ORGANIC COMPOUNDS

1. **Organic Compounds:** There exist a large number of organic compounds. The property of carbon responsible to form so many compounds is due to following reasons:
    1. **Tendency to form multiple bonds:** Carbon has covalency of four and forms multiple bonds (double bonds and triple bonds) with other carbon atoms, oxygen and nitrogen.
    2. **Stability of bonds:** Carbon forms stable bonds with elements having electronegativity close to it.
    3. **Catenation:** Ability of carbon to bond successively with other carbon atoms to form chains of varying lengths and shapes. This property of carbon is called as catenation and it is one of the main reasons of carbon to form so many compounds.

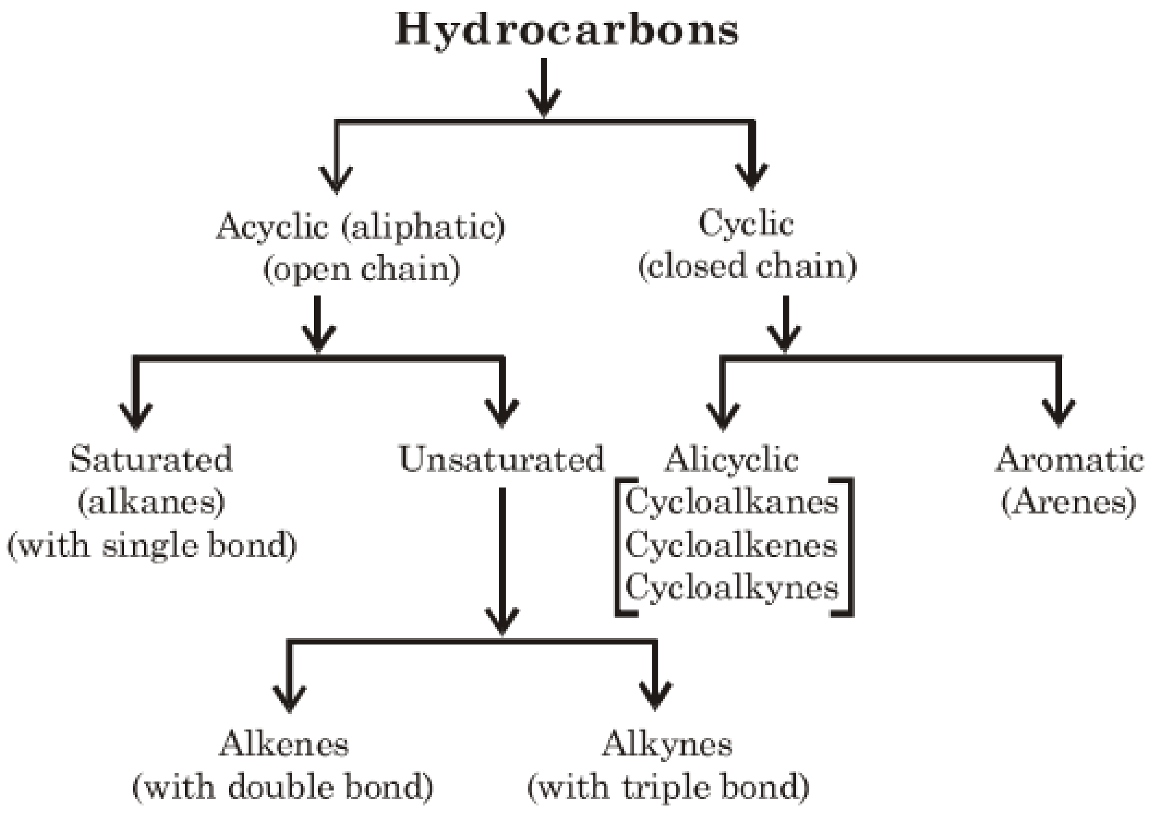
4. **Isomerism:** Compounds having same molecular formula but different structural formula are called isomers and this phenomenon is called as isomerism. Such as Molecular formula C_2H_6O represents two different compounds.

CH_3-CH_2-OH $\quad$ CH_3-O-CH_3

Ethyl alcohol $\quad$ Dimethyl ether.

2. **Hydrocarbons:** Hydrocarbons are the organic compounds having carbon atoms and hydrogen atoms only.

Classification of hydrocarbons

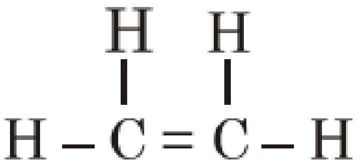


A. **Acyclic or aliphatic or open chain hydrocarbons :** These hydrocarbons contains open chain of carbon atoms in their molecules.

- (a) **Saturated aliphatic hydrocarbons:** These compounds have carbon atoms linked to another by single bonds. Alkanes are saturated aliphatic hydrocarbons having general formula C_nH_{2n+2}. Such as methane (CH_4), ethane (C_2H_6), propane (C_3H_8) etc.

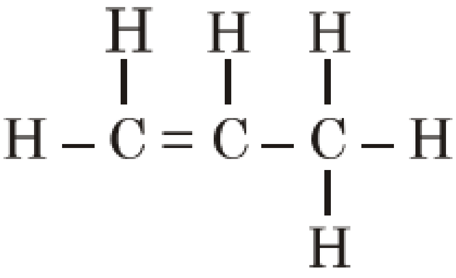
- (b) **Unsaturated aliphatic hydrocarbons:** Unsaturated compounds have carbon atoms bonded either through double bond (in alkenes) or through triple bond (in alkynes).

Alkenes (C_nH_{2n})



$$\mathrm{H-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H}$$

Ethene (C_2H_4)



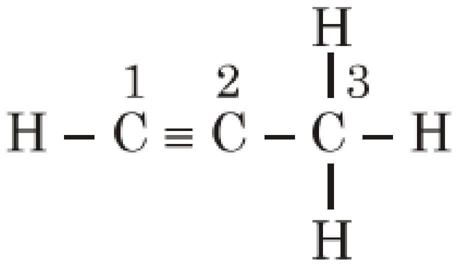
$$\mathrm{H-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-\underset{\underset{H}{|}}{\overset{H}{\overset{|}{C}}}-H}$$

Propene (C_3H_6)

Alkynes (C_nH_{2n-2})

$H-C\equiv C-H$

Ethyne (C_2H_2)



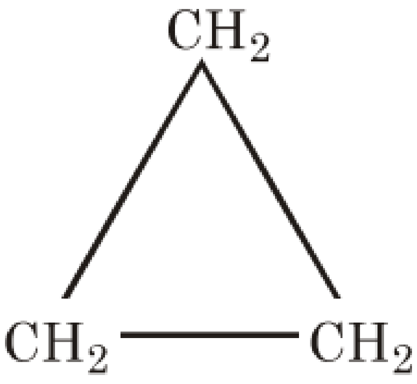
$$H-\overset{1}{C}\equiv\overset{2}{C}-\overset{\overset{H}{|}\,3}{\underset{\underset{H}{|}}{C}}-H$$

Propyne (C_3H_4)

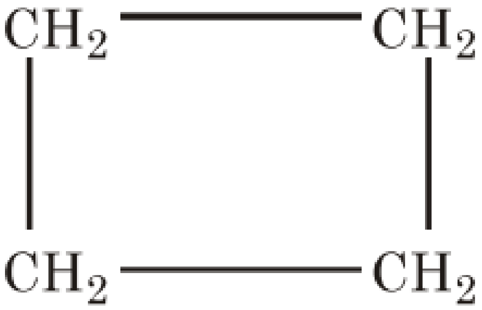
B. Cyclic or closed chain hydrocarbons : Cyclic hydrocarbons have their both the ends joined. These compounds may be saturated or unsaturated.

(a) Alicyclic: These are the cyclic hydrocarbons having properties similar to corresponding aliphatic hydrocarbons. These are classified into following types:

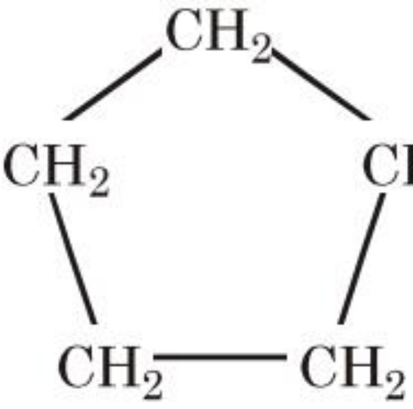
(i) Cycloalkanes: Cycloalkanes are saturated alicyclic hydrocarbons.



Cyclopropane

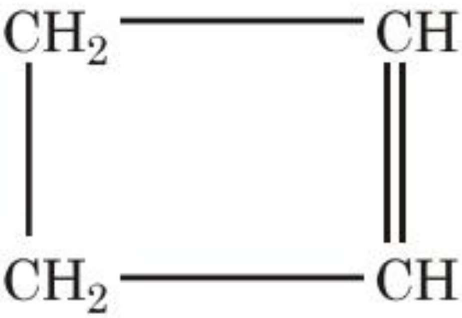


Cyclobutane

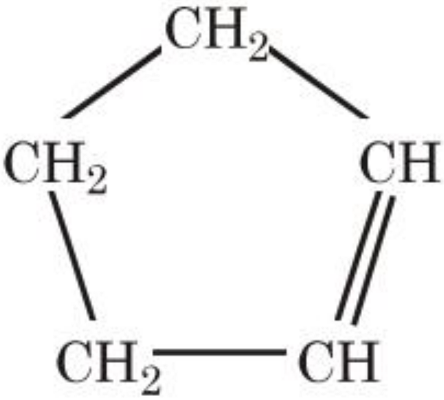


Cyclopentane

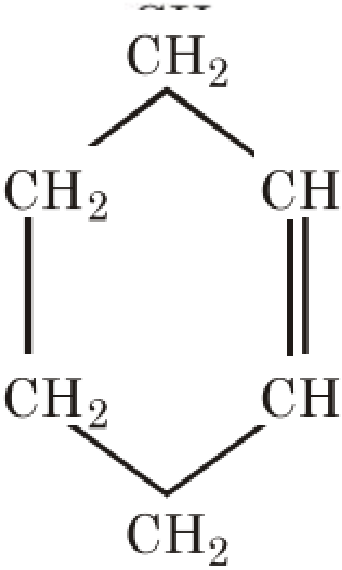
(*ii*) ***Cycloalkenes:*** Cycloalkenes are unsaturated hydrocarbons containing one carbon-carbon double bond.



Cyclobutene

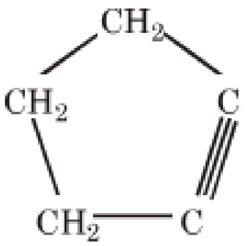


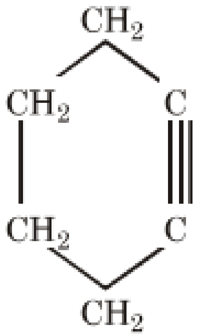
Cyclopentene



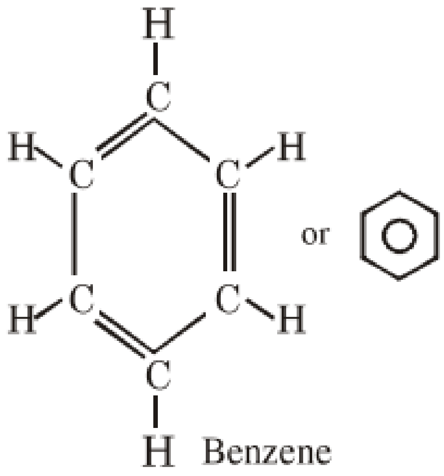
Cyclohexene

(*iii*) *Cycloalkynes:* Cycloalkynes are unsaturated hydrocarbons containing one carbon-carbon triple bond.

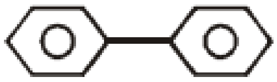

Cyclopentyne

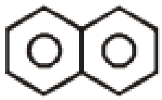

Cyclohexyne

(b) Aromatic hydrocarbons: Benzene is the parent hydrocarbon having six carbon atoms with alternate single and double bonds. Aromatic hydrocarbons are those compounds which contain one or more benzene rings either fused or isolated in their molecules.



Benzene


Diphenyl or biphenyl


Naphthalene


Anthracine

3. **Homologous Series:** A homologous series is a class of organic compounds in which adjacent members differ by CH_2 unit. Individual member is called homologue and this phenomenon is called homology.

4. **Nomenclature of organic compounds:** Now-a-days, naming of organic compounds is done according to a set of rules laid down by International Union of Pure and Applied Chemistry (IUPAC), according to which, name of an organic compound has three parts :

   (i) Word root (ii) Suffix (iii) Prefix

(*i*) Word root: Word root signifies the number of carbon atoms in principal chain of organic compounds, as follows:

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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_4	But–	C_{14}	Tetradec–
C_5	Pent–	C_{15}	Pentadec–
C_6	Hex–	C_{16}	Hexadec–
C_7	Hept–	C_{17}	Heptadec–
C_8	Oct–	C_{18}	Octadec–
C_9	Non–	C_{19}	Nonadec–
C_{10}	Dec–	C_{20}	Icosa–

(*ii*) Suffix

(a) ***Primary suffix:*** It indicated the saturated or insturated nature of principal carbon chain.

Principal carbon chain	Primary suffix
C – C (Saturated)	–ane
C = C (Unsaturated)	–ene
C ≡ C (Unsaturated)	–yne

If principal carbon chain has two, three or more double or triple bonds, following suffix are used.

Number of bonds	Double bond	Triple bond
2	– diene	– diyne
3	– triene	– triyne

(a) **Secondary suffix:** It indicated the type of functional group present in the organic compound.

Class of organic compounds	Functional group	Secondary suffix
Alcohols	–OH	– ol
Aldehydes	–CHO	– al
Ketones	>CO	– one
Carboxylic acids	–COOH	– oic acid
Esters	–COOR	alkyl ... oate

Acid amides	$-CONH_2$	– amide
Acid chlorides	$-COCl$	– oly chloride
Amines	$-NH_2$	– amine
Imines	$=NH$	– imine
Thio alcohols	$-SH$	– thiol
Nitriles	$-CN$	– nitrile

The terminal 'e' of primary suffix is dropped if secondary suffix starts with a vowel. However, if secondary suffix starts with a consonant, then the terminal 'e' of primary suffix is retained.

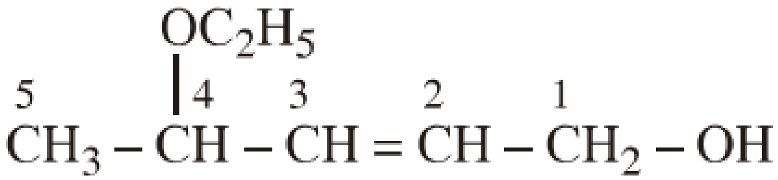
(*iii*) Prefix : Certain groups which are considered as substituents are indicated by prefixes. Prefixes are added immediately before the word root.

Substituent groups	**Prefix**	**Substituent groups**	**Prefix groups**
$-CH_3$	Methyl	$-F$	Fluoro
$-C_2H_5$	Ethyl	$-Cl$	Chloro
$-C_3H_7$	Propyl	$-Br$	Bromo
$-C_6H_5$	Phenyl	$-I$	Iodo
$-CH(CH_3)_2$	Iso-propyl	$-NO_2$	Nitro
$-C(CH_3)_3$	t-Butyl	$-NO$	Nitroso
$-OCH_3$	Methoxy	$-N=N-$	Diazo
$-OC_2H_5$	Ethoxy	$-OH$	Hydroxo

Hence complete IUPAC name of an organic compound can be written as follows:

Prefix + Word root + Primary suffix + Secondary suffix → IUPAC name

(i)



$$\overset{5}{CH_3} - \overset{\overset{OC_2H_5}{|\,4}}{CH} - \overset{3}{CH} = \overset{2}{CH} - \overset{1}{CH_2} - OH$$

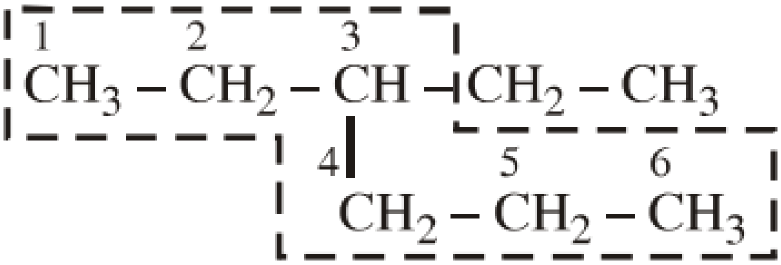
Here, Prefix : Ethoxy
Word root : Pent –
Primary suffix : –ene
Secondary suffix : –ol
Hence, IUPAC name : 4–ethoxy–2–pentenol.

Nomenclature of Saturated Hydrocarbons (Alkanes)

Alkanes are those aliphatic hydrocarbons which contain single covalent bond between carbon atoms. Following rules are given below:

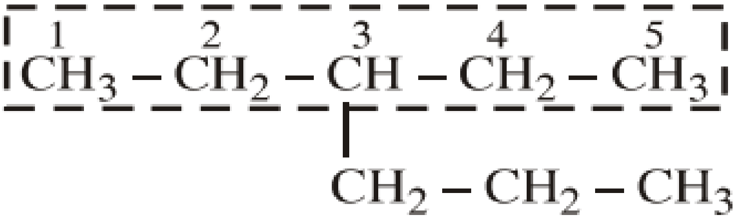
Rule1. Longest chain rule

Select the longest continuous chain, having maximum number of carbon atoms in the molecule. This chain is known as parent chain and word root is selected according to this chain. The other parts not included in the parent chain are considered as substituents.



$$\overset{1}{CH_3} - \overset{2}{CH_2} - \underset{\underset{\overset{4}{CH_2} - \overset{5}{CH_2} - \overset{6}{CH_3}}{|}}{\overset{3}{CH}} - CH_2 - CH_3$$

Correct chain
Chain Containing 6 C-atoms)

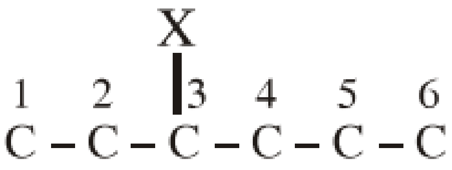


$$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{\underset{\displaystyle CH_2-CH_2-CH_3}{\underset{|}{CH}}}-\overset{4}{CH_2}-\overset{5}{CH_3}$$

Incorrect chain
Chain Containing 5 C-atoms)

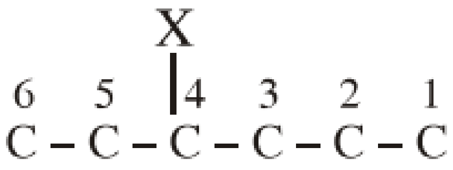
Rule 2. Lowest set of locants

Number the parent chain, starting from the end, in such a way that carbon atom linked to substituent gets the lowest possible number.



$$\overset{1}{C}-\overset{2}{C}-\overset{\displaystyle X}{\overset{|3}{C}}-\overset{4}{C}-\overset{5}{C}-\overset{6}{C}$$

Correct

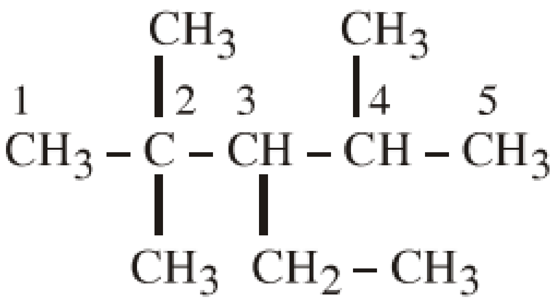


$$\overset{6}{C}-\overset{5}{C}-\overset{\displaystyle X}{\overset{|4}{C}}-\overset{3}{C}-\overset{2}{C}-\overset{1}{C}$$

Incorrect

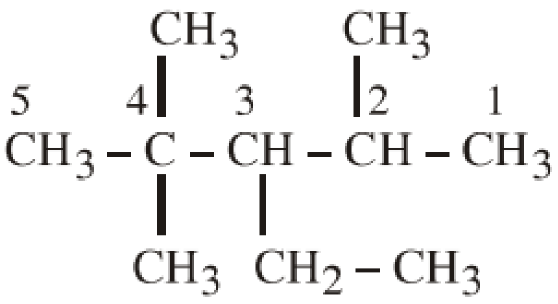
Rule 3. Lowest sum rule

If more than one substituents are attached to the longest continuous carbon chain, the numbering is done in such a way that sum of numbers given to substituents is the lowest.



$$\overset{1}{CH_3}-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|2}{C}}}}-\underset{\displaystyle CH_2-CH_3}{\underset{|}{\overset{3}{CH}}}-\overset{\displaystyle CH_3}{\overset{|4}{CH}}-\overset{5}{CH_3}$$

(Correct)



$$\overset{5}{CH_3}-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{4|}{C}}}}-\underset{\displaystyle CH_2-CH_3}{\underset{|}{\overset{3}{CH}}}-\overset{\displaystyle CH_3}{\overset{|2}{CH}}-\overset{1}{CH_3}$$

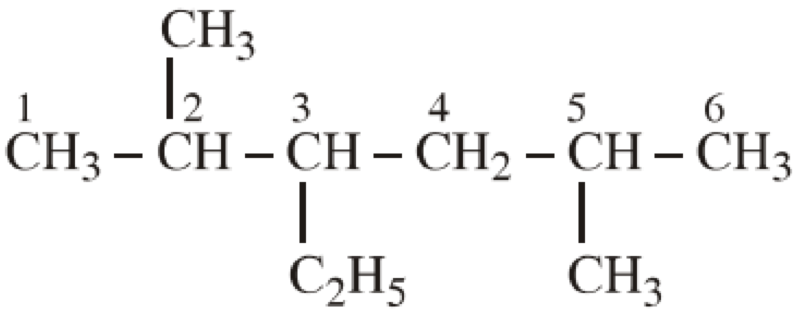
(Incorrect)

Sum of locants = 2 + 2 + 3 + 4 = 11

Sum of locants = 2 + 3 + 4 + 4 = 13

According to latest rule, if two sets of locants are possible for same chain then the set having lowest number at first point of difference is correct even if it violates the lowest sum rule. Such as,

I.

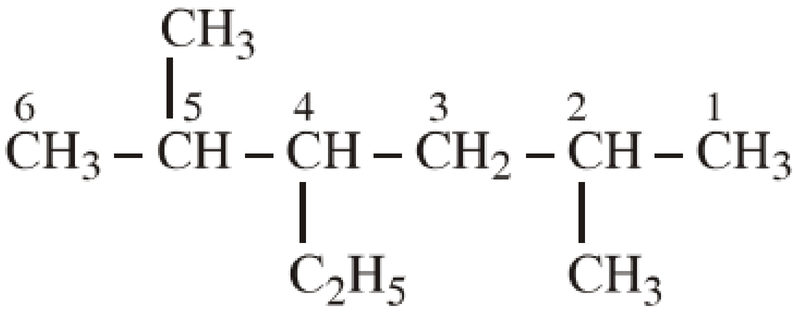


$$\overset{1}{CH_3}-\overset{CH_3}{\underset{2}{\overset{|}{CH}}}-\underset{C_2H_5}{\underset{|}{\overset{3}{CH}}}-\overset{4}{CH_2}-\underset{CH_3}{\underset{|}{\overset{5}{CH}}}-\overset{6}{CH_3}$$

(Correct)

Set of locants = 2, 3, 5

II.



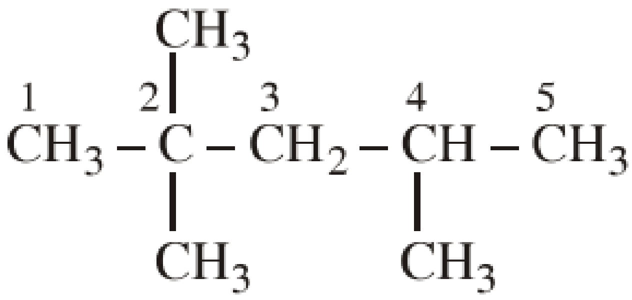
$$\overset{6}{CH_3}-\overset{CH_3}{\underset{5}{\overset{|}{CH}}}-\underset{C_2H_5}{\underset{|}{\overset{4}{CH}}}-\overset{3}{CH_2}-\underset{CH_3}{\underset{|}{\overset{2}{CH}}}-\overset{1}{CH_3}$$

(Incorrect)

Set of locants = 2, 4, 5

On comparing these two sets first number is same 2, 2. At first point of difference 3 of A is lower than 4 of B, so set of locants of structure A is correct.

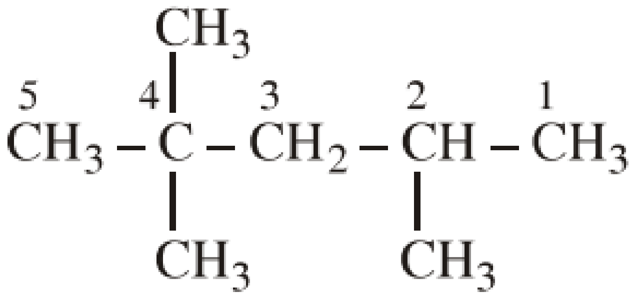
I.



$$\overset{1}{C}H_3-\overset{2}{\underset{CH_3}{\overset{CH_3}{C}}}-\overset{3}{C}H_2-\overset{4}{\underset{CH_3}{C}}H-\overset{5}{C}H_3$$

(Correct)
Set of locants = 2, 2, 4

II.



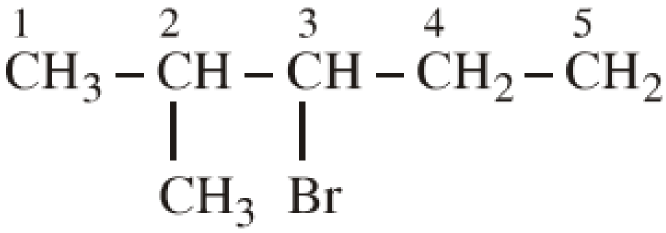
$$\overset{5}{C}H_3-\overset{4}{\underset{CH_3}{\overset{CH_3}{C}}}-\overset{3}{C}H_2-\overset{2}{\underset{CH_3}{C}}H-\overset{1}{C}H_3$$

(Incorrect)
Set of locants = 2, 4, 4

Comparing these two sets first number is same 2, 2. At first point of difference (2, 4), 2 of structure A is lower than 4 of structure B, so set of locants of structure A is correct.

Rule 4. Naming of different substituents

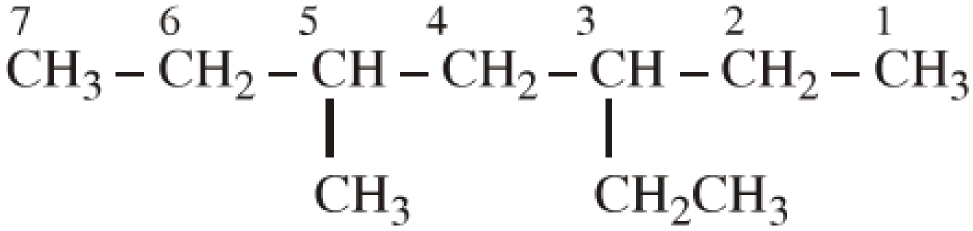
(*a*) When two or more than two substituents are present on the parent chain, they are arranged in alphabetical order irrespective of their positional number.



$$\overset{1}{CH_3}-\underset{\displaystyle CH_3}{\overset{2}{CH}}-\underset{\displaystyle Br}{\overset{3}{CH}}-\overset{4}{CH_2}-\overset{5}{CH_2}$$

3- bromo-2-methylpentane (correct)
2-methyl-3-bromopentane (wrong)

(*b*) When two different substituents are present at equivalent positions, the substituent first in alphabetical order gets the lower number.



$$\overset{7}{CH_3}-\overset{6}{CH_2}-\underset{\displaystyle CH_3}{\overset{5}{CH}}-\overset{4}{CH_2}-\underset{\displaystyle CH_2CH_3}{\overset{3}{CH}}-\overset{2}{CH_2}-\overset{1}{CH_3}$$

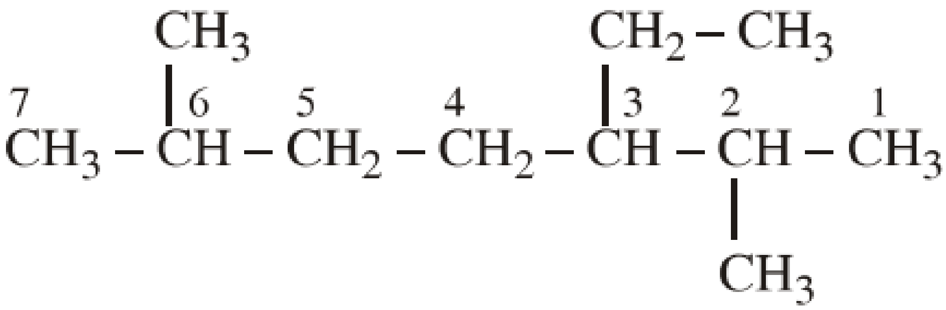
3-ethyl-5-methyl heptane (correct)
5-ethyl-3-methyl heptane (wrong)

Rule 5.

For same substituents occuring more than once, perfixes di, tri, tetra, etc. are used. Which are not considered while deciding alphabetical order.

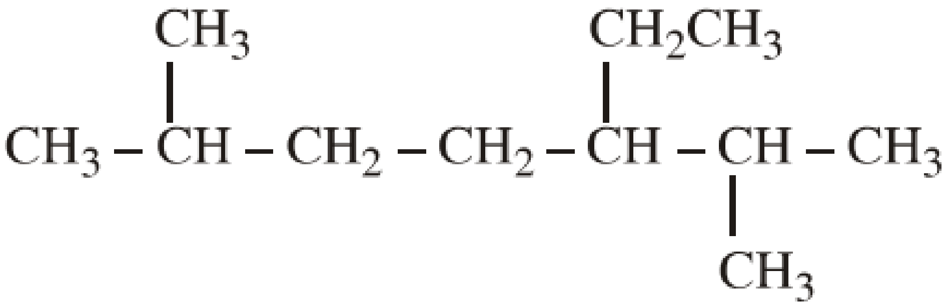
Rule 6.

If two possiblities are there for the same length of parent chain, number the compound so as to get maximum number of side chains or alkyl groups.



$$\overset{7}{\mathrm{CH_3}}-\overset{\overset{\mathrm{CH_3}}{|}}{\overset{6}{\mathrm{CH}}}-\overset{5}{\mathrm{CH_2}}-\overset{4}{\mathrm{CH_2}}-\overset{\overset{\mathrm{CH_2-CH_3}}{|}}{\overset{3}{\mathrm{CH}}}-\underset{\underset{\mathrm{CH_3}}{|}}{\overset{2}{\mathrm{CH}}}-\overset{1}{\mathrm{CH_3}}$$

(Correct)
3-ethyl-2, 6-dimethyl heptane (3 side chains)

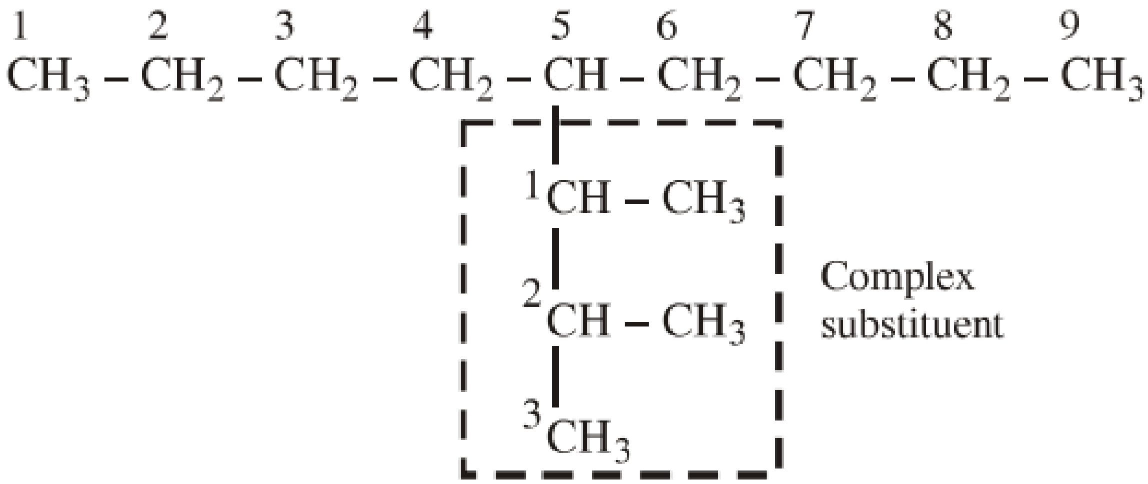


$$\mathrm{CH_3}-\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{CH}}-\mathrm{CH_2}-\mathrm{CH_2}-\overset{\overset{\mathrm{CH_2CH_3}}{|}}{\mathrm{CH}}-\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{CH}}-\mathrm{CH_3}$$

(Incorrect)
5-isopropyl-2, 6-methyl heptane (2 side chains)

Rule 7.

When the substituent on the parent chain is complex, then it is numbered separately and carbon atom to which this substituent is linked to parent chain is numbered as 1. The name of complex substituent is written in bracket.



5–(1, 2- dimethyl propyl) nonane

Nomenclature of Alkenes

The general rules for nomenclature of alkenes are exactly the same as for alkanes, with only following differences –

(*a*) Double bond should be in the longest continuous parent carbon chain.

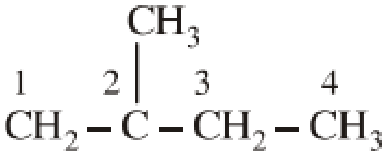
(*b*) Numbering of carbon atoms should be done in such a way that double bond gets the lowest possible number.

(*c*) Suffix 'ane' is replaced by 'ene'.

Molecular formula	IUPAC name (Common name)
$CH_2=CH_2$	Ethene (Ethylene)
$CH_3-CH=CH_2$	1-Propene (Propylene)
$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{CH}=\overset{1}{CH_2}$	1-Butene (α- Butylene)

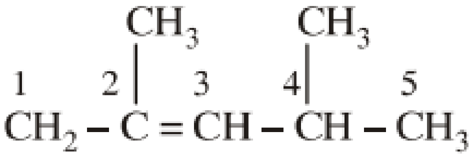
$\overset{4}{\mathrm{CH_3}}-\overset{3}{\mathrm{CH}}=\overset{2}{\mathrm{CH}}-\overset{1}{\mathrm{CH_2}}$

2-Butene (β-Butylene).



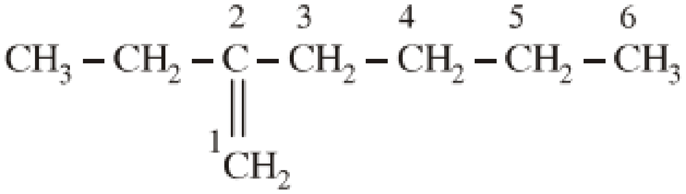
$\overset{1}{\mathrm{CH_2}}-\overset{\overset{\mathrm{CH_3}}{|}}{\overset{2}{\mathrm{C}}}-\overset{3}{\mathrm{CH_2}}-\overset{4}{\mathrm{CH_3}}$

2-methyl-1-butene.



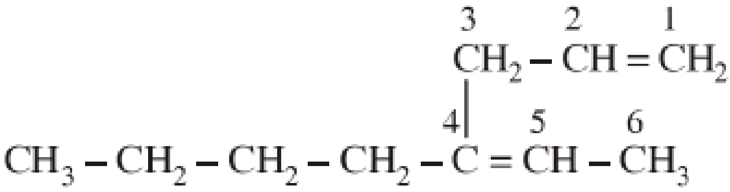
$\overset{1}{\mathrm{CH_2}}-\overset{\overset{\mathrm{CH_3}}{|}}{\overset{2}{\mathrm{C}}}=\overset{3}{\mathrm{CH}}-\overset{\overset{\mathrm{CH_3}}{|}}{\overset{4}{\mathrm{CH}}}-\overset{5}{\mathrm{CH_3}}$

2,4-dimethyl-2-pentene



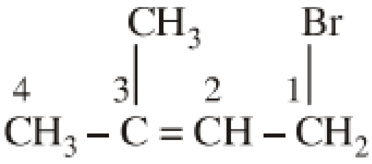
$\mathrm{CH_3}-\mathrm{CH_2}-\underset{\underset{\overset{1}{\mathrm{CH_2}}}{\|}}{\overset{2}{\mathrm{C}}}-\overset{3}{\mathrm{CH_2}}-\overset{4}{\mathrm{CH_2}}-\overset{5}{\mathrm{CH_2}}-\overset{6}{\mathrm{CH_3}}$

2-ethyl-2-hexene.



$\mathrm{CH_3}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_2}-\overset{\overset{\overset{3}{\mathrm{CH_2}}-\overset{2}{\mathrm{CH}}=\overset{1}{\mathrm{CH_2}}}{|}}{\overset{4}{\mathrm{C}}}=\overset{5}{\mathrm{CH}}-\overset{6}{\mathrm{CH_3}}$

4-butyl-hexa-1, 4-diene

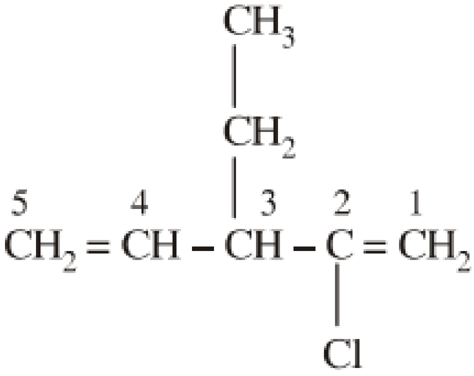


$\overset{4}{\mathrm{CH_3}}-\overset{\overset{\mathrm{CH_3}}{|}}{\overset{3}{\mathrm{C}}}=\overset{2}{\mathrm{CH}}-\overset{\overset{\mathrm{Br}}{|}}{\overset{1}{\mathrm{CH_2}}}$

1-bromo-3-methyl-
2-butene

$\overset{1}{\mathrm{CH_3}}-\overset{2}{\mathrm{CH}}=\overset{3}{\mathrm{C}}=\overset{4}{\mathrm{CH}}-\overset{5}{\mathrm{CH_2}}-\overset{6}{\mathrm{CH_3}}$

2, 3-hexadiene.



$\overset{5}{\mathrm{CH_2}}=\overset{4}{\mathrm{CH}}-\overset{\overset{\overset{\mathrm{CH_3}}{|}}{\overset{\mathrm{CH_2}}{|}}}{\overset{3}{\mathrm{CH}}}-\underset{\underset{\mathrm{Cl}}{|}}{\overset{2}{\mathrm{C}}}=\overset{1}{\mathrm{CH_2}}$

2-chloro-3ethyl-1,
4-pentadiene

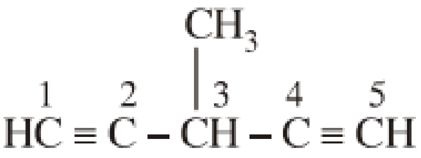
Nomenclature of Alkynes

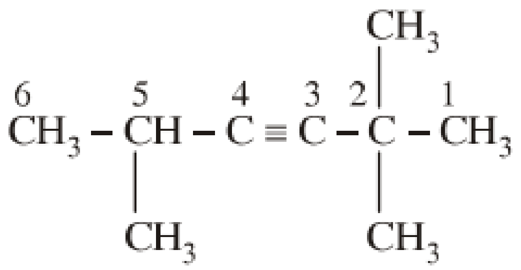
The general rules for nomenclature of alkynes are exactly the same as for alkanes, with only following differences:

(*a*) Triple bond should be in the longest continuous parent carbon chain.

(*b*) Numbering of carbon atoms should be done is such a way that triple bond gets the lowest possible number.

(*c*) Suffix 'ane' is replaced by 'yne'.

Molecular formula	IUPAC name (Common name)
$CH\equiv CH$	Ethyne (Acetylene)
$CH_3-C\equiv CH$	Propyne (Methyl acetylene)
$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{C}\equiv\overset{1}{CH}$	1-Butyne (Ethyl acetylene)
$\overset{4}{CH_3}-\overset{3}{C}\equiv\overset{2}{C}-\overset{1}{CH_3}$	2-Butyne (Dimethyl acetylene)
$CH\equiv C-CH_2-CH_2-Cl$	4-chloro-1-butyne.
 $\overset{1}{HC}\equiv\overset{2}{C}-\overset{3}{\underset{}{CH}}(CH_3)-\overset{4}{C}\equiv\overset{5}{CH}$	3-methyl penta-1, 4-diyne
$\overset{1}{HC}\equiv\overset{2}{C}-\overset{3}{CH}=\overset{4}{CH}-\overset{5}{C}\equiv\overset{6}{CH}$	Hex-3-ene-1, 5-diyne



$$\overset{6}{CH_3}-\underset{CH_3}{\overset{5}{CH}}-\overset{4}{C}\equiv\overset{3}{C}-\underset{CH_3}{\overset{CH_3}{\overset{2}{C}}}-\overset{1}{CH_3}$$

2,2,5-trimethyl-3-hexyne

---

5. **Isomerism:** Compounds which have the same molecular formula but different chemical or physical properties are called as isomers and this phenomenon is called as isomerism.

Types of isomerism

(*a*) Structural isomerism.

(*b*) Stereoisomerism.

(*a*) Structural isomerism: If isomerism is due to difference in the arrangement of atoms within the molecule, the phenomenon is called structural isomerism.

Types of structural isomerism

(*i*) Chain isomerism: Chain isomers have the same molecular formula but differ in the order in which the carbon atoms are bonded to each other.

(*ii*) Position isomerism: Position of a functional group on the carbon atom differs in position isomerism.

(*iii*) **Functional isomerism:** Functional isomers have the same molecular formula but different functional groups.

(*iv*) **Metamerism:** Unequal distribution of carbon atoms on either side of the functional group results in this type of isomerism.

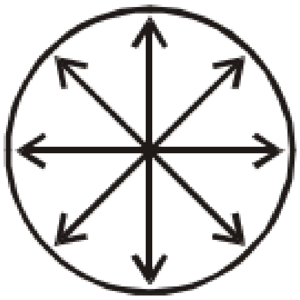
(*v*) **Tautomerism:** In this isomerism, isomers are in dynamic equilibrium with each other.

(*b*) **Stereoisomerism:** Isomerism caused due to its different arrangements of atoms in space is called as stereoisomerism.

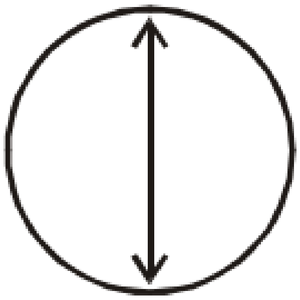
Types of stereoisomerism

(*i*) ***Geometrical isomerism:*** Geometrical isomerism results from a restriction in rotation about double bonds.

(*ii*) ***Optical isomerism:*** Atoms of optical isomers have different spatial arrangement. Optical isomers have the ability to rotate plane polarised light.



Ordinary light



Plane polarised light

6. **Optical activity and chairality:** Those compounds which have ability to rotate the plane of polarised light are optically active. This property of a compound is called **optical activity**.

The compound which rotates the plane of polarised light to the right, is called dextro-rotatory. The compound which rotates the plane of polarised light to the left, is called laevo-rotatory.

Plane of symmetry: A plane which divides a compound into two symmetrical halves, is known to be the plane of symmetry.

Chirality: The chiral atoms do not have any plane of symmetry and are not superimposable on its mirror image. This property is known as chirality.

Enantiomers: Non-superimposable mirror images are known as enantiomers. Enantiomers rotate the plane polarised light equally but in opposite directions.

7. **Conformations (Conformation isomers of alkanes):** Alkanes have carbon-carbon single sigma (σ) bond that is symmetrical about internuclear axis and is capable of free rotation. The various arrangements of atoms in a molecule that may arise due to free rotation about a single bond are known as conformations of the molecule. The conformational forms are as follows:
   - (*i*) **The eclipsed form:** In eclipsed form atoms are as close to each other as possible. The hydrogen atoms bonded with back carbon atoms are eclipsed by hydrogen atoms bonded with front carbon atoms.
   - (*ii*) **The staggered form:** In staggered form atoms are as far as possible.
   - (*iii*) **The skew form:** Except from these two forms there are a large number of possible arrangements in between these two forms which are known as skew forms.

Preparation of Alkanes

I. By hydrogenation of unsaturated hydrocarbons

$$\underset{\text{Alkene}}{R-CH=CH_2} + H_2 \xrightarrow[523\ -\ 573\ K]{\text{Ni or Pt or Pd}} \underset{\text{Alkane}}{R-CH_2-CH_3}$$

$$\underset{\text{Ethene}}{CH_2=CH_2} + H_2 \xrightarrow[523\ -\ 573\ K]{\text{Ni or Pt or Pd}} \underset{\text{Ethane}}{CH_3-CH_3}$$

$$\underset{\text{Alkyne}}{R-C\equiv CH} + 2H_2 \xrightarrow[523\ -\ 573\ K]{\text{Ni or Pt or Pd}} \underset{\text{Alkane}}{R-CH_2-CH_2}$$

$$\underset{\text{Ethyne}}{CH\equiv CH} + 2H_2 \xrightarrow[523\ -\ 573\ K]{\text{Ni or Pt or Pd}} \underset{\text{Ethane}}{CH_3-CH_3}$$

II. From alkyl halides

(*a*) By Wurtz reaction:

$$\underset{\text{Alkyl halide}}{R-}\boxed{X + \underset{\text{Sodium}}{2Na} + X}-R \xrightarrow{\text{Dry ether}} \underset{\text{Alkane}}{R-R} + 2NaX$$

$$\underset{\text{Bromomethane}}{CH_3-Br} + 2Na + Br-CH_3 \xrightarrow{\text{Dry ether}} \underset{\text{Ethane}}{CH_3-CH_3} + 2NaBr$$

Methane cannot be prepared by Wurtz reaction.

(*b*) By reduction with nascent hydrogen:

$$\underset{\text{Alkyl halide}}{R-X} + \underset{\text{Nascent hydrogen}}{2[H]} \rightarrow \underset{\text{Alkane}}{R-H} + HX$$

$$\underset{\text{Bromoethane}}{CH_3CH_2Br} + 2[H] \rightarrow \underset{\text{Ethane}}{CH_3{-}CH_3} + HBr$$

III. From aldehydes and ketones

$$\underset{\text{Propanone}}{CH_3COCH_3} + 2H_2 \xrightarrow{\text{Zn+conc.HCl}} \underset{\text{Propane}}{CH_3CH_2CH_3} + H_2O$$

$$\underset{\text{Ethanal}}{CH_3CHO} + 2H_2 \xrightarrow{\text{Zn+conc.HCl}} \underset{\text{Ethane}}{CH_3CH_3} + H_2O$$

IV. From carboxylic acid

(a) By decarboxylation (Removal of CO_2)

$$\underset{\text{Sodium carboxylate}}{R-COONa} + \underset{\text{Sodium hydroxide}}{NaOH} \xrightarrow{\text{CaO, 630 K}} \underset{\text{Alkane}}{R-H} + Na_2CO_3$$

$$\underset{\text{Sodium acetate}}{CH_3-COONa} + \underset{\text{Sodium hydroxide}}{NaOH} \xrightarrow{\text{CaO, 630 K}} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

Calcium oxide keeps sodium hydroxide dry. In laboratory, methane is prepared by this method.

(b) By electrolysis of sodium or potassium salts of carboxylic acid.

$$\underset{\text{Sodium carboxylate}}{2RCOONa} + 2H_2O \xrightarrow{\text{Electrolysis}} \underset{\text{Alkane (at anode)}}{R-R} + 2NaOH + H_2 + 2CO_2$$

$$\underset{\text{Sodium ethanoate}}{2CH_3COONa} + 2H_2O \xrightarrow{\text{Electrolysis}} \underset{\text{Ethane}}{CH_3{-}CH_3} + 2NaOH + H_2 + 2CO_2$$

Properties of Alkanes

I. **Boiling points:** Boiling points of alkanes increase with the increase in their molecular mass. Branched alkanes have lower boiling points than corresponding straight chain alkanes.

II. **Melting points:** Alkanes do not show regular variation in melting points. Alkanes with even number of carbon atoms have higher melting points than with odd number of carbon atoms.

III. **Density:** Densities of alkanes increase with increase in molecular mass. Alkanes are lighter than water.

IV. **Solubility:** Hydrocarbons are soluble in non-polar solvents (benzene, carbon tetrachloride, petroleum, ether etc.) and insoluble in polar solvents (water, alcohols etc.)

V. **Combustion**

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{Heat}$$

While in limited supply of air CO and H_2O are obtained.

$$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$$

VII. Substitution reactions:

(a) Halogenation :

$$CH_4 + Cl_2 \xrightarrow{\text{Sunlight}} CH_3Cl + HCl$$

$$CH_3Cl + Cl_2 \rightarrow \underset{\text{Dichloro methane}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \rightarrow \underset{\substack{\text{Trichloro Methane} \\ \text{(Chloroform)}}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \rightarrow \underset{\text{Tetrachloro methane}}{CCl_4} + HCl$$

The order of reactivity of halogens with alkanes is $F_2 > Cl_2 > Br_2 > I_2$.

(b) Sulphonation :

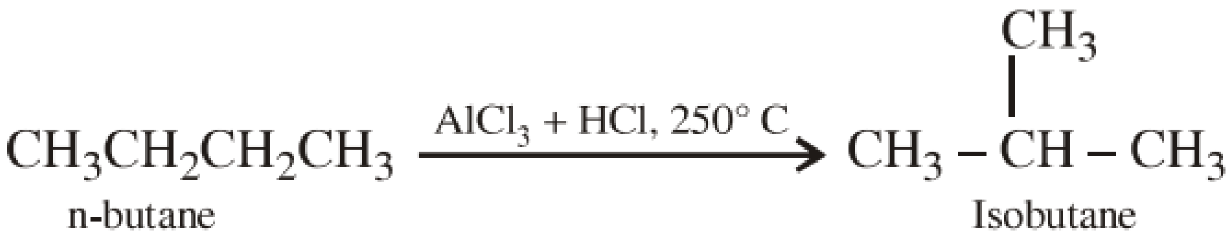
$$\underset{\text{Alkane}}{R-H} + \underset{\text{Sulphuric acid (fuming)}}{HO-SO_3H} \xrightarrow{\Delta} \underset{\text{Alkane sulphonic acid}}{R-SO_3H} + H_2O$$

Where $R = C_6H_{13}$ or larger alkyl group.

(c) Nitration :

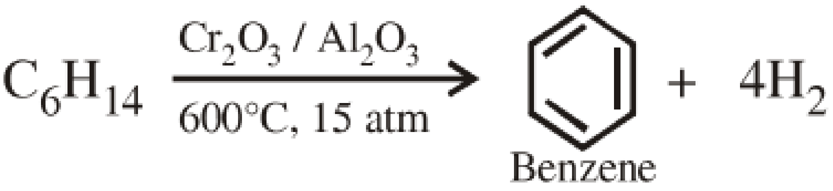
$$CH_4 + HNO_3 \xrightarrow{400-500^\circ C} CH_3NO_2 + H_2O$$

(d) Isomerization:



$$\underset{\text{n-butane}}{CH_3CH_2CH_2CH_3} \xrightarrow{AlCl_3 + HCl,\ 250^\circ C} \underset{\text{Isobutane}}{CH_3-\overset{\overset{\large CH_3}{|}}{C}H-CH_3}$$

VI. Aromatization:



Preparation of Alkenes

I. By dehydration of alcohols:

$$\underset{\text{Primary alcohol}}{R-CH_2-CH_2OH} \xrightarrow[\text{or } Al_2O_3,\ 623-633\ K]{\text{Conc. } H_2SO_4,\ 440K} \underset{\text{Alkene}}{R-CH=CH_2} + H_2O$$

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{or } Al_2O_3,\ 623-633\ K]{\text{Conc. } H_2SO_4,\ 440K} \underset{\text{Ethene}}{CH_2=CH_2} + H_2O$$

II. By cracking of alkanes:

$$\underset{\text{Ethane}}{CH_3-CH_3} \xrightarrow{600°C} \underset{\text{Ethene}}{CH_2 = CH_2} + H_2$$

III. By controlled hydrogenation of alkynes:

$$\underset{\text{Alkyne}}{R-C\equiv C-H} + H_2 \xrightarrow[\text{quinoline}]{\text{Pd-CaCO}_3} \underset{\text{Alkene}}{R-CH=CH_2}$$

$$\underset{\text{Propyne}}{CH_3-C\equiv C-H} + H_2 \xrightarrow[\text{quinoline}]{\text{Pd-CaCO}_3} \underset{\text{Propene}}{CH_3-CH=CH_2}$$

IV. By dehydrohalogenation of alkyl halides:

$$R{-}CH_2{-}CH_2X + KOH \xrightarrow[353-363\text{ K}]{\text{(Alcoholic)}} R{-}CH=CH_2 + KX + H_2O$$

Alkyl halide Potassium hydroxide Alkene

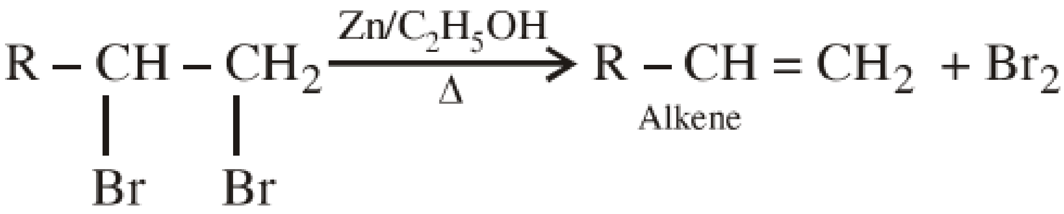
$$CH_3CH_2{-}I + KOH \xrightarrow{353-363\text{ K}} CH_2=CH_2 + KI + H_2O$$

Iodoethane Potassium Hydroxide (alc.) Ethene

$$CH_3CH_2CH_2-Br + KOH \xrightarrow{353-363\text{ K}} CH_3CH=CH_2 + KBr + H_2O$$

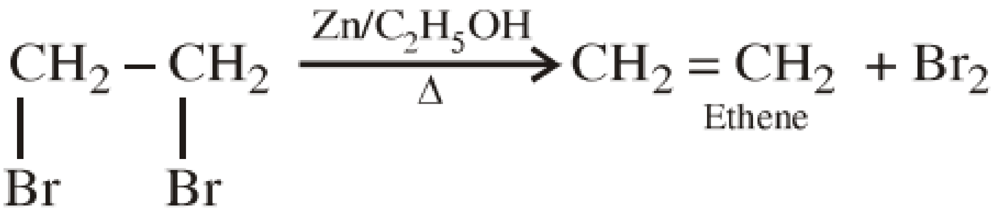
1- bromopropane Potassium hydroxide (atc.) Propene

V. By dehalogenation of vic-dihalides (having two halogen atoms on adjacent carbon atoms.)



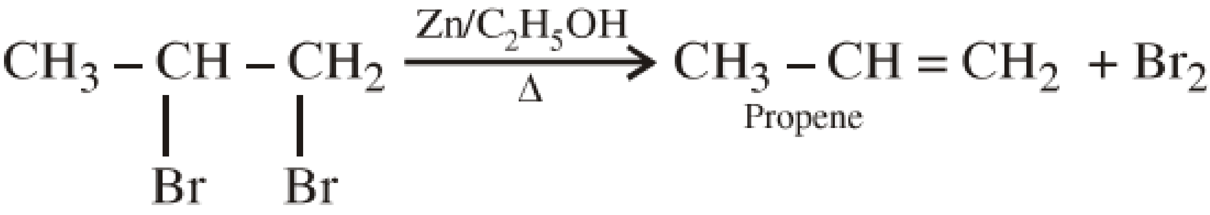
$$R-\underset{\displaystyle Br}{\underset{|}{CH}}-\underset{\displaystyle Br}{\underset{|}{CH_2}} \xrightarrow[\Delta]{Zn/C_2H_5OH} R-CH=CH_2 + Br_2$$

Dibromo-alkane Alkene



$$\underset{\displaystyle Br}{\underset{|}{CH_2}}-\underset{\displaystyle Br}{\underset{|}{CH_2}} \xrightarrow[\Delta]{Zn/C_2H_5OH} CH_2=CH_2 + Br_2$$

1, 2-dibromoethane Ethene



$$CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-\underset{\displaystyle Br}{\underset{|}{CH_2}} \xrightarrow[\Delta]{Zn/C_2H_5OH} CH_3-CH=CH_2 + Br_2$$

1, 2-dibromopropane Propene

Properties of Alkenes

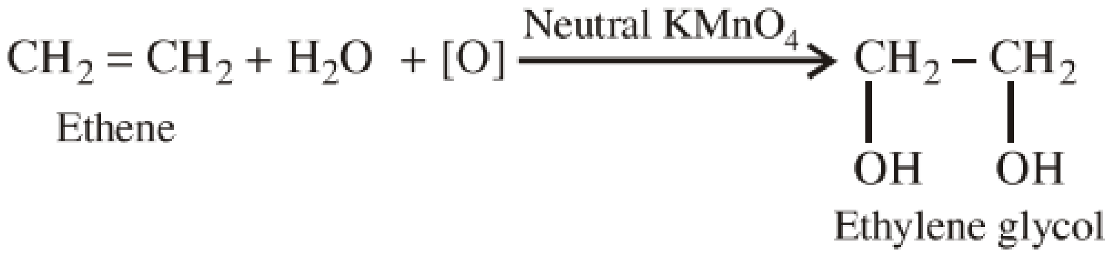
I. **State:** Alkenes having carbon atoms upto 4 are gases, having 5-15 carbon atoms are liquids, but members having more than 15 carbon atoms are solids.

II. **Boiling points and melting points:** Alkenes have higher boiling and melting points than corresponding alkanes. The boiling points and melting points of alkenes also increase with increase in molecular mass like alkanes.

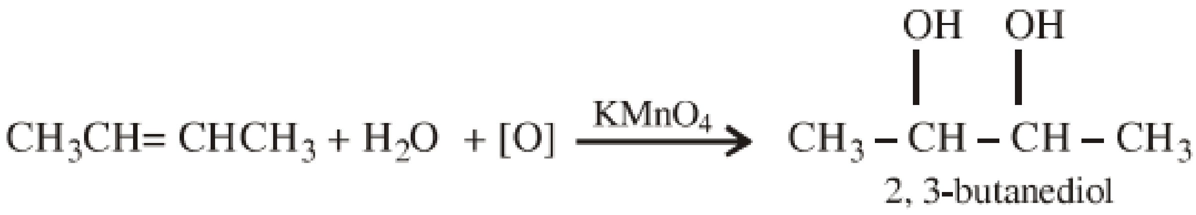
III. **Combustion:**

$$CH_2=CH_2 + 3O_2 \rightarrow 2CO_2 + 2H_2O + \text{Heat}$$

IV. **Oxidation:** With cold and dilute potassium permanganate solution ($KMnO_4$).



$$\underset{\text{Ethene}}{CH_2=CH_2} + H_2O + [O] \xrightarrow{\text{Neutral } KMnO_4} \underset{\text{Ethylene glycol}}{\underset{OH\quad\ OH}{CH_2-CH_2}}$$



$$CH_3CH=CHCH_3 + H_2O + [O] \xrightarrow{KMnO_4} \underset{\text{2, 3-butanediol}}{CH_3-\overset{OH}{CH}-\overset{OH}{CH}-CH_3}$$

V. Addition reactions: Addition of hydrogen:

$$\underset{\text{Alkene}}{R - CH = CH_2} + H_2 \xrightarrow[475 - 525\ K]{\text{Ni or Pt}} \underset{\text{Alkane}}{R - CH_2 - CH_3}$$

$$\underset{\text{Ethene}}{CH_2 = CH_2} + H_2 \xrightarrow[475 - 525\ K]{\text{Ni or Pt}} \underset{\text{Ethane}}{CH_3 - CH_3}$$

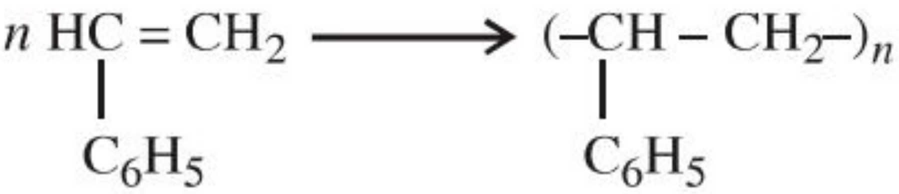
VI. Polymerization:

$$\underset{\text{Ethene}}{n\, CH_2 = CH_2} \xrightarrow{473 - 673\ K,\ \text{High pres.}} \underset{\text{Polyethene}}{(-CH_2 - CH_2-)_n}$$

$$n\, CH_2 = CH - Cl \longrightarrow (-CH_2 - \underset{\substack{|\\ Cl}}{CH_2}-)_n$$

Chloro ethane
(Vinyl chloride)

Polyvinyl chloride (PVC)



$$n\, \underset{\substack{|\\ C_6H_5}}{HC} = CH_2 \longrightarrow (-\underset{\substack{|\\ C_6H_5}}{CH} - CH_2-)_n$$

Styrene

Poly styrene

$$\underset{\text{Tetrafluoroethane}}{n\, CF_2 = CF_2} \longrightarrow \underset{\text{Polytetrafluoroethane (Teflon)}}{(-CF_2 - CF_2-)_n}$$

VII. Isomerization:

$$\underset{\text{1-butene}}{CH_3 - CH_2 + CH = CH_2} \xrightarrow{AlCl_3,\ 500\text{-}700^\circ C} \underset{\text{2-butene}}{CH_3 - CH = CH - CH_3}$$

Preparation of Alkynes

I. From ethyne (for higher alkynes):

$$\underset{\text{Ethyne}}{HC \equiv CH} + \underset{\text{Sodamide}}{NaNH_2} \xrightarrow{196\text{ K, Liq. }NH_3} \underset{\text{Sodium acetylide}}{HC \equiv C^{-}Na^{+}} + NH_3$$

$$HC \equiv C^{-}Na^{+} + \underset{\text{Bromomethane}}{CH_3 - Br} \rightarrow \underset{\text{Propyne}}{HC \equiv C - CH_3} + NaBr$$

$$HC \equiv C^{-}Na^{+} + \underset{\text{Bromoethane}}{CH_3 - CH_2 - Br} \rightarrow \underset{\text{1-Butyne}}{HC \equiv C - CH_2CH_3} + NaBr$$

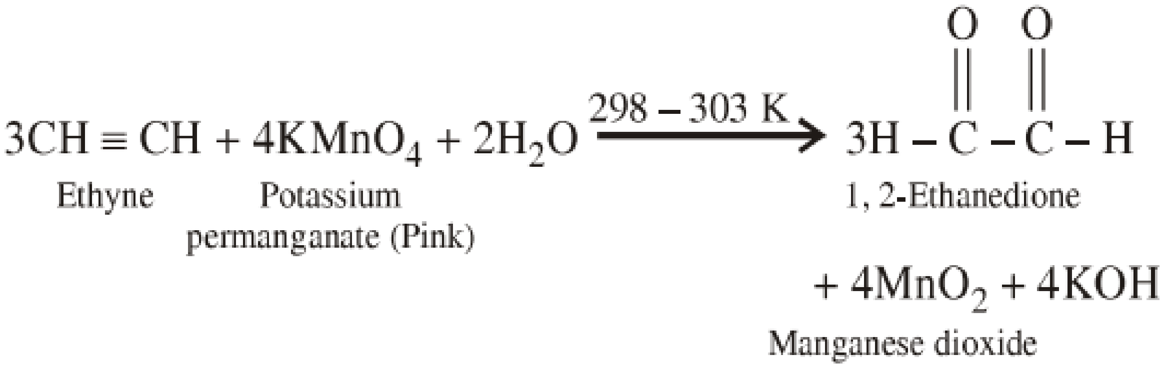
II. From calcium carbide:

$$CaC_2 + 2H_2O \rightarrow \underset{\text{Ethyne}}{HC = CH} + Ca(OH)_2$$

Properties of Alkynes

I. M.P., B.P, solubility and density of alkynes are similar to those of alkanes.

II. Oxidation: With cold potassium permanganate solution:



$$\underset{\text{Ethyne}}{3CH \equiv CH} + \underset{\text{permanganate (Pink)}}{\underset{\text{Potassium}}{4KMnO_4}} + 2H_2O \xrightarrow{298 - 303\text{ K}} \underset{\text{1, 2-Ethanedione}}{3H - \overset{\overset{\displaystyle O}{\|}}{C} - \overset{\overset{\displaystyle O}{\|}}{C} - H} + \underset{\text{Manganese dioxide}}{4MnO_2} + 4KOH$$

III. Addition reaction: Addition of hydrogen.

$$\underset{\text{Alkyne}}{R-C\equiv CH}\xrightarrow{H_2/Ni}\underset{\text{Alkene}}{R-CH=CH_2}\xrightarrow{H_2/Ni}\underset{\text{Alkane}}{RCH_2CH_3}$$

$$\underset{\text{Ethyne}}{HC\equiv CH}\xrightarrow{H_2/Ni}\underset{\text{Ethene}}{CH_2=CH_2}\xrightarrow{H_2/Ni}\underset{\text{Ethane}}{CH_3-CH_3}$$

$$\underset{\text{Propyne}}{CH_3C\equiv CH}+H_2\xrightarrow[\text{Lindlar's catalyst}]{Pd/CaCO_3+\text{lead acetate}}\underset{\text{Propene}}{CH_3-CH=CH_2}$$

IV. Acidic character of alkynes: Hydrogen bonded with carbon atom having triple bond is acidic in nature.

(a) Formation of heavy metal acetylides:

$$\underset{\text{Acetylene}}{H-C\equiv C-H}+\underset{\text{Silver nitrate}}{2AgNO_3}+\underset{\substack{\text{Ammonium}\\\text{hydroxide}}}{2NH_4OH}\rightarrow\underset{\substack{\text{Silver acetylide}\\\text{(white ppt)}}}{Ag-C\equiv C-Ag}$$

$$+2NH_4NO_3+2H_2O$$

$$\underset{\text{Acetylene}}{H-C\equiv C-H}+\underset{\text{Cuprous chloride}}{Cu_2Cl_2}+2NH_4OH\rightarrow\underset{\substack{\text{Cuprous acetylide}\\\text{(red ppt)}}}{Cu-C\equiv C-Cu}$$

$$+2NH_4Cl+2H_2O$$

(b) Formation of alkali metal cynides :

$$\underset{\text{Acetylene}}{H-C\equiv C-H}+Na\rightarrow\underset{\text{Sodium acetylide}}{H-C\equiv C-Na}+H$$

$$\underset{\text{Acetylene}}{H-C\equiv C-H}+\underset{\text{Sodamide}}{NaNH_2}\rightarrow\underset{\text{Sodium acetylide}}{HC\equiv C-Na}+NH_3$$

Some Important Facts

I. Alkanes are also called as **paraffins**.

II. Alkanes and cycloalkanes show conformational isomerism.

III. Pi (π) bond lacks symmetry about internuclear axis.

IV. Pi (π) bond is weaker than sigma (σ) bond.

V. Cis-form has substituent on the same side and trans-form has substituent on opposite side.

VI. Alkenes show position and the chain isomerism, as well as geometrical isomerism.

VII. Alkynes show position and chain isomerism but do not show geometrical isomerism.

VIII. For geometrical isomerism, the molecule must have a double bond.

IX. Ethyne does not show isomerism.

X. Bond length decreases in following order:
$C-C > C=C > C\equiv C$

XI. **Reforming:** It is the process of conversion of alicyclic or aliphatic hydrocarbons having 6-8 carbon atoms into aromatic hydrocarbons.

XII. **Cracking:** It is the process of conversion of higher hydrocarbons into lower hydrocarbons.

XIII. **Cetane number:** Cetane number of a diesel fuel is defined as the percentage of cetane in a mixture of centane and α-methyl naphthalene which has the same ignition qualities as the test fuel.

XIV. **Octane number:** Octane number of a fuel is defined as the percentage of iso-octane in the mixture of n-heptane and iso-octane which has the same anti-knocking property as the test fuel.

XV. **Carbonization** is the process of transformation of organic matter into coal in absence of oxygen.

XVI. Gaseous mixture found with crude petroleum is known as **natural gas**.

XVII. Petroleum is also known as **rock oil**.

XVIII. Branched chain compounds, alkenes, cycloalkanes and aromatic compounds have high octane numbers.

XIX. Methane is the chief constituent of natural gas.

XX. Thermal cracking is difficult to control.

XXI. Lead compounds are poisonous and responsible for air pollution.

XXII. Acidic nature of alkynes can be used to separate, to purify and to identify them from other hydrocarbons.

XXIII. Alkymides are generally explosive and unstable in dry state.

XXIV. Wurtz reaction is not suitable for preparation of unsymmetrical alkanes.

XXV. On addition of H_2O, only C_2H_2 gives aldehyde and rest of all alkynes give ketones.

XXVI. Alkymides are ionic in nature.