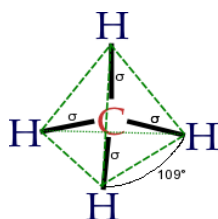


Principles of Organic Chemistry

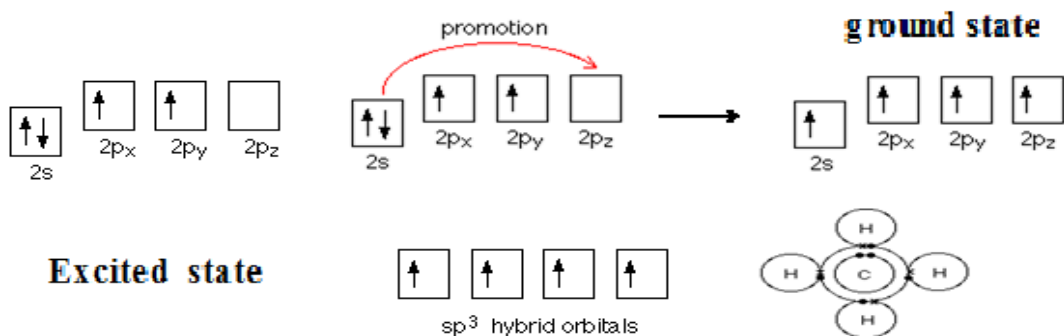
ALKANES

Alkanes - Saturated Hydrocarbons

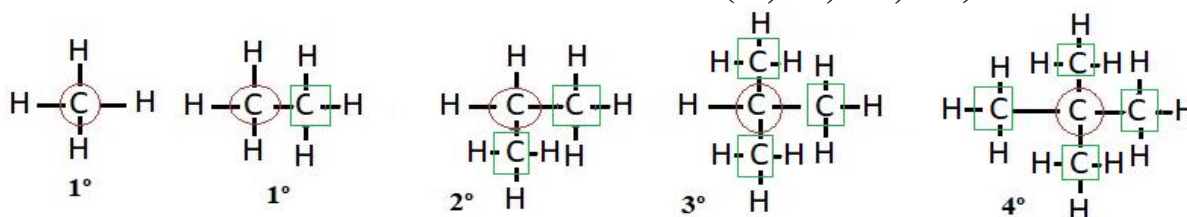
Alkanes, or paraffin's (a still-used historical name for alkanes), are saturated hydrocarbons. They consist only of hydrogen and carbon atoms, all bonds are single bonds. The simplest alkane is methane, CH_4 . Methane molecule has four equivalent carbon-hydrogen bonds arranged tetrahedrally.



The carbon atom is joined to each hydrogen atom by a sigma bond. In methane, the four sp^3 hybrid orbitals of carbon atom overlap with s orbital of four hydrogen atom to form four σ C-H bond



The types of carbon atom are classified to four types depend on the number of carbon atom attachments with center carbon (1° , 2° , 3° , 4°).



Saturated hydrocarbons contain only carbon-carbon single bond. Alkanes with carbon chains that are unbranched are sometime called normal alkanes.

Open-chain alkanes (without rings) all have the general formula C_nH_{2n+2} , where n equals the number of carbon atoms.

IUPAC System of naming alkanes: -

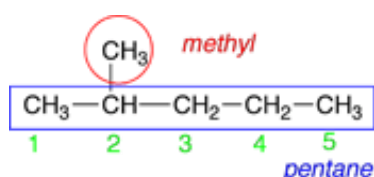
Although many different types of nomenclature, or naming systems, were employed in the past, today only the International Union of Pure and Applied Chemistry (IUPAC) nomenclature is acceptable for all scientific publications. In this system, a series of rules has been created that is adaptable to all classes of organic compounds. For alkanes, the following rules apply:

1- The ending for all alkanes and cycloalkanes is –ane

2- For alkanes with branched carbon chains, the principal chain is the longest continuous carbon chain. This chain is called the parent chain. For example, the branched chain alkane. Methane , ethane , propane.

$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_3 \end{array}$$
 the parent chain: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ it has 5 carbon atoms; therefore, it is a derivative of pentane.

3- The carbon atoms of parent chain are numbered from one end to another giving the lowest number to the first branching point.

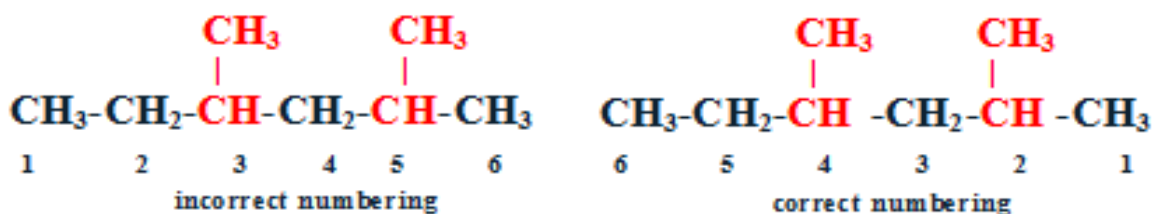


The branch is therefore located on the second carbon.

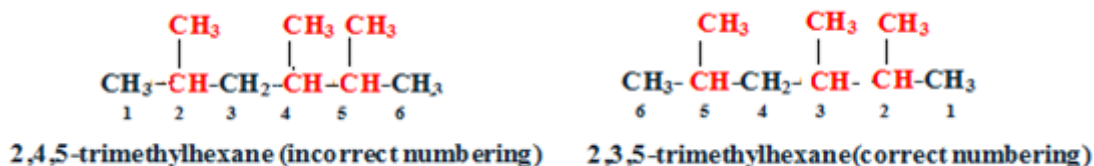
a- Name each branch attached to the parent chain according to alkyl group. In this case, the branch would be *methyl*.

b- Attach the name of alkyl group to the name of the parent chain as a prefix. Place the location number of the alkyl group in the front of resulting name. In this case, it would be 2- methyl pentane.

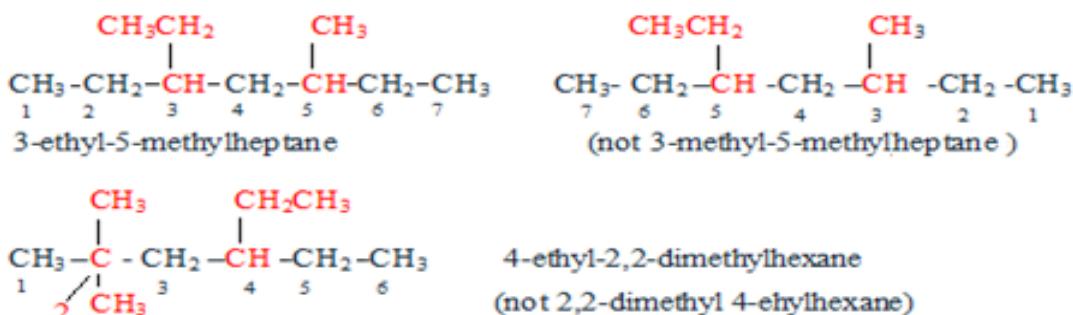
4- If there are two or more identical substituents the parent chain from the end that gives the lower number to the substituent closest to the end of the chain. If there are two or more substituent, the number of times they occur is indicated by the prefixes *di-*, *tri-*, *tetra-*, *penta-*, *hexa-* and so on. A comma is used to separate position number. Of the two possibilities below, we choose the one that numbers the carbon atoms to which the methyl groups are attached as 2 and 4, rather than 3 and 5.



5- If step 4 leads to more than one possibility, number the parent chain, such that the first point of difference has the lowest possible number. Of the two possibilities below, we choose the one that numbers the methyl 3 rather than 4.



6- If there are two or more different substituent, list them alphabetical order, using the base name (ignore the prefixes). The only prefix which is used when putting the substituents in alphabetical order is iso as in isopropyl or isobutyl. The prefixes sec- and tert- are not used in determining alphabetical order except when compared with each others



7- There must always be commas between numbers and dashes between numbers and names. Here are some examples:

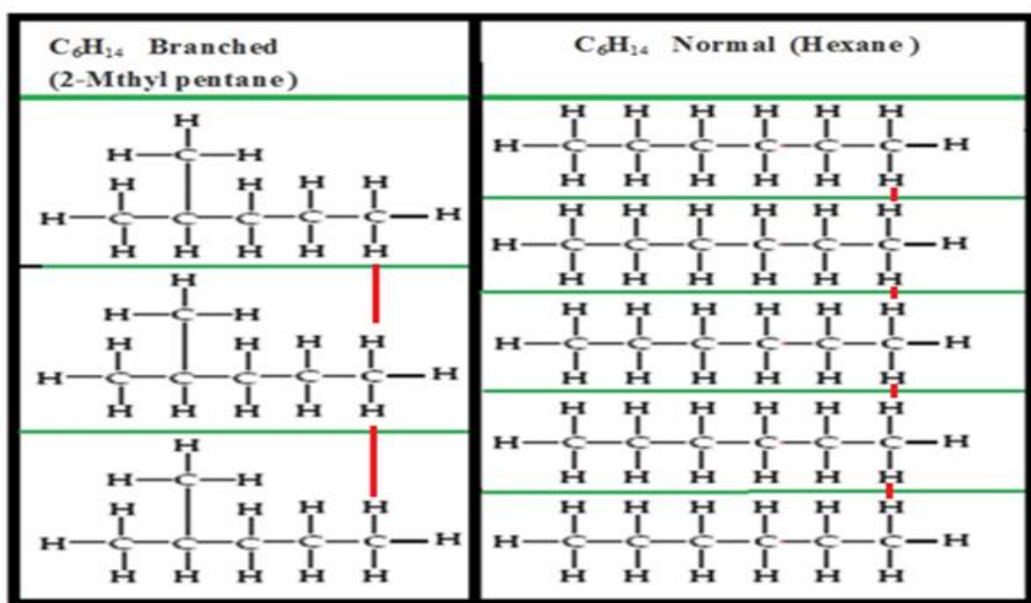


Physical Properties of Alkanes:-

-The attractive forces between the molecules of alkanes are weak. There are only Van der Waals intermolecular forces between alkane molecules. The alkanes can exist as gases, liquids, or solids at room temperature. The unbranched alkanes methane, ethane, propane, and butane are gases. pentane through hexadecane are liquids; the homologues larger than hexadecane are solids. Solid alkanes are normally soft, with low melting points

Name	State	Formula	MP °C	BP °C	Density(g/ml)
Methane	Gas	CH ₄	-190	-162	0.42
Ethane	Gas	C ₂ H ₆	-183	-89	0.55
Propane	Gas	C ₃ H ₈	-172	-45	0.58
Butane	Gas	C ₄ H ₁₀	-135	-0.5	0.60
Pentane	Liquide	C ₅ H ₁₂	-130	36	0.63
Hexane	Liquide	C ₆ H ₁₄	- 95	69	0.66
Heptane	Liquide	C ₇ H ₁₆	- 91	98	0.68

As the chain length of linear (numbers of carbons) increases the boiling points of the alkanes gradually increase. larger molecules have more surface area, so there is more space for interaction between molecules. Because this makes the molecules harder to separate, you need more heat to boil the liquid to the gas. - Branched alkanes normally exhibit lower boiling points than unbranched alkanes of the same carbon content. For example; n-pentane (CH₃-CH₂-CH₂-CH₂-CH₃) a straight chain alkane has 36°C b.p., but **isopentane** CH₃CH(CH₃)CH₂CH₃ and **neopentane** C(CH₃)₄ (which are isomers and branched chain carbon atoms) have lower b.p 28 degrees and 10 degree respectively.



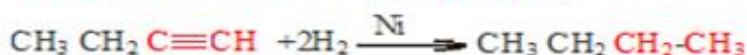
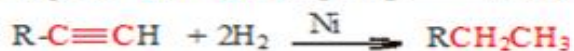
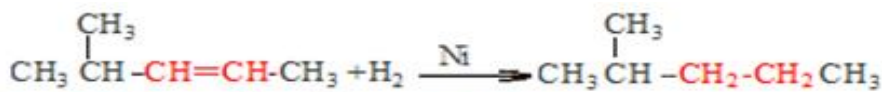
This occurs because of the greater van der Waals forces that exist between molecules of the unbranched alkanes.

The unbranched alkanes have greater van der Waals forces of attraction because of their greater surface areas. -Finally, alkanes are almost completely insoluble in water (hydrophobic). This is because, the water molecule is polar, In other hands, alkanes dissolve in most organic solvent

Preparation of Alkanes: -

Alkane can be prepared by the following methods:

1- By catalytic hydrogenation of unsaturated hydrocarbons (alkenes and alkynes)



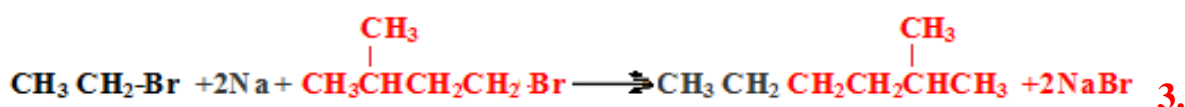
Methane

cannot be prepared by this method because alkenes or alkynes will have two carbons at their lowest level.

2. From alkyl halides via coupling (Wurtz reaction):

When

an alkyl halide (usually bromide or iodide) is treated with sodium in dry ether, a symmetrical alkane containing twice the number of carbon atoms of alkyl halide is obtained.

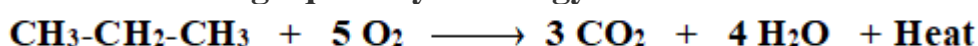


Reactions of Alkanes: -

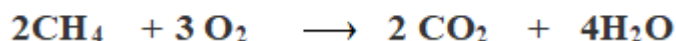
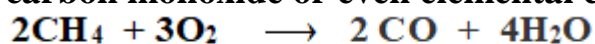
The alkanes are the least reactive organic compounds. Among the few reactions that alkanes undergo are their reactions with oxygen and halogens.

1-Oxidation Reaction:-

In the presence of excess oxygen and spark, alkanes burn to form carbon dioxide, water and a large quantity of energy released:



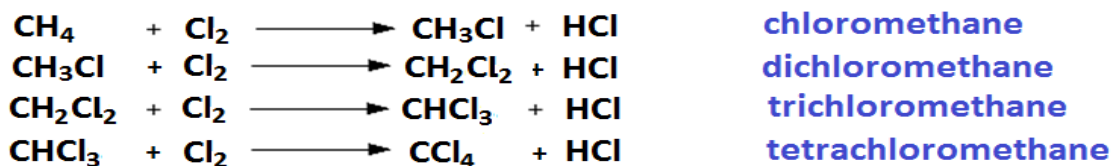
If insufficient oxygen is available, partial oxidation of alkanes occurs to form carbon monoxide or even elemental carbon:



2- Halogenation Reactions: -

Halogenation is the replacement of one or more hydrogen atoms in an organic compound by a halogen (fluorine, chlorine, bromine or iodine). Unlike the complex transformations of combustion, the halogenation of an alkane appears to be a simple substitution reaction in which a C-H bond is broken and a new C-X bond is formed. The reactivity of the halogens decreases in the following order: $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$. The chlorination of methane provides a simple example of this reaction.

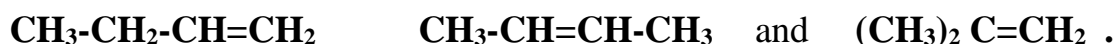
Methane and chlorine substitution reactions happen in which hydrogen atoms in the methane are replaced one at a time by chlorine atoms. You end up with a mixture of chloromethane, dichloromethane, trichloromethane and tetrachloromethane.



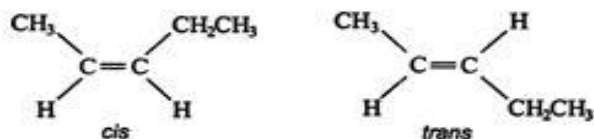
ALKENES

Molecular and Structural Formulas

The alkenes are hydrocarbons that composed of carbon and hydrogen atoms with at least one double bond in the carbon chain. Alkenes with only one double bond have the general formula of C_nH_{2n} , where n equals any integer greater than one. The simplest alkene, ethene, has two carbon atoms and a molecular formula of C_2H_4 . The structural formula for ethene is $\text{CH}_2=\text{CH}_2$. In longer alkene chains, the additional carbon atoms are attached to each other by single covalent bonds. Each carbon atom is also attached to sufficient hydrogen atoms to produce a total of four single covalent bonds about itself. In chains with four or more carbon atoms, the double bond can be located in different positions, leading to the formation of **structural isomers**. For example, the alkene of molecular formula C_4H_8 has three isomers.



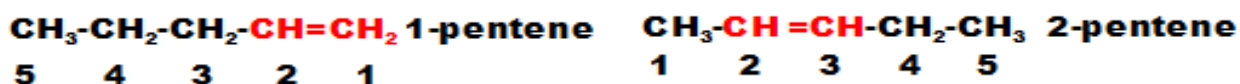
In addition to structural isomers, alkenes also form geometric isomers (cis-trans isomers). Because rotation around a multiple bond is impossible without breaking it, groups attached to the double bonded carbon atoms always remain in the same relative positions. The *cis-trans* isomers differ from each other by the position of attached groups relative to double bond, one having similar groups on the same side is called *cis* and one having similar groups on opposite side called *trans*. An example of geometric isomerism is 2-pentene



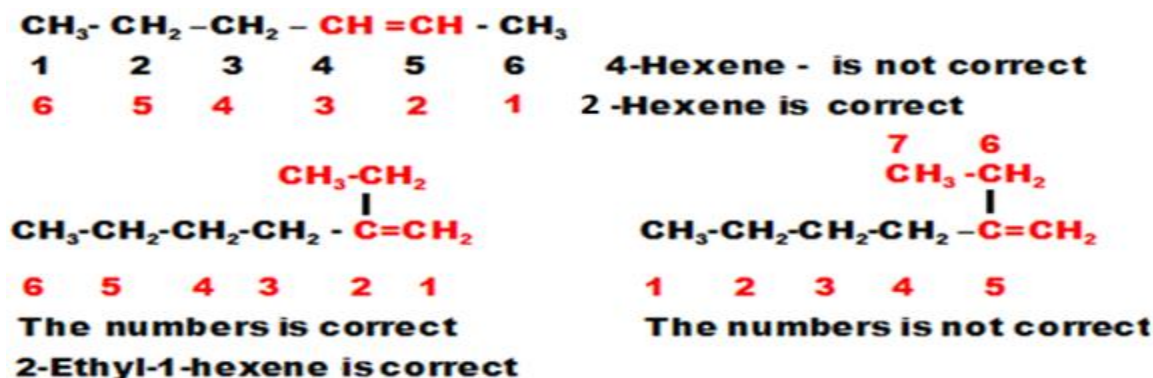
IUPAC System of naming alkenes:-

Alkenes are normally named using the IUPAC system. The rules for alkenes are similar to those used for alkanes. The following rules summarize alkenes naming.

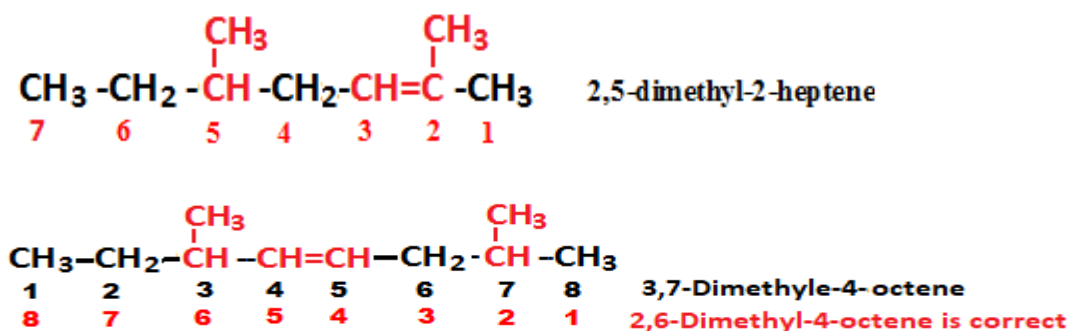
- 1-The **ene** suffix (ending) indicates an alkene or cycloalkene.
- 2- Number the carbon atoms of the longest continuous chain, starting at the end closest to the double bond



3- The position of double bond (C=C) is indicated by placing the lower of the pair of numbers assigned to the double bonded carbon atoms in the front of the name of alkene.. The longest chain chosen for the root name **must include both carbon atoms of the double bond**



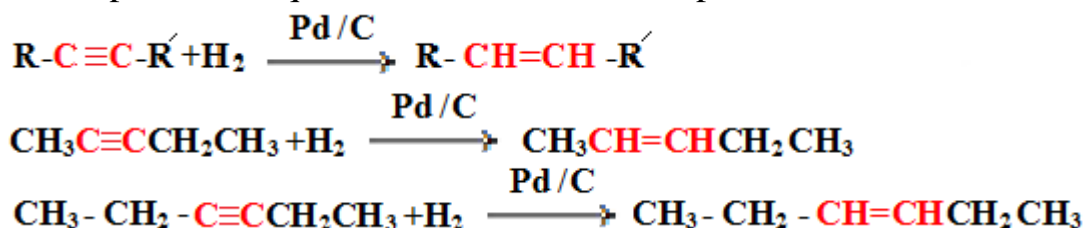
4. The location and name of any substituent molecule or group is indicated. For example, **If the double bond is in the center of the chain, the nearest substituent rule is used to determine the end where numbering starts.**



Preparation of Alkenes :-

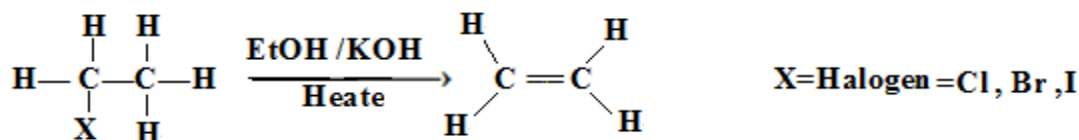
1-Preparation of Alkenes from Alkynes

Alkynes undergo partial reduction with a particular quantity of dihydrogen to produce alkenes. The reaction takes place in the presence of palladised charcoal that has been deactivated with poisonous compounds such as quinolone or sulfur compounds, also known as Lindlar's catalyst. The reaction leads to the formation of compounds having cis-geometric conformation. However, if the same alkynes reduction takes placed with sodium present in liquid ammonia, the resultant product will be trans alkenes

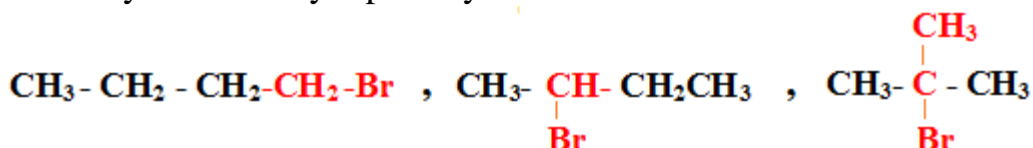


2-Preparation of Alkenes from Alkyl Halides :-

R-X or Alkyl Halides undergo heating with alcoholic potash to form alkenes. Dissolving potassium hydroxide in an alcohol such as ethanol leads to the formation of alcoholic potash. In this reaction, the heating of alkyl halides with alcoholic potash will remove one molecule from halogen acid leading to the formation of alkenes. Thus, it is a β -elimination reaction example because removal of hydrogen atom takes place from the β carbon atom.

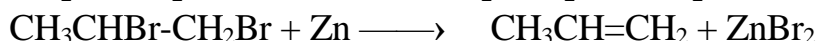
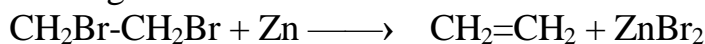


The rate of reaction is dependent on the alkyl group and nature of halogen atom. The order, in this case, is iodine > bromine > chlorine. The rate of reaction according to the alkyl group is tertiary > secondary > primary.



3- Preparation of Alkenes from Vicinal Dihalides :-

Vicinal halides are compounds containing two halogen atoms present on two adjacent carbon atoms. Vicinal dihalides undergo treatment zinc metal to form an alkene. The treatment of vicinal dihalides with zinc metal will help in removal of a molecule from ZnX_2 thereby resulting in the formation of the alkene. The reaction is an example dehalogenation.

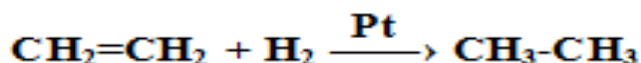


Reaction of alkenes:-

Alkenes are relatively stable compounds, but are more reactive than alkanes due to the presence of a carbon-carbon double bond. The majority of the reactions of alkenes involve the rupture of this double bond, forming new single bonds.

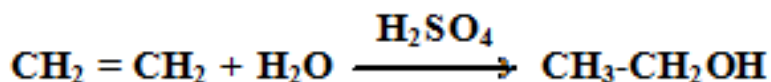
1-Hydrogenation:-

Hydrogenation of alkenes produces the corresponding alkanes. The reaction is carried out under pressure at a temperature of 200 °C in the presence of a metallic catalyst. Common industrial catalysts are based on Pt, Ni or Pd. The simplest example of this reaction is the catalytic hydrogenation of ethylene (ethane) to yield ethane:



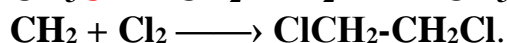
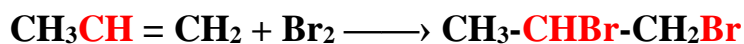
2-Hydration :-

Hydration, the addition of water across the double bond of alkenes, yields alcohol. The reaction is catalyzed by strong acids such as sulfuric acid. This reaction is carried out on an industrial scale to make ethanol.



3- Halogenation:-

In halogenation, the addition of elemental Br₂ or Cl₂ to alkenes yields vicinal dibromo- and dichloroalkanes (1,2-dihalides), respectively.



4- Hydrohalogenation:-

Hydrohalogenation is the addition of hydrohalic such as HCl or HI to alkenes to yield the corresponding alkanhalides.

