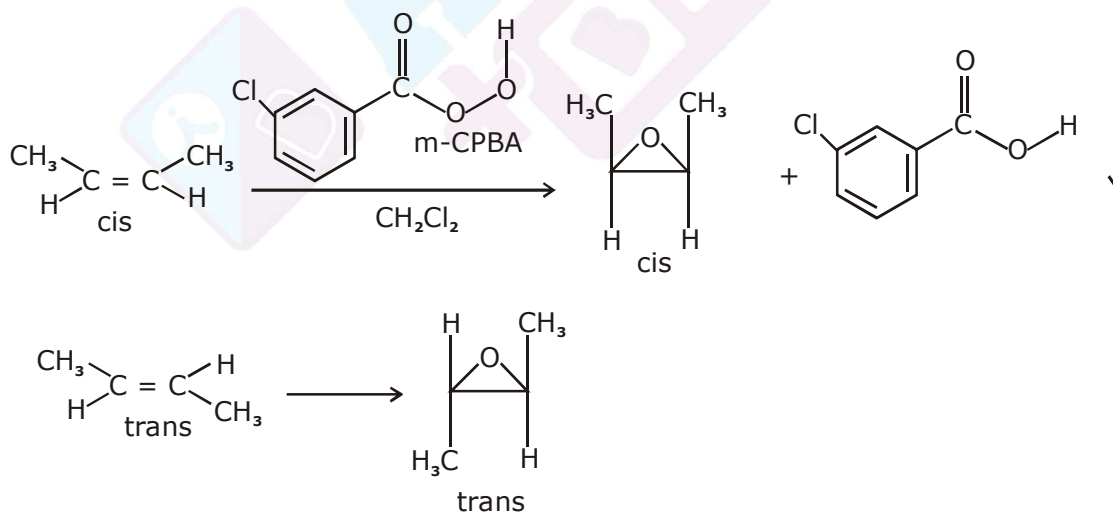
The epoxidation of an alkene is clearly an oxidation, since in oxidation, an oxygen atom is added. Peroxyacids are highly selective oxidizing agents. Some simple peroxyacids (sometimes called per acids) and their corresponding carboxylic acids are shown below :



Mech.

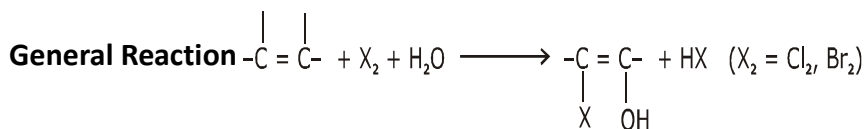


e.g.



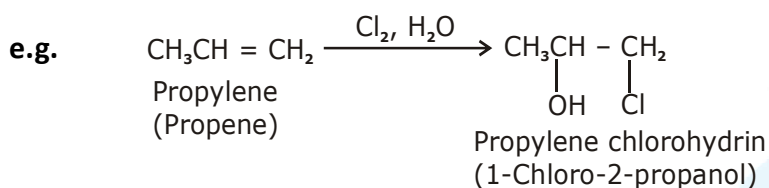


(IV) HALOHYDRIN FORMATION:



Addition of the electrophile X^+ (from X_2) to form a bridged halonium ion, followed by Nu attack by H_2O

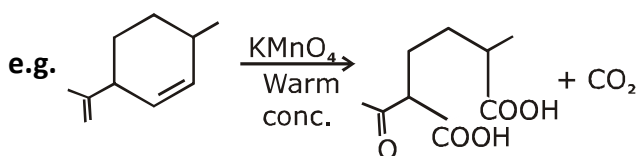
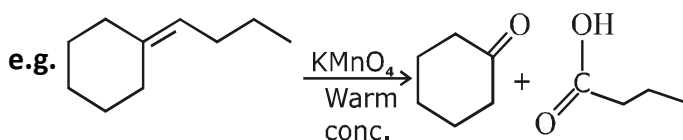
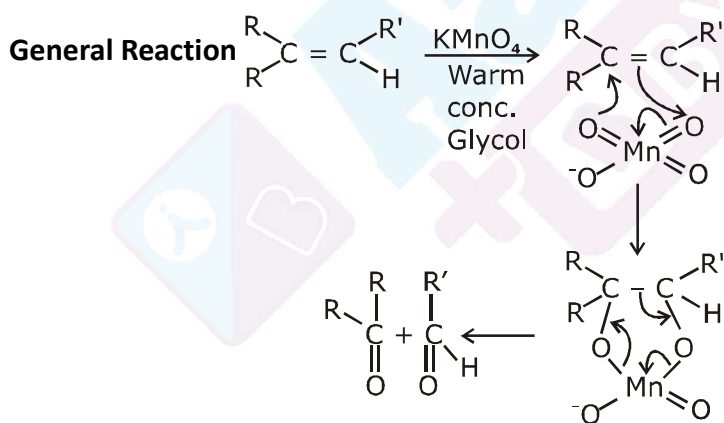
Halohydrin formation commences when the π electrons of the alkene react with electrophilic bromine to form a bridge intermediate called a bromonium ion. Water, acting as a nucleophile, uses a lone pair of electron to open the three-membered bromonium ion ring and forms a bond with the carbon in an S_N2 process.



(V) OXIDATIVE CLEAVAGE OF ALKENES:

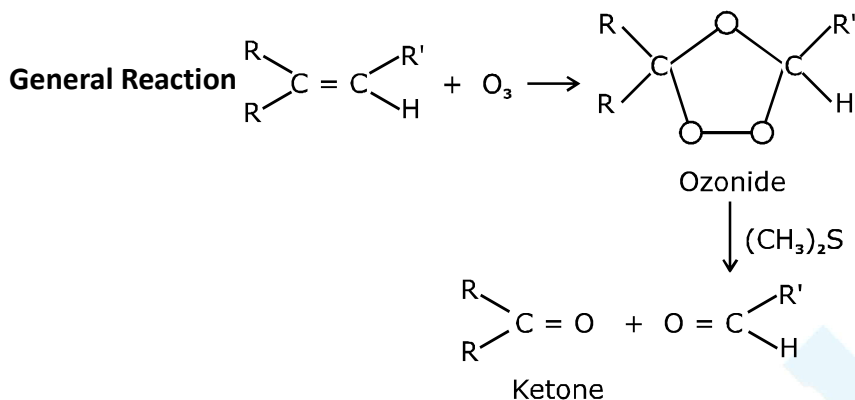
(i) Cleavage by permanganate

In a $KMnO_4$ hydroxylation, if the solution is warm or acidic or too concentrated, oxidative cleavage by $KMnO_4$ starts with an addition to the π bond forming a cyclic intermediate which eventually breaks down to an aldehyde or a ketone. The aldehyde is further oxidized to a carboxylic acid by the $KMnO_4$. The mechanism of this transformation is covered in the oxidation of alcohols.

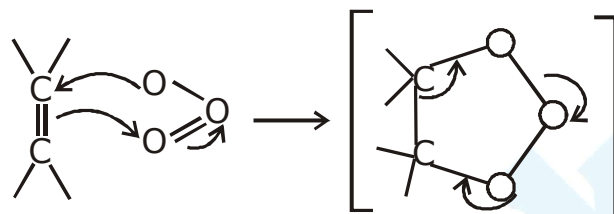




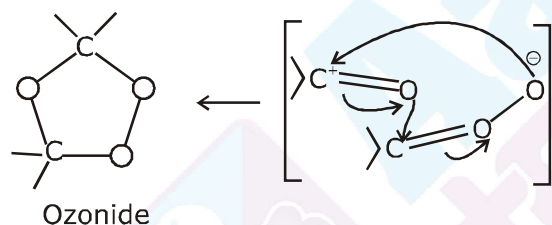
(ii) Ozonolysis : Like permanganate, ozone cleaves double bonds to give ketones and aldehydes. However, ozonolysis is milder, and both ketones and aldehydes can be recovered without further oxidation.



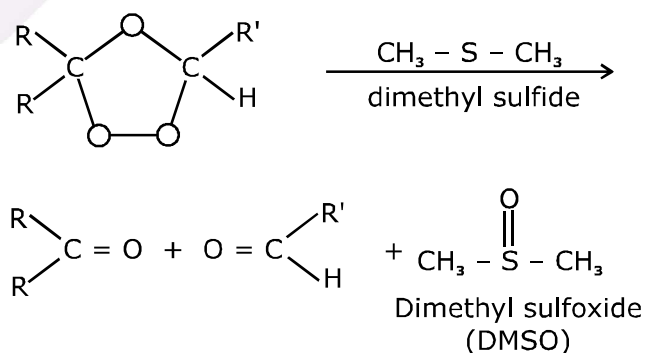
Mechanism



Molozonide
(Primary ozonide)

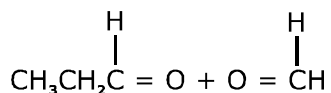
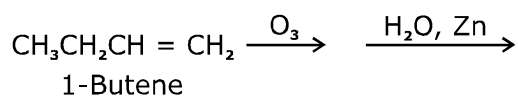


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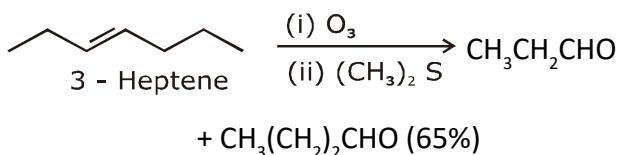




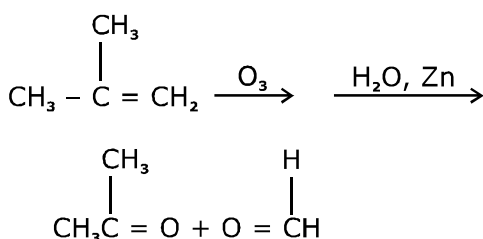
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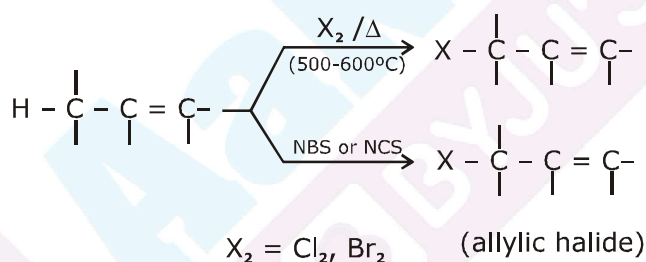


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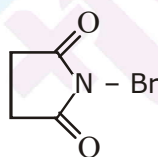


(VI) HALOGENATION, ALLYLIC SUBSTITUTION

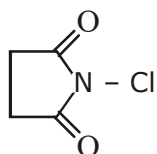
General Reaction



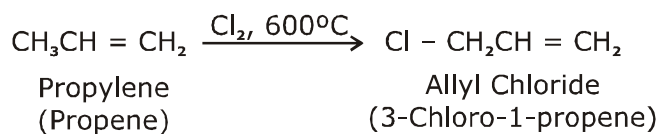
NBS = N-Bromosuccinimide



NCS = N-Chlorosuccinimide



e.g.





HYDROCARBON (ALKYNES)

ALKYNES

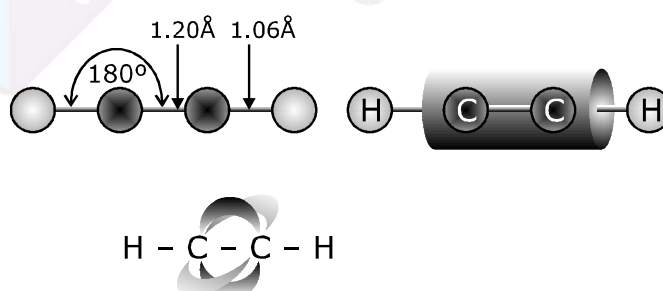
Introduction

A triple bond gives an alkyne with four fewer hydrogen atoms than the corresponding alkane. Therefore the triple bond contributes two degree of unsaturation (DU).

Alkynes are not as common in nature as alkenes, but some plants do use alkynes to protect themselves against disease or predators. Acetylene as far as we know, is the the most important commercial alkyne. Acetylene is an important industrial feedstock but its largest use is as the fuel for the oxyacetylene welding torch.

Structure and bonding in Alkynes

- (1) Alkynes are hydrocarbons that contain carbon-carbon triple bond.
- (2) Alkynes are also called acetylenes because they are derivatives of acetylene.
- (3) The general formula is : C_nH_{2n-2} . (one triple bond)
- (4) In alkyne $C \equiv C$ bond length is 1.20 \AA .
- (5) Its bond energy is $192 \text{ kcal mol}^{-1}$
- (6) The hybridization of carbon atoms having triple bond ($C \equiv C$) in alkynes is sp .
- (7) Overlapping of these sp hybrid orbitals with each other and with the hydrogen orbitals gives the sigma bond framework which is linear (180°) structure.
- (8) Two π bonds result from overlap of the two remaining unhybridized p orbitals on each carbon atom. These orbitals overlap at **right angles** (90°) to each other, forming one π bond with electron density above and below the $C-C$ sigma bond, and the other with electron density in front and in back of the sigma bond. This results in a cylindrical π electron cloud around σ bonded structure.



Note :

Any type of stereochemistry does not arise in acetylenic bond due to linearity of $C \equiv C$ bond.



Physical Properties of Alkynes

- (1) Alkynes are relatively nonpolar (w.r.t. alkyl halides and alcohols) and are nearly insoluble in water (but they are more polar than alkenes and alkanes). They are quite soluble in most organic solvents, (acetone, ether, methylene chloride, chloroform and alcohols).
- (2) Acetylene, propyne, and butynes are gases at room temperature, just like the corresponding alkanes and alkenes. In fact, the boiling point of alkynes are nearly the same as those of alkanes and alkenes with same number of carbon atoms.

Table

| Name | Formula | M.p., °C | B.P., °C | Relative density (at 20°C) |
|-------------------|---|----------|----------|----------------------------|
| Acetylene | $\text{HC} \equiv \text{CH}$ | - 82 | - 75 | |
| Propyne | $\text{HC} \equiv \text{CCH}_3$ | - 101.5 | - 23 | |
| 1-Butyne | $\text{HC} \equiv \text{CCH}_2\text{CH}_3$ | - 122 | 9 | |
| 1-Pentyne | $\text{HC} \equiv \text{C}(\text{CH}_2)_2\text{CH}_3$ | - 98 | 40 | 0.695 |
| 2-Butyne | $\text{CH}_3\text{C} \equiv \text{CCH}_3$ | - 24 | 27 | 0.694 |
| 2-Pentyne | $\text{CH}_3\text{C} \equiv \text{CCH}_2\text{CH}_3$ | - 101 | 55 | 0.714 |
| 3-Methyl-1-butyne | $\text{HC} \equiv \text{CCH}(\text{CH}_3)_2$ | | 29 | 665 |

TABLE - COMPARATIVE STUDY OF ALKANES, ALKENES, ALKYNES

| S.No. | Properties | Alkanes | Alkenes | Alkynes |
|-------|---|------------------------------------|------------------------------------|------------------------------------|
| 1. | Bond length (angstrom) | 1.54 (C - C) | 1.32 (C = C) | 1.20 (C \equiv C) |
| 2. | Bond energy (kJmol^{-1}) | 415 (C - C) | 615 (C = C) | 835 (C \equiv C) |
| 3. | Hybridization | sp^3 | sp^2 | sp |
| 4. | % s character | 25% | 33% | 50% |
| 5. | pK_a | 50 | 44 | 25 |
| 6. | Electronegativity of 'C' | | Increases | → |
| 7. | Polarity | | Increases | → |
| 8. | Rate of hydrogenation | | less | more |
| 9. | Rate of electrophilic addition reaction | | more | less |
| 10. | Heat of combustion | C_2H_6 (-373 kcal) | C_2H_4 (-337 kcal) | C_2H_2 (-317 kcal) |



| S.No. | Properties | Alkanes | Alkenes | Alkynes |
|-------|------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| 11. | Density (g/cm ³) | C ₃ H ₈ (0.49) | C ₃ H ₆ (0.52) | C ₃ H ₄ (0.67) |
| 12. | Structure | | | |
| 13. | Shape | Tetrahedral | Planar | Linear |

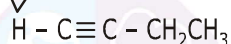
Laboratory Test of Alkyne :

| Functional Group | Reagent | Observation | Reaction | Remarks |
|------------------|---|-------------------------|---|--------------------------|
| - C ≡ C - | (1) Baeyer's Reagent alk.dil. cold KMnO ₄ | Pink colour disappears | $\text{HC} \equiv \text{CH} + \text{H}_2\text{O} + \text{O} \xrightarrow{\text{alk. KMnO}_4} \text{OHC} - \text{CHO}$ | Hydroxylation |
| | (2) Br ₂ /H ₂ O | Red colour decolourises | $\text{Br}_2 + \text{HC} \equiv \text{CH} \rightarrow \text{CHBr}_2 - \text{CHBr}_2$ | Bromination White ppt |
| | (3) O ₃ (ozone) | Acid Formed | $\text{R} - \text{C} \equiv \text{C} - \text{R}' \xrightarrow{\text{O}_3} \text{RCOOH} + \text{R}'\text{COOH}$ | Ozonolysis |

Laboratory Test of Terminal Alkynes :

When triple bond comes at the end of a carbon chain, the alkyne is called a terminal alkyne.

acetylenic hydrogen



1-Butyne, terminal alkyne

| Functional Group | Reagent | Observation | Reaction |
|------------------|---|----------------|---|
| R-C≡C-H | (1) Cuprous chloride +NH ₄ OH | Red ppt | $\text{R} - \text{C} \equiv \text{CH} + \text{CuCl} \xrightarrow{\text{NH}_4\text{OH}} \text{R} - \text{C} \equiv \text{C} \text{Cu} \downarrow (\text{red})$ |
| | (2) AgNO ₃ + NH ₄ OH | White ppt | $\text{R} - \text{C} \equiv \text{CH} + \text{Ag}^+ \rightarrow \text{R} - \text{C} \equiv \text{C} \text{Ag} \downarrow (\text{white})$ |
| | (3) Na in ether | Colourless gas | $\text{HC} \equiv \text{CH} + 2\text{Na} \longrightarrow \text{Na} - \text{C} \equiv \text{C} - \text{Na} + \text{H}_2 \uparrow$ |



Acidity of Terminal Alkynes :

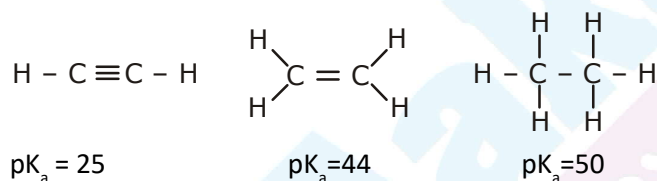
Terminal alkynes are much acidic than other hydrocarbons due to more electronegative sp hybridised carbon. The polarity (acidity) of a C–H bond varies with its hybridization, increases with the increase in percentage of s character of the orbitals. $sp^3 < sp^2 < sp$

| S.No. | Compound | Conjugate Base | Hybridization of C | % s-Character | pK _a |
|-------|--|---|--------------------|---------------|-----------------|
| 1. | $\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$ | $\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}: \\ \quad \\ \text{H} \quad \text{H} \end{array}$ | sp ³ | 25% | 50 |
| 2. | $\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad / \\ \text{C} = \text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{H} \end{array}$ | $\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad / \\ \text{C} = \text{C}: \\ / \quad \diagdown \\ \text{H} \quad \text{H} \end{array}$ | sp ² | 33% | 44 |
| 3. | :NH ₃ | : $\ddot{\text{N}}\text{H}_2^-$ | | | |
| 4. | H – C≡C – H | H – C≡C [⊖] | sp | 50% | 25 |
| 5. | R – OH | R – $\ddot{\text{O}}^-$ | | | 16-18 |

Weakest acid

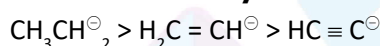
Stronger acid

The hydrogen bonded to the carbon of a terminal alkyne is considerably more acidic than those bonded to carbons of an alkene and alkane (see section). The pK_a values for ethyne, ethene & ethane illustrate this point.



The order of basicity of their anions is opposite to that of their relative acidity:

Relative Basicity



Relative acidity

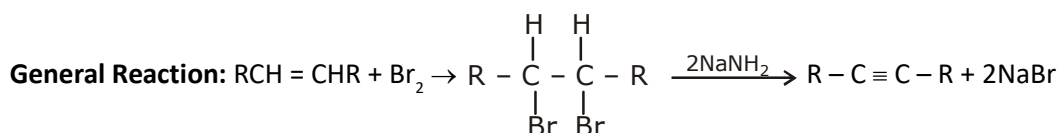


Relative Basicity



Preparation methods of Alkyne :

(I) By dehydrohalogenation of gem and vic dihalide:



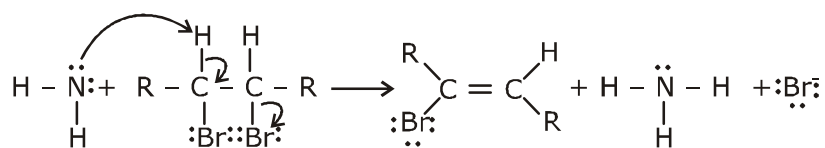
vic - Dibromide

The dehydrohalogenations occur in two steps, the first yielding a bromoalkene and the second alkyne.



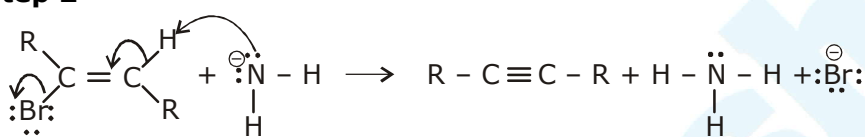
Mechanism :

Step 1

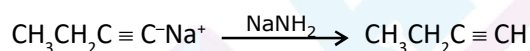
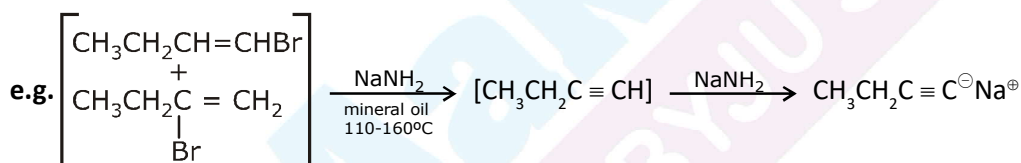
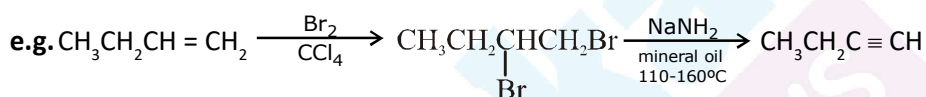


Amide ion vic-Dibromide Bromoalkene Ammonia Bromide ion
 (The strongly basic amide ion brings about an E2 reaction.)

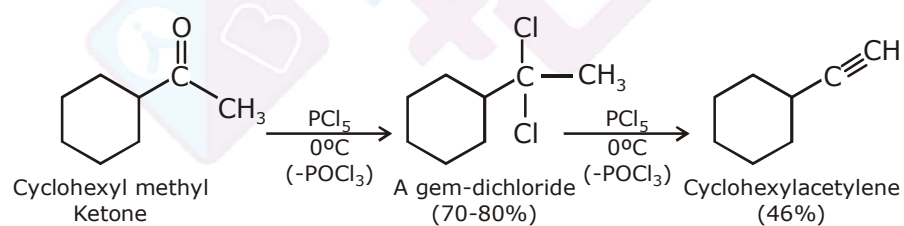
Step 2



Bromoalkene Amide ion Alkyne Ammonia Bromide ion
 (A second E2 reaction produces the alkyne)

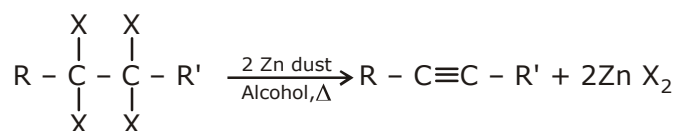


General Reaction



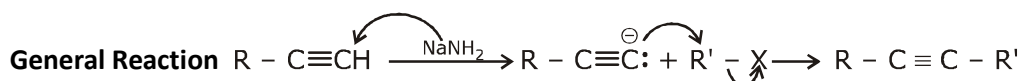
(II) By dehalogenation of tetrahaloalkane:

General Reaction

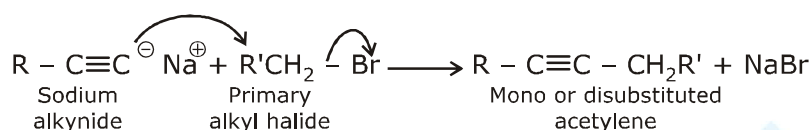
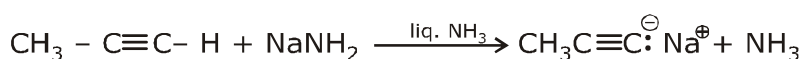




(III) Replacement of The acetylenic hydrogen atom of terminal alkynes:

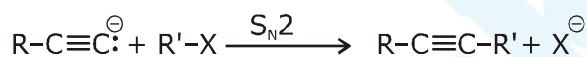
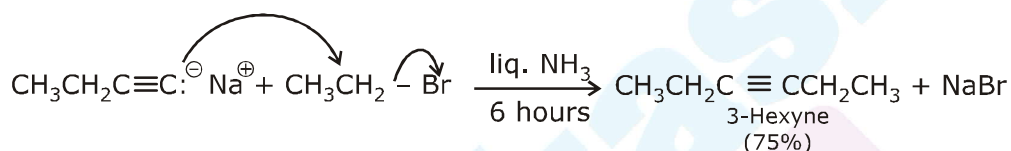


Sodium ethynide and other sodium alkynides can be prepared by treating terminal alkynes with sodium amide in liquid ammonia.



(R or R' or both may be hydrogen)

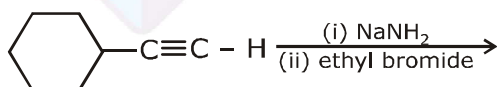
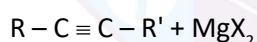
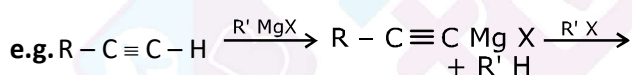
The following example illustrates this synthesis of higher alkyne homologues.



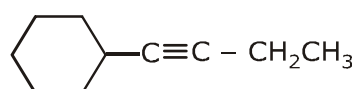
(R'-X must be an unhindered primary halide or tosylate)

The unshared electron pair of the alkynide ion attacks the back side of the carbon atom that bears the halogen atom and forms a bond to it. The halogen atom departs as a halide ion.

e.g.



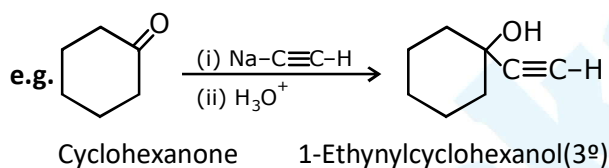
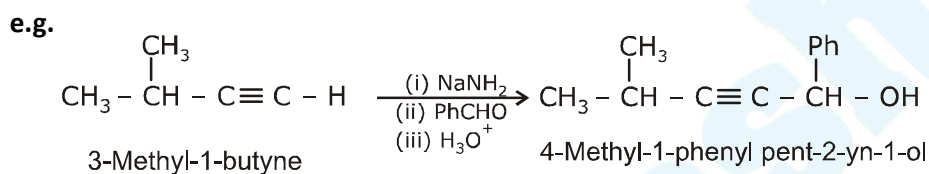
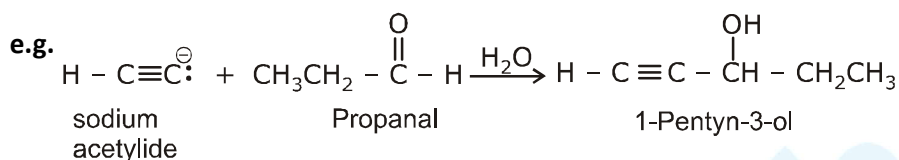
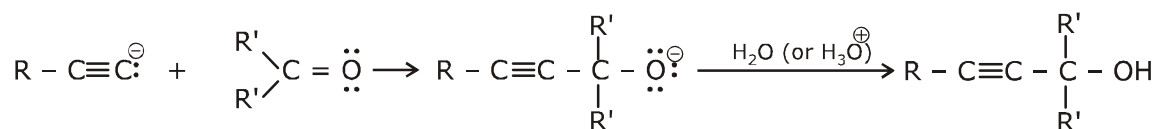
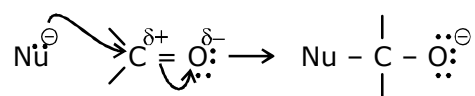
e.g. Ethynylcyclohexane



1-Cyclohexyl-1-butyne
(ethylcyclohexyl acetylene)



Addition of acetylide ions to carbonyl groups :

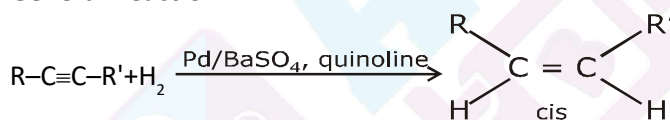


Chemical reaction of Alkyne

(I) Reduction to alkenes

(a) By Lindlar's reagent

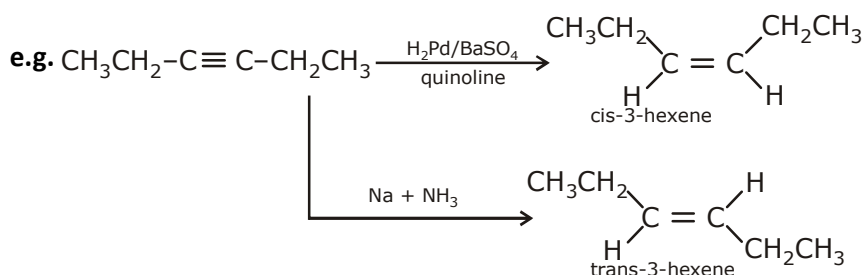
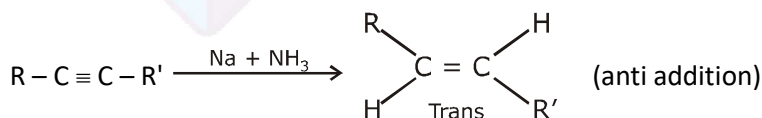
General Reaction



(syn addition)

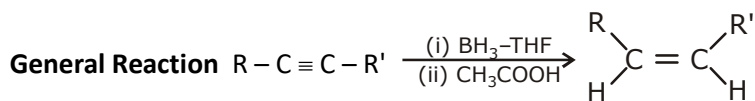
(b) By Birch reduction

General Reaction

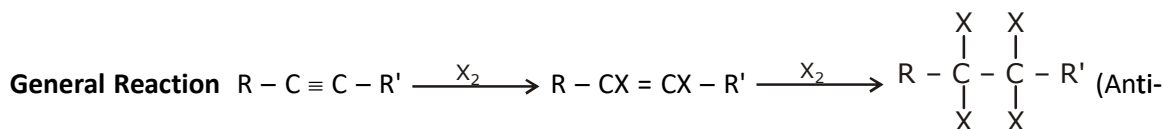




(c) By hydroboration reduction

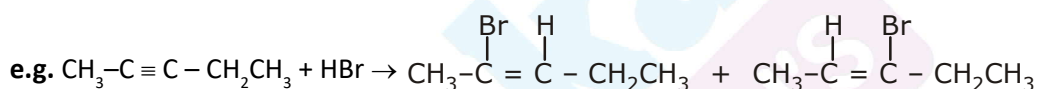
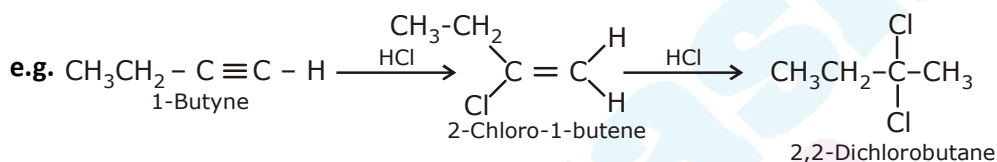
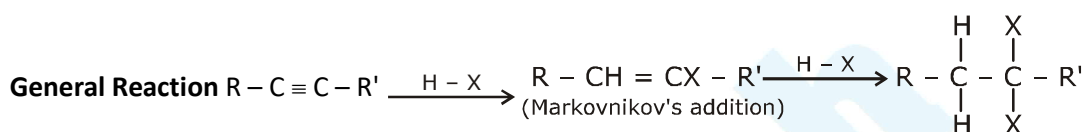


(II) Addition of halogen ($X_2 = Cl_2, Br_2$)

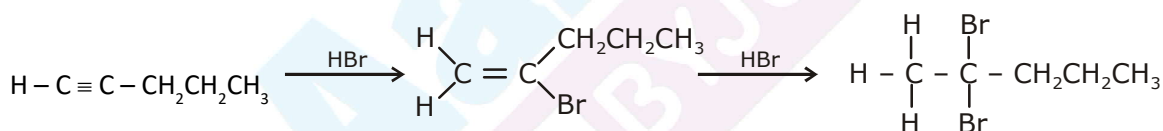


addition)

(III) Addition of hydrogen halides (Where $HX = HCl, HBr, HI$)

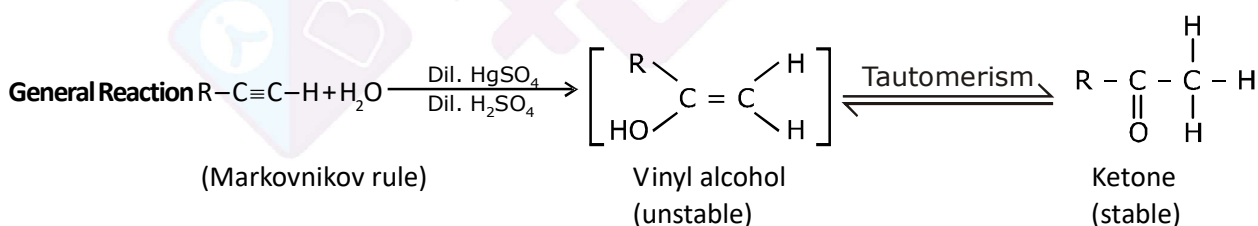


e.g.



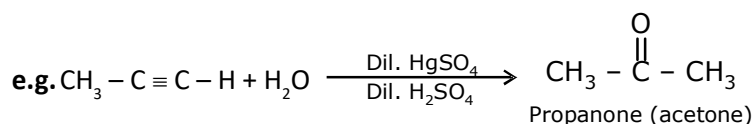
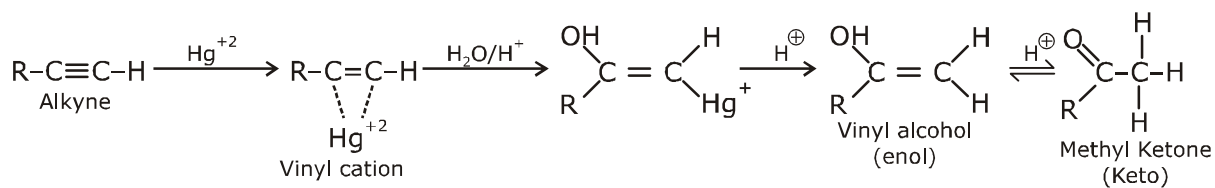
(IV) Addition of water

(a) Mercuric ion catalyzed hydration:



Electrophilic addition of mercuric ion gives a vinyl cation, which reacts with water and loses a proton to give an organomercuri alcohol. Under the acidic reaction condition, Hg is replaced by hydrogen to give a vinyl alcohol, called an enol.

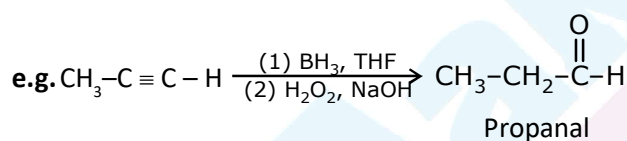
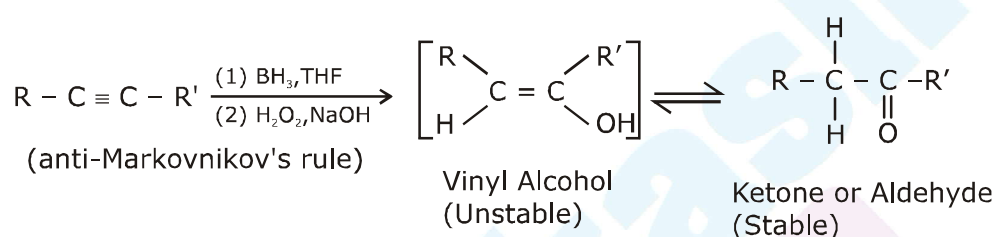
Mech.



(b) Hydroboration-oxidation:

In alkyne, except that a hindered dialkylborane must be used to prevent addition of two molecules of borane across the triple bond.

General Reaction

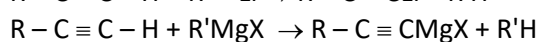
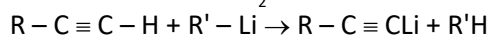
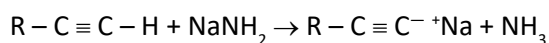


| Reactant | Product obtained by | |
|---|---|---|
| | Hydroboration oxidation | Hg ²⁺ ion-catalysed hydration |
| (a) $\text{CH}_3\text{C}\equiv\text{CCH}_3$ | $\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}_2\text{CH}_3$ | $\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}_2\text{CH}_3$ |
| (b) $\text{C}\equiv\text{CH}$ | CH_2CHO | |

(V) Formation of alkylide anions (Alkynides)

Sodium, lithium and magnesium alkynide

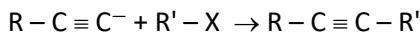
General Reaction



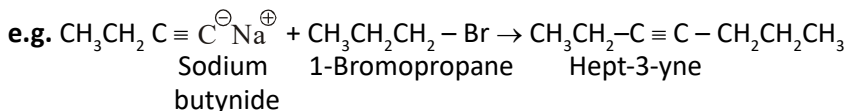


(VI) Alkylation of alkylide ions

General Reaction

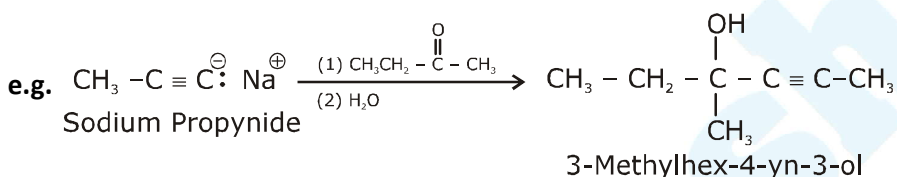
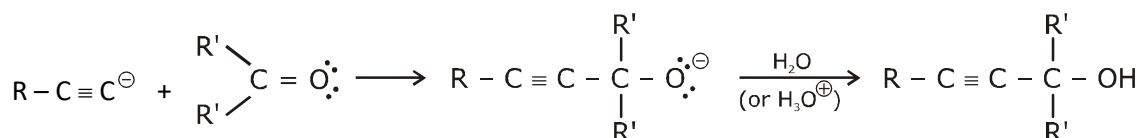


(R' - X must be an unhindered primary halide or tosylate)



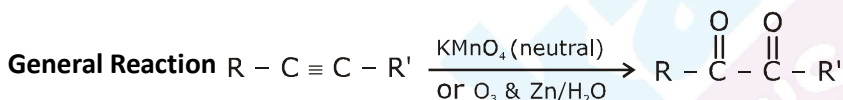
(VII) Reactions with carbonyl groups

General Reaction

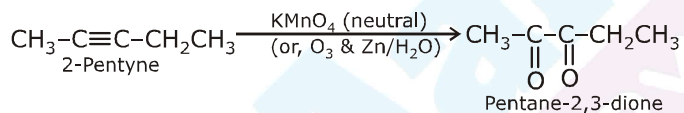


(VIII) Oxidation of alkyne

If an alkyne is treated with aqueous $KMnO_4$ under nearly neutral conditions, an α -diketone results.

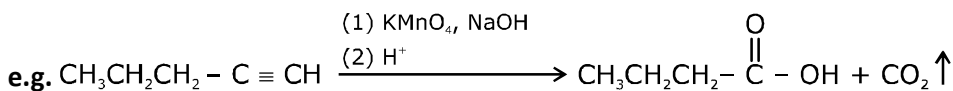
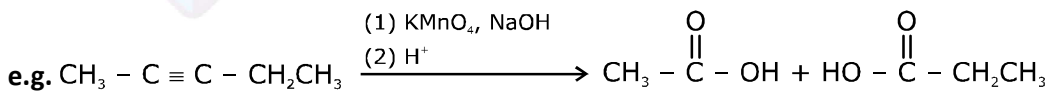
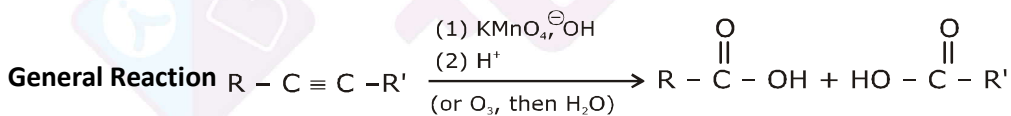


e.g.

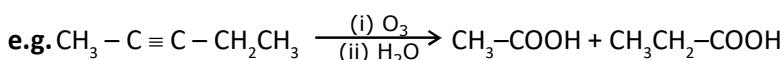
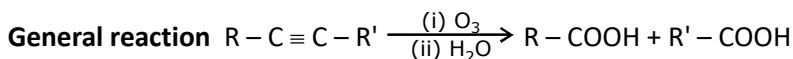


(IX) Oxidative cleavage

If the reaction mixture becomes warm or too basic the diketone undergoes oxidative cleavage. The products are the salts of carboxylic acids, which can be converted to the free acids by adding dilute acid.



Ozonolysis :





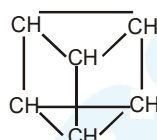
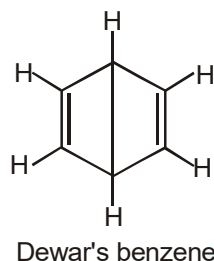
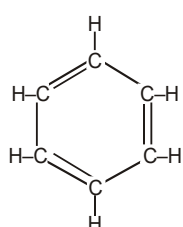
AROMATIC COMPOUNDS

BENZENE

Introduction :

All organic compounds classify into two broad classes, aliphatic compounds and aromatic compounds. Aromatic compounds are those that resemble with benzene in chemical behaviour.

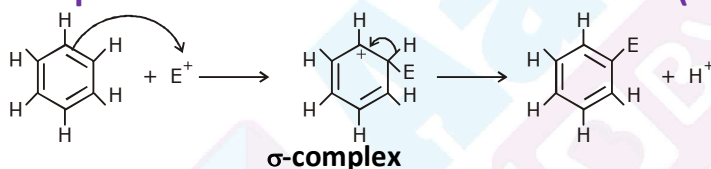
Proposed structure of benzene :



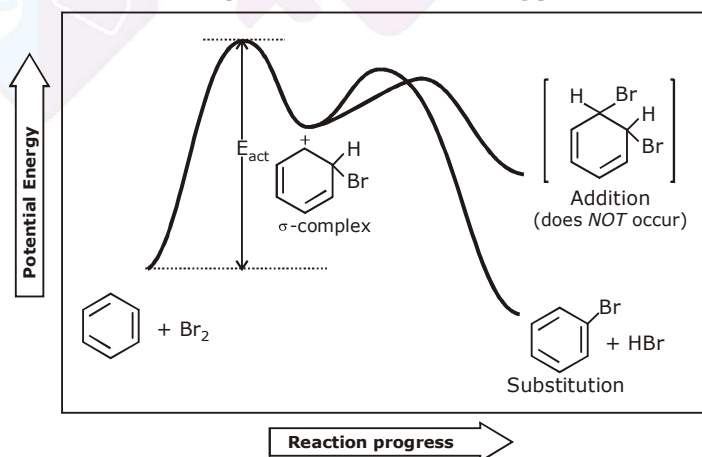
[Prism like structure proposed by Albert Ladenberg]

* Benzene mostly represents by Kekule structure.

Electrophilic aromatic substitution reaction (AR_5E reaction)

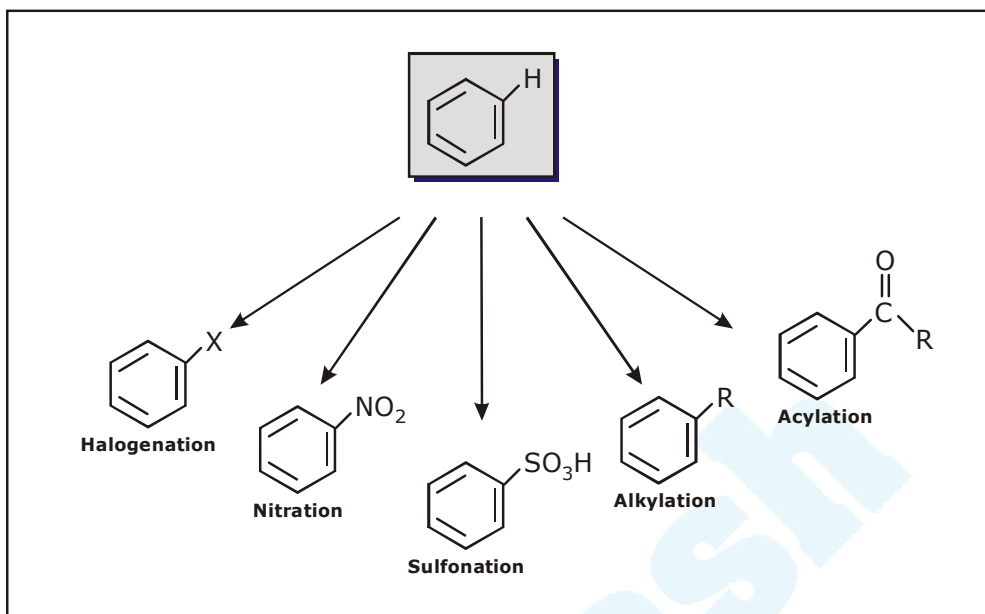


A reaction energy diagram for the electrophilic bromination of benzene
The reaction occurs in two steps and releases energy





Some Electrophilic Aromatic substitution Reactions of Benzene :



- (i) **Ortho- and para-directing activators** : Groups like -OH and -NH_2 present on a ring direct an electrophile, E^+ , to ortho or para position and they react faster than benzene.
 - (ii) **Ortho- and para-directing deactivators** : Halogens present on a ring direct an electrophile, E^+ , to ortho or para positions, and they react slower than benzene.
 - (iii) **Meta-directing deactivators** : Groups containing a carbonyl ($>\text{C} = \text{O}$) or a -CN group direct an electrophile, E^+ , to the meta positions, but they react slower than benzene.
- No meta-directing activators are known. Figure 5.8 shows how the directing effects of the groups correlate with their reactivities. All meta directing groups are deactivating and most ortho - and para - directing groups are activating. The halogens are unique in being ortho and para directing and deactivating.

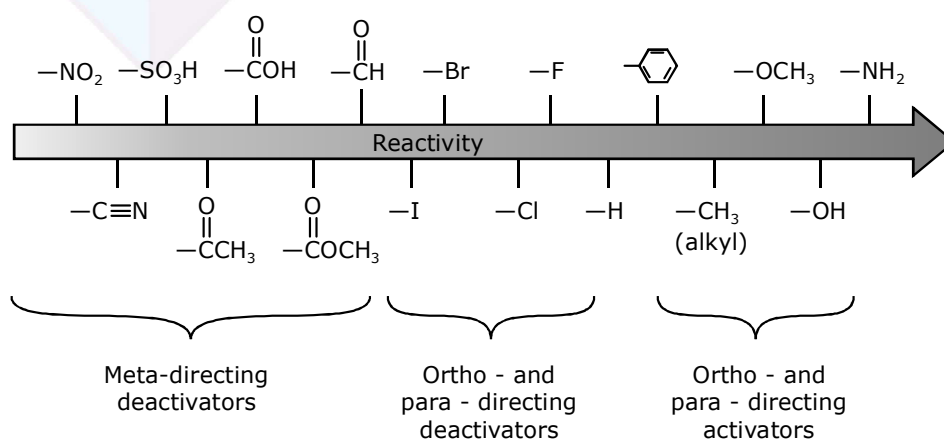
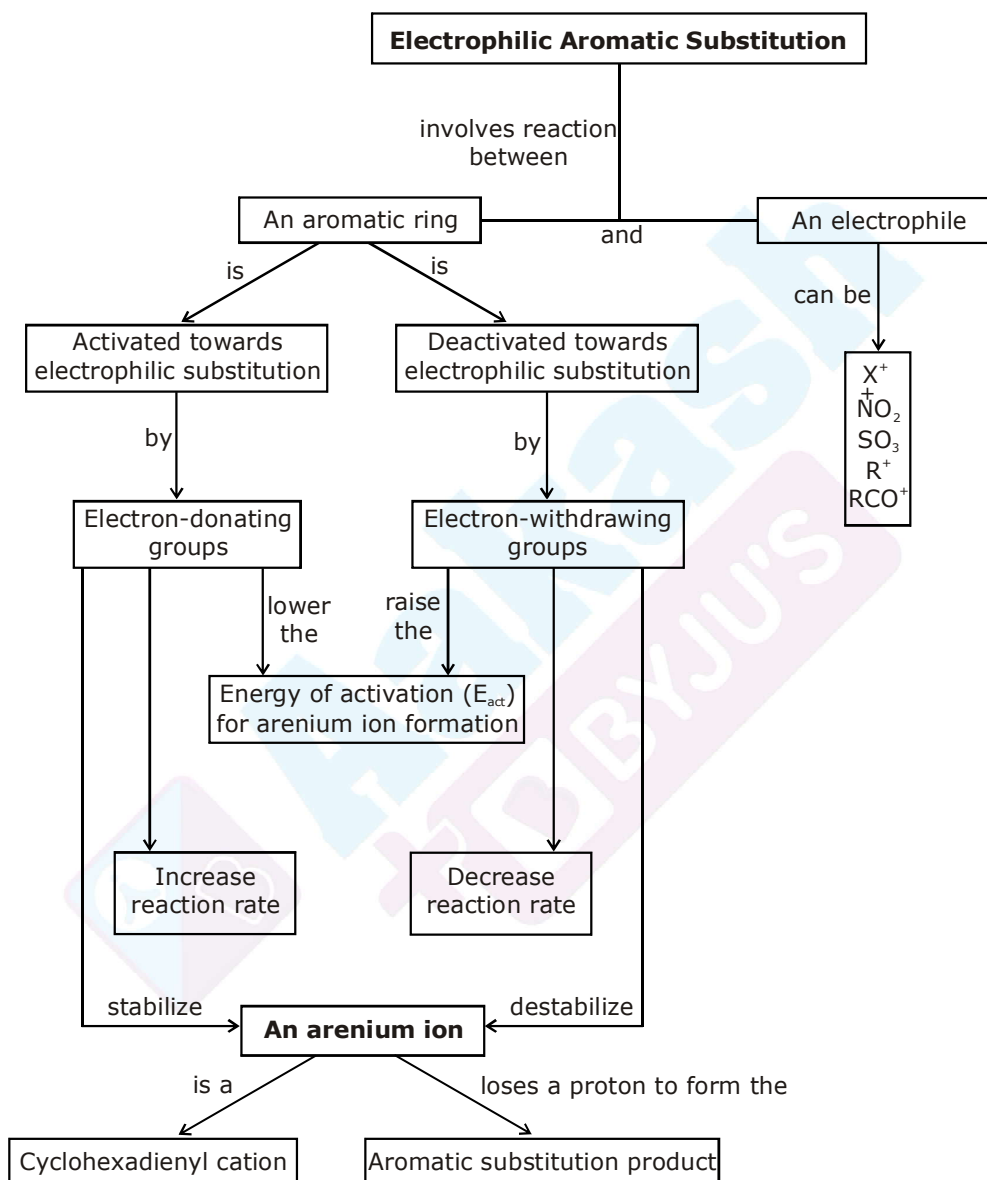




Figure: Effects of Substituents in electrophilic aromatic substitutions. All activating groups are ortho - and para - directing, and all deactivating groups other than halogen are meta-directing. The halogens are ortho and para-directing deactivators.

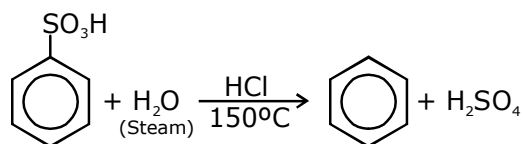
Concept Map :



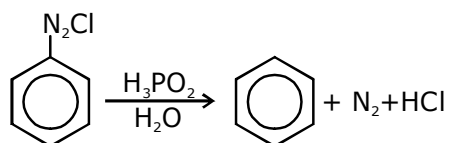


Method of Preparation of Benzene :

(I) **From Sulphonic Acid:** When benzene sulphonic acid is heated with steam under pressure benzene is formed.

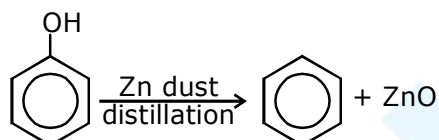


(II) **From Diazonium Salts:**

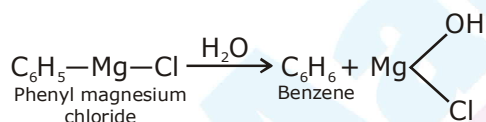


When benzene diazonium chloride undergoes reduction with H_3PO_2 in presence of H_2O , benzene is formed.

(III) **From phenol:** When phenol is distilled with zinc dust, benzene is formed.

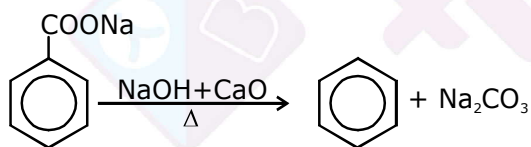


(IV) **From Grignard Reagent:**



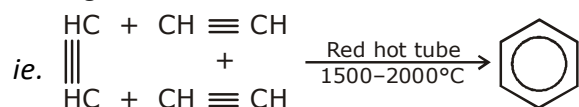
Note: $\text{C}_6\text{H}_5\text{—Cl} \xrightarrow[\text{dry ether}]{\text{Mg}} \text{C}_6\text{H}_5\text{—MgCl}$

(V) **From Decarboxylation of Sodium Benzoate:**



Note: Benzene is prepared in the laboratory by heating the mixture of sodalime and sodium benzoate. This reaction is called decarboxylation.

(VI) **From Acetylene: [Synthesis]** Acetylene polymerizes to give benzene when passed through a heated metallic tube.



Note: (i) This reaction is called cyclic polymerisation.

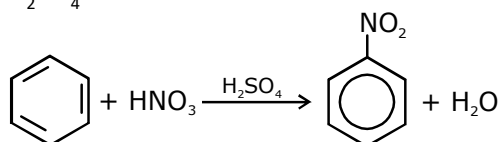
(ii) Red hot tube or a tube containing a complex organo-nickel catalyst at 70°C .



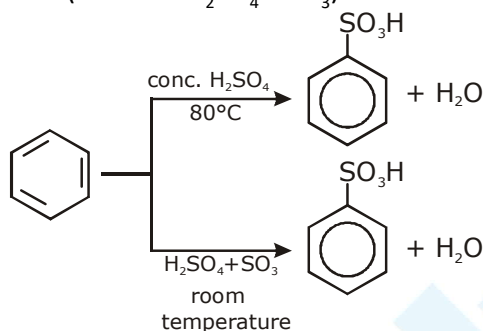
Chemical reactions of Benzene

The characteristic reaction of benzene are aromatic substitution. In these reaction one of the ring hydrogen is replaced by some other group.

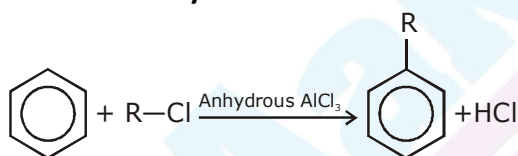
(I) Nitration: The treatment of benzene with conc. HNO_3 in the presence of concentrated H_2SO_4 . Then nitrobenzene is formed.



(II) Sulphonation: The treatment of benzene with conc. H_2SO_4 at 80°C or fuming sulphuric acid (i.e conc. $\text{H}_2\text{SO}_4 + \text{SO}_3$) at room temperature.

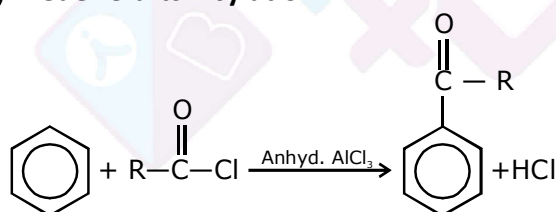


(III) Friedel-Crafts Alkylation:



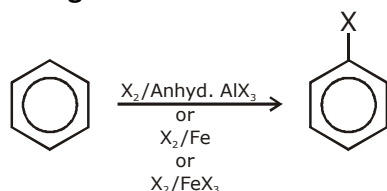
This involves the treatment of benzene with alkyl chlorides in the presence of anhydrous AlCl_3 .

(IV) Friedel-Crafts Acylation:



The treatment of benzene with acyl chlorides in the presence of anhydrous AlCl_3 .

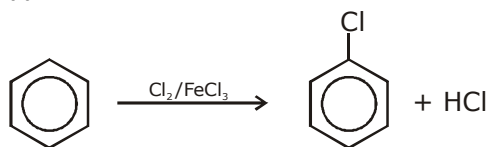
(V) Halogenation:



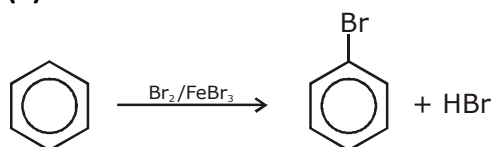


Example:

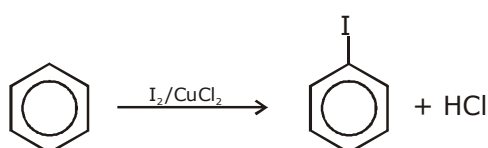
(i) Chlorination:



(ii) Bromination:



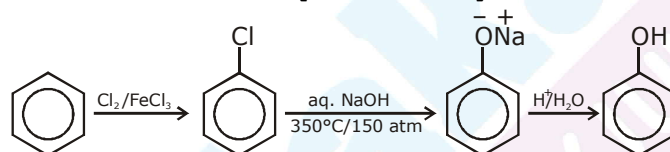
(iii) Iodination:



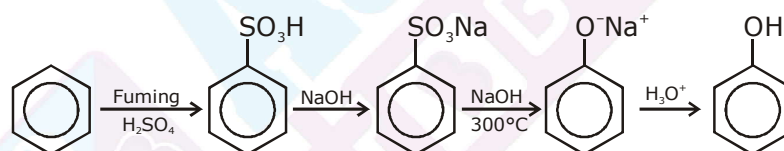
Note: Fluorobenzene cannot be prepared by a direct method.

(VI) Phenol From Benzene:

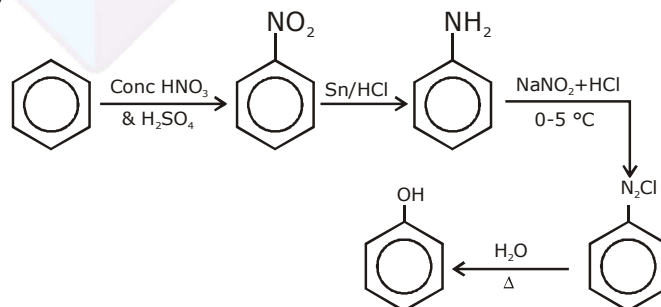
(i) From Chlorobenzene: [Dow Process]



(ii) From Benzene Sulphonic Acid:

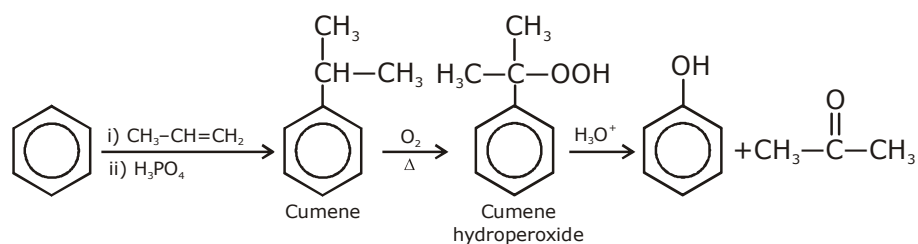


(iii) From Benzene Diazonium Chloride:



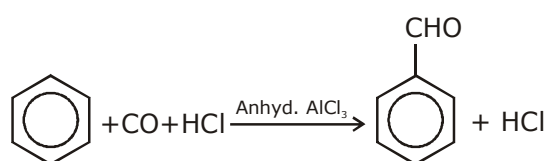


(iv) From Cumene Hydroperoxide: [Cumene Process]



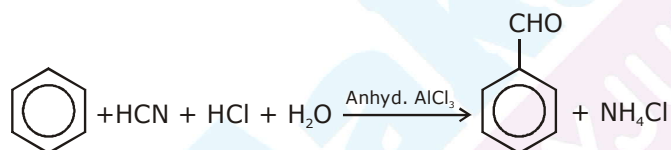
(VII) Benzaldehyde From benzene:

1. Method:- Gattermann-Koch Synthesis:



This reaction involves the treatment of benzene with carbon monoxide and hydrogen chloride (CO + HCl) in the presence of anhydrous AlCl₃ catalyst.

2. Method: Gattermann-Aldehyde Synthesis:



This reaction involves the treatment of benzene with (HCN + HCl + H₂O) in the presence of anhydrous AlCl₃ catalyst.