

# HYDROCARBON

Organic compounds composed of only carbon and hydrogen are called hydrocarbon.

## CLASSIFICATION OF HYDROCARBONS

On the basis of structure, hydrocarbons are broadly divided into main types

1. Acyclic or open chain hydrocarbon
2. Cyclic or closed chain hydrocarbon

### Acyclic hydrocarbon

These hydrocarbon contains open chain of carbon atom in their molecule. These are also called as aliphatic hydrocarbon

These are further classified as

- i) Alkanes: C – C bond ( saturated compounds)
- ii) Alkene : C = C bond ( Unsaturated compounds)
- iii) Alkyne: C≡ C bond ( Unsaturated compounds)

### Cyclic hydrocarbon

These contains closed chain or rings of carbon atom in their molecule

These are further divided in two groups

- (i) Alicyclic hydrocarbon: The hydrocarbon which contains ring of carbon atom in a molecule and resemble aliphatic hydrocarbon in their properties
- (ii) Aromatic hydrocarbon: These hydrocarbon contains at least one special type of hexagonal ring of carbon atom with three double bonds in alternate position.

The major source of aliphatic hydrocarbon are petroleum and natural gas, where as aromatic hydrocarbons are main obtained from coal

## PETROLEUM

(Petra = rock , oleum = oil)

- It is dark viscous fluid with unpleasant smell found at various depth under the earth crust.

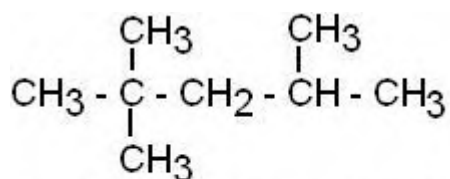
- Crude petroleum is a mixture of hydrocarbons containing 80-85% of carbon 10-14% hydrogen and small amount of oxygen, nitrogen and sulphur.

## Petroleum products

1. Gaseous (  $C_1 - C_4$  )  
Boiling range : 113 – 303 K  
Uses: As a fuel, for production of carbon black
2. Petroleum ether (  $C_5 - C_7$  )  
Boiling range : 303 – 363K  
Use : As a solvent for rubber, oil, fats and varnishes, for dry cleaning
3. Gasoline or Petrol (  $C_8 - C_{11}$  )  
Boiling range : 343 -373K  
Uses: As a motor fuel, for dry cleaning
4. Kerosene oil or Paraffin oil (  $C_{12} - C_{15}$  )  
Boiling range : 448 – 548K  
Uses: As an illuminant fuel, jet engine fuel and for making oil gas
5. Gas oil, fuel and diesel gas (  $C_{15} - C_{18}$  )  
Boiling range : 573 – 673  
Use: Furnace fuel, fuel for diesel engine
6. Lubrication or Mineral oil (  $C_{16} - C_{20}$  )  
Boiling range : 623 K and above  
Uses: As a lubricant
7. Grease, Vaseline, petroleum jelly (  $C_8 - C_{22}$  )  
Use: pharmaceutical preparations
8. Paraffin wax (  $C_{20} - C_{30}$  )  
Uses: In the manufacture of candles, waxed papers and for water proofing.

## OCTANE NUMBER

- Quality of petrol or gasoline is graded in terms of octane number
- Octane number is defined as the percentage by volume of iso-octane present in the mixture of iso-octane and n-heptane which has same knocking properties.
- Metallic sound which arises due to violent jerk in piston is known as knocking  
 $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$   
( n – heptanes , octane number = 0 )

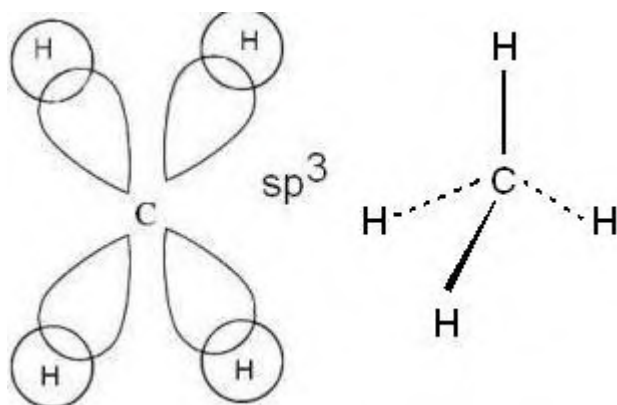


iso-octane [ 2,2,4 - trimethylpentane]  
octane number = 100

- Higher the octane number of fuel, better is the fuel. Octane number of gasoline is 80
- Straight chain hydrocarbon have low octane number.
- Presence of multiple bond increases octane number.
- Aromatic hydrocarbon have higher octane number.
- Octane number decreases with increase in chain length but increases with branching of chain
- Octane number follows the following order  
Aromatic hydrocarbons > cycloalkanes > branched chain alkane  
> straight chain alkanes

## ALKANES

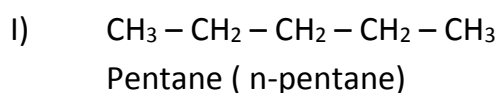
- Alkanes are saturated open chain hydrocarbon containing carbon-carbon single bond
- General formula of alkanes is  $C_nH_{2n+2}$



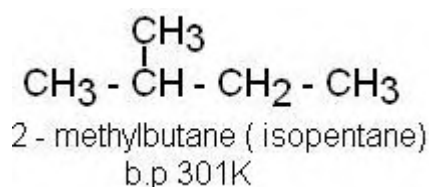
- Methane has a tetrahedral structure which is multiplanar, in which carbon lies at the centre and four hydrogen atoms lie at the four corners of a regular tetrahedron. All H-C-H bond angles are of  $109.5^\circ$
- In alkanes, tetrahedral are joined together in which C – C and C – H bond lengths are 154 pm and 112pm

## ISOMERISM OF ALKANES

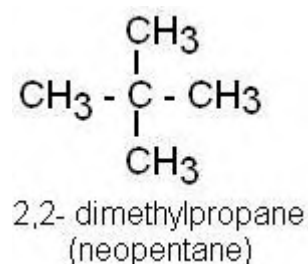
- Difference in properties due to difference in their structures are known as structural isomers
- Structural isomers which differ in chain of carbon atoms are known as chain isomers

Eg.  $C_5H_{12}$ 

II)

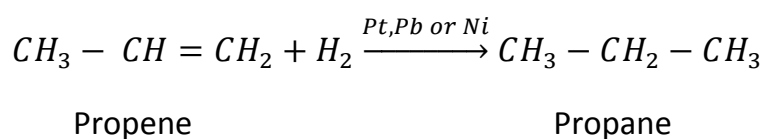
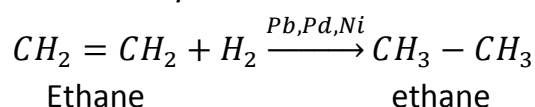


III)



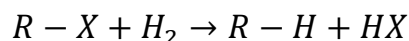
## PREPARATION OF ALKANES

## 1. Hydrogenation of unsaturated hydrocarbons

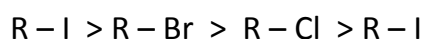


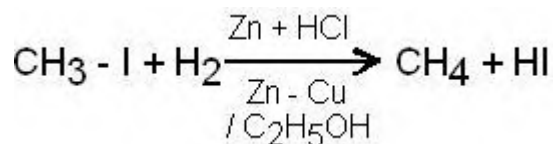
- Metals like platinum, palladium adsorb dihydrogen gas on their surface and activate the hydrogen bond
- Platinum and Palladium catalyse the reaction at room temperature
- Nickel requires high temperature and pressure

## 2. Reduction of alkyl halide

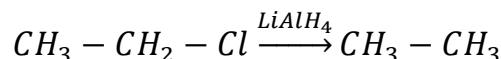


Order of reactivity of different alkyl halides is

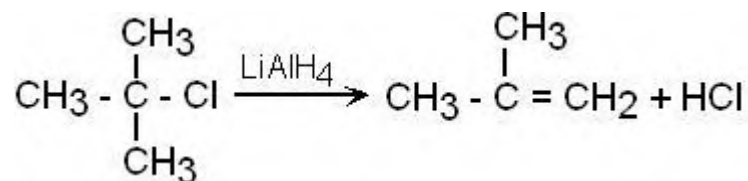




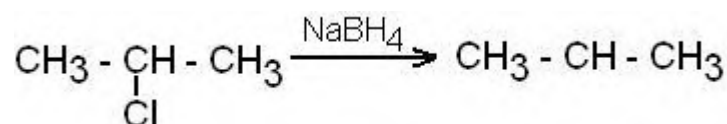
- The purpose of using of red phosphorus is to remove iodine
- 1<sup>o</sup> and 2<sup>o</sup> alkyl halides are readily reduced by LiAlH<sub>4</sub> but 3<sup>o</sup> halides give **alkene**



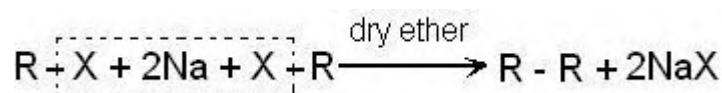
BUT



- NaBH<sub>4</sub> reduces 2<sup>o</sup> and 3<sup>o</sup> halides but 1<sup>o</sup>

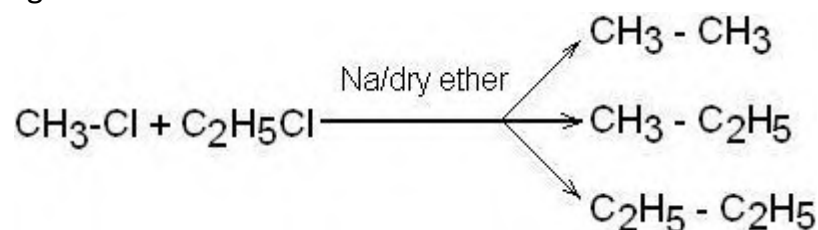


### 3. Wurts reaction



- If two different alkyl halides are used mixture of three different alkanes are obtained.

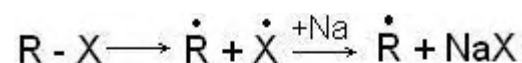
Eg



The separation of the mixture into individual members is not easy

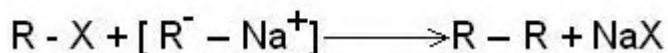
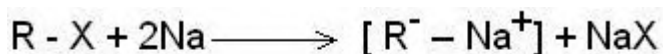
- Wurtz reaction is used for the preparation of higher alkanes containing even number of carbon atoms

Mechanism



Wurtz reaction is supposed to follow free radical mechanism

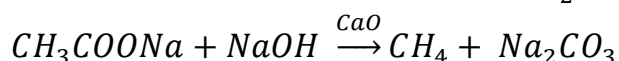
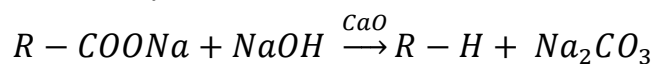
- Ionic mechanism is suggested for Wurtz reaction



Reactivity order of alkyl halides towards Wurtz reaction is

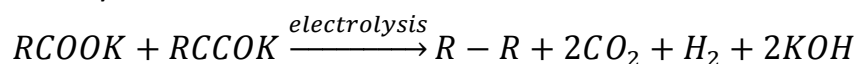


4. Decarboxylation of carboxylic acid.

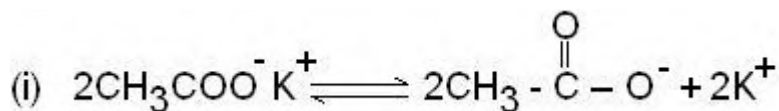


Alkane obtained in this method have one carbon less than the parent compounds

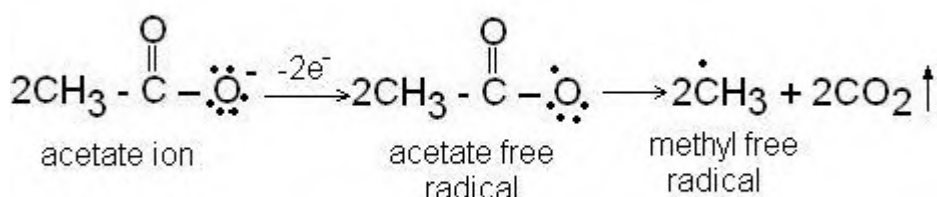
5. Kolbe's electrolytic method



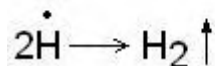
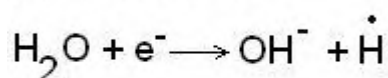
Mechanism



(ii) At anode:



(iii) At cathode

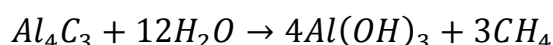


If number of carbon atoms in potassium carboxylate = n

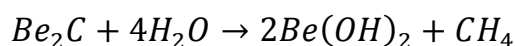
Number of carbon atoms in alkane formed = 2(n-1)

Therefore, methane cannot be prepared by this method

6. Hydrolysis of aluminium and beryllium carbide



Aluminium carbide



Beryllium carbide

## PHYSICAL PROPERTIES OF ALKANES

## (1) Physical state

Due to weak intermolecular forces, alkanes from C<sub>1</sub> to C<sub>4</sub> are colourless gas, next thirteen C<sub>5</sub> to C<sub>17</sub> are colourless, odourless liquid. Higher members from C<sub>18</sub> onwards are waxy solids

## (2) Solubility

Alkanes are non-polar, hence insoluble in polar solvents like water but readily soluble in non-polar solvents like benzene, ether etc.

The solubility decreases with increase in molecular mass

## (3) Density

The relative densities of alkanes increases with increase in molecular mass, but very slowly till it becomes constant at about 0.8. thus all alkanes are lighter than water

## (4) Boiling point

Boiling point of alkane increases with increasing molecular mass

The greater the branching of the chain, lower is the boiling point. This is because surface area of branched chain alkanes is less than that of straight chain alkanes. As a result they experience lower magnitude of van der Waals forces

## (5) Melting point

Melting point of alkanes also increases with the increase in molecular weight. Alkanes with odd number of carbon atoms have lower melting point than the next lower or next higher alkanes having even number of carbon atoms.

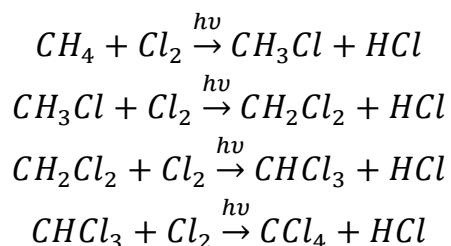
## (6) Viscosity

Viscosity of alkanes (in liquid states) increases with chain length

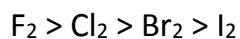
For isomeric alkanes, viscosity increases with branching

## CHEMICAL PROPERTIES OF ALKANES

## 1) Halogenation

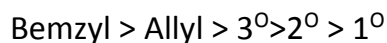


Reactivity of halogens is in order



For a given halogen, abstraction of  $1^\circ, 2^\circ, 3^\circ$  hydrogen follows the order  
 $3^\circ > 2^\circ > 1^\circ$

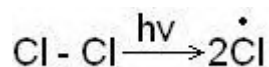
Reactivity of different hydrogen towards halogenations is



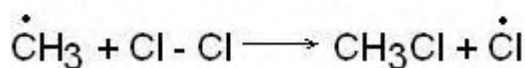
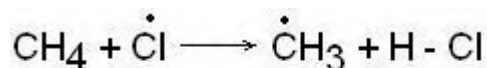
Mechanism

Free radical substitution

(1) Chain initiation step

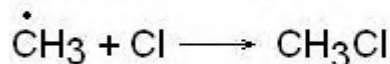
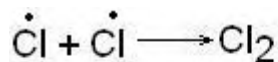


(2) Chain propagation step

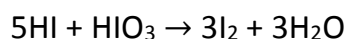
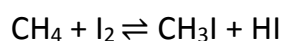


And so on.....

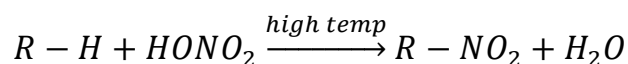
(3) Chain terminating step



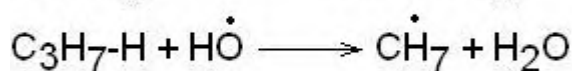
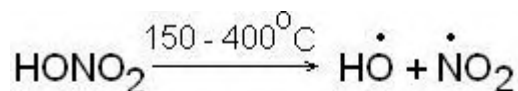
Iodination is very slow and reversible reaction. It can be carried out in the presence of oxidizing agents like  $HNO_3$  or  $HIO_3$



2) Nitration



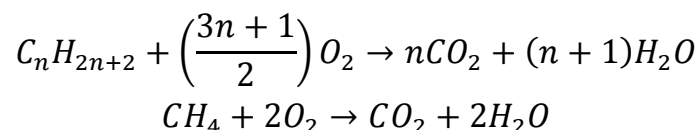
Nitration follows free radical mechanism



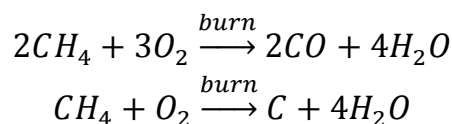


## 3) Oxidation

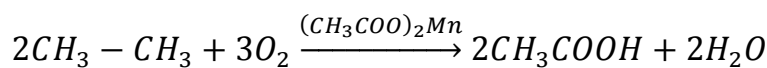
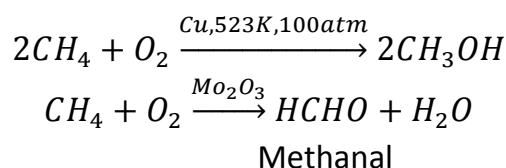
(a) Combustion or complete oxidation



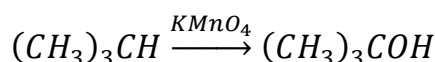
(b) Incomplete combustion



(c) Catalytic oxidation



Ethanoic acid

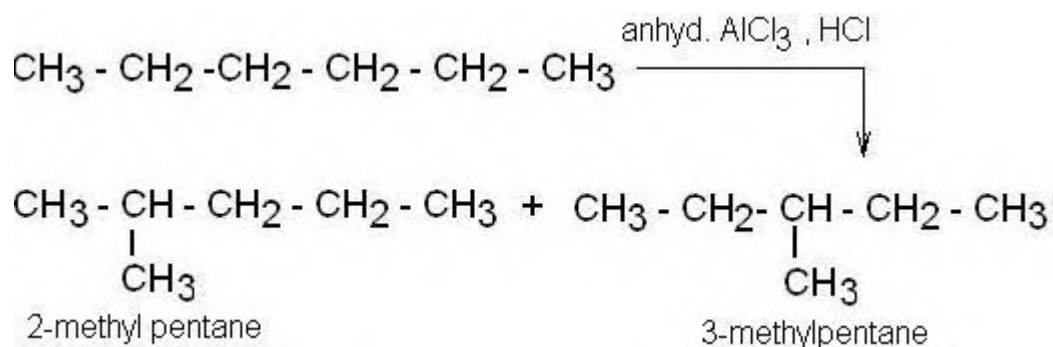


2-methyl propane

2-methylpropan-2-ol

## 4) Isomerisation

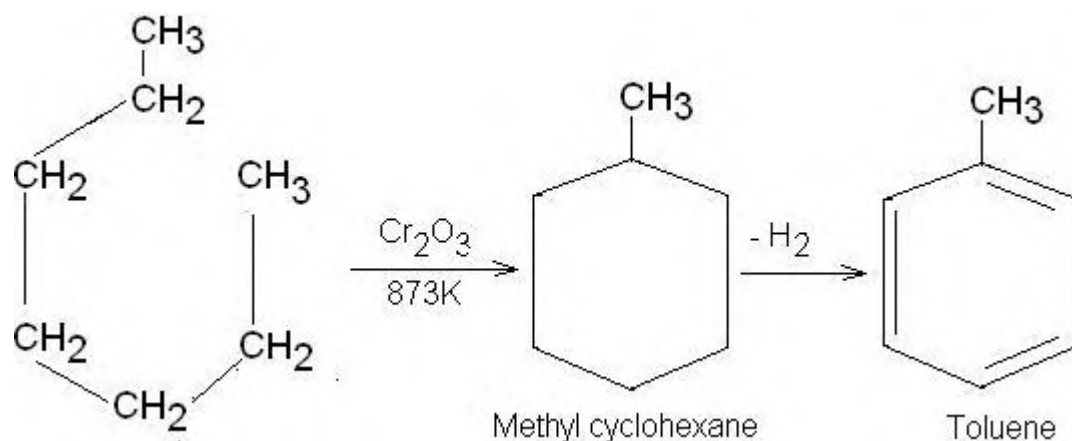
The process of conversion of one isomer into another isomer is called isomerisation.



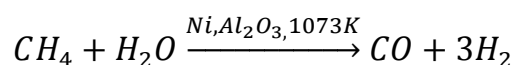
Isomerisation involves 1, 2 shift of hydride or methyl group

## 5) Aromatization

The conversion of aliphatic compounds into aromatic compounds is known as aromatization

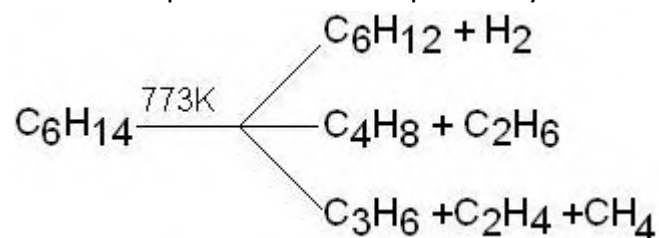


6) Reaction with steam

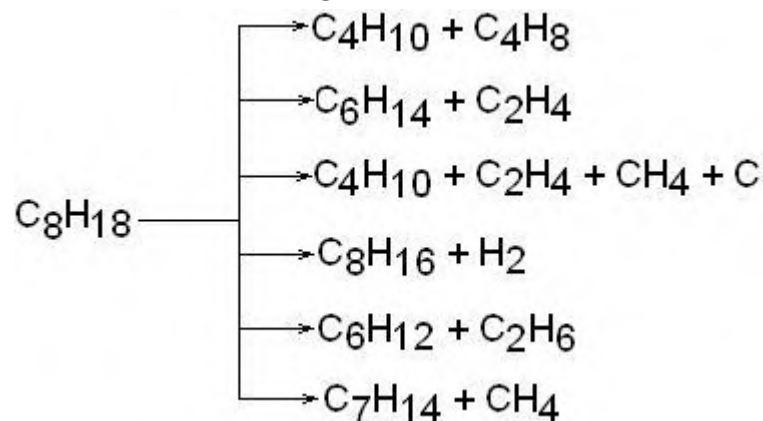


7) Pyrolysis

The decomposition of a compound by heat is called pyrolysis.



Mechanism of cracking follows free radical mechanism



Use of alkanes

- Methane is used in the preparation of carbon black which is used for making printing ink, black paint
- Methane in the form of natural gas used for running the cars, buses etc
- Ethane is used for making hexachloroethane which is artificial camphor.

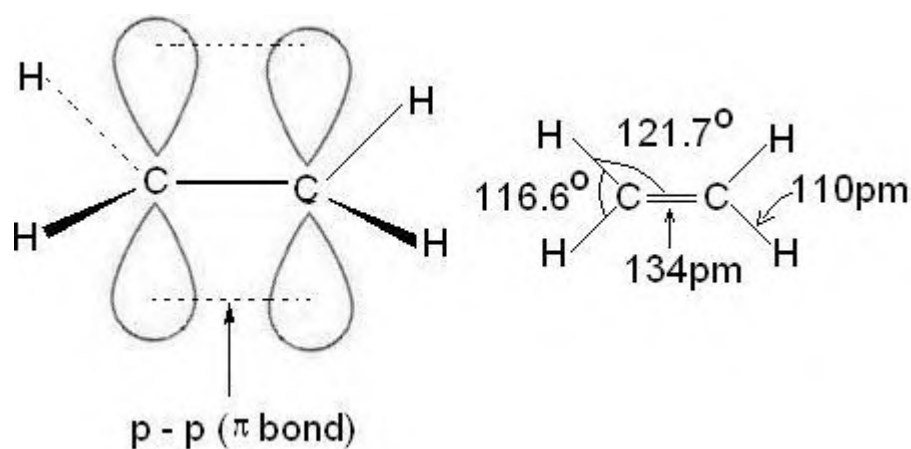
## ALKENES

Alkenes are unsaturated hydrocarbons having double bond ( C = C )

Their general formula is  $C_nH_{2n}$

They are also known as olefins since the lower members form oily product on treatment with chlorine or bromine.

### STRUCTURE OF ALKENES



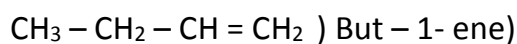
Carbon-Carbon double bond in alkenes consists of one strong sigma ( $\sigma$ ) bond due to head on overlapping of  $sp^2$  hybridised orbitals and one weak pi ( $\pi$ ) bond obtained by sideways overlapping of the two  $2p$  orbitals of the two carbon atoms

The double bond is shorter in bond length ( $134\text{pm}$ ) than the C-c single bond ( $154\text{pm}$ )

The bond enthalpy of double bond is  $681\text{kJ/mol}$  which is greater than single bond ( $348\text{kJ/mol}$ )

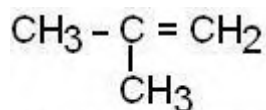
### ISOMERISM IN ALKENES

(a) Position isomerism: This is due to the position of double bond in the same molecular formula



(b) Chain isomerism: This is due to the difference in the nature of carbon skeleton

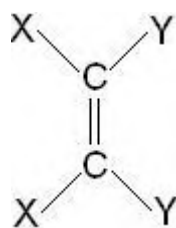




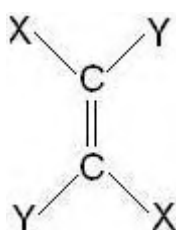
2 - methylpropane

(c) Geometrical isomerism : Isomers, which possess the same molecular and structural but differ in the arrangement of atom or groups in space due to restricted rotation around the double bonded atom are known as geometrical isomer and the phenomenon is known as geometrical isomerism

(1) If two identical atoms or groups lie on the same side of the double bond is called cis-isomer



(2) If two identical atoms or groups lie on the opposite side of the double bond is called trans-isomer.

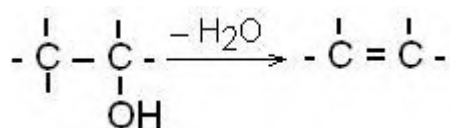


#### Physical properties of cis-trans isomers

- (i) Melting point of trans-isomer is more than that of cis-isomer
- (ii) Boiling point : p.pt. of cis-isomer is more than that of trans isomer
- (iii) Solubility: The solubility viscosity and refractive index of cis-isomer is more than the trans isomer in a given solvent
- (iv) Dipole moment: Cis-isomer has higher dipole moment than trans –isomer
- (v) Stability: Trans-isomer is more stable but less reactive than cis-isomer

#### PREPARATION METHODS OF ALKENES

1. By dehydration of alcohol

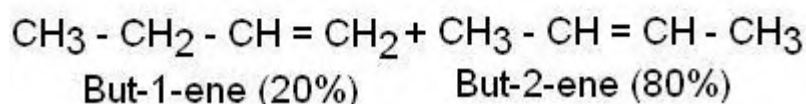
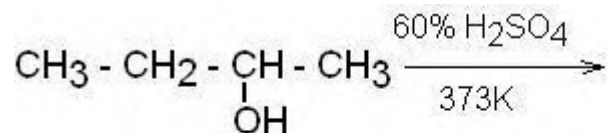


Ease of dehydration follows the order

Tertiary (3°) > Secondary(2°) > Primary(1°)

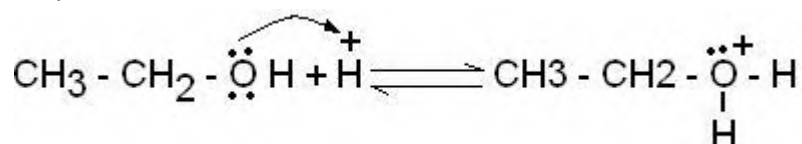
In the dehydration of secondary and tertiary alcohol, when there is a possibility of formation of two isomers, the hydrogen atom is preferentially eliminated from the number of hydrogen atom

This is Saytzeff's rule

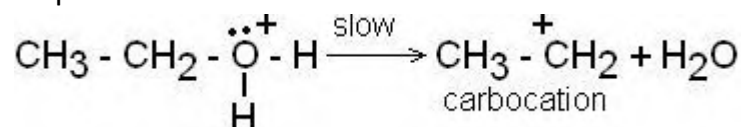


Mechanism

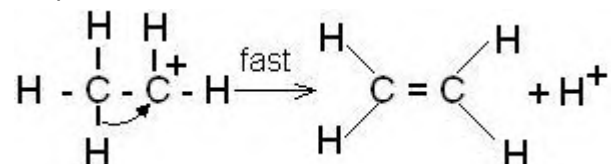
Step I



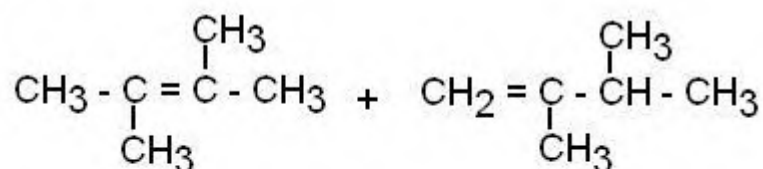
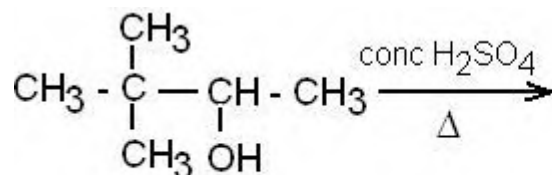
Step II



Step III



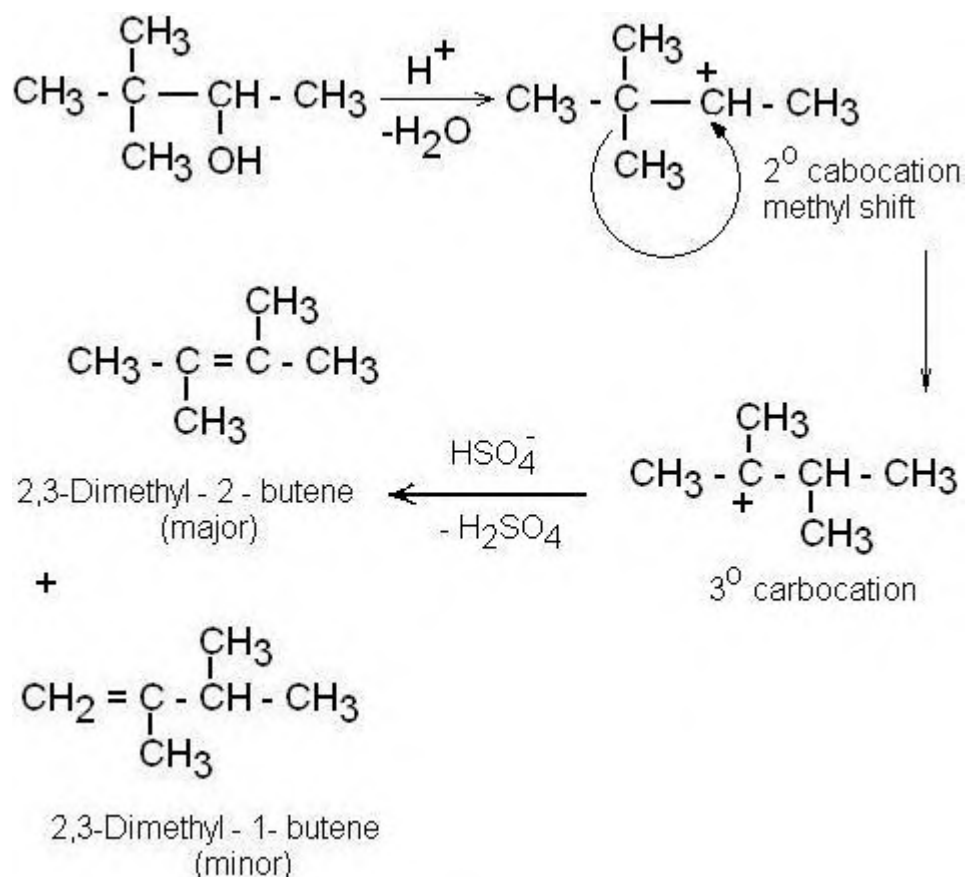
Retropinacol rearrangement ( Wagner – rearrangement)



2,3-Dimethyl - 2 - butene  
(major)

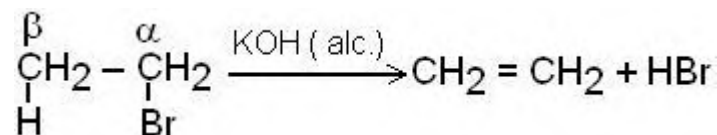
2,3-Dimethyl - 1- butene  
(minor)

The above reaction can be explained as follows

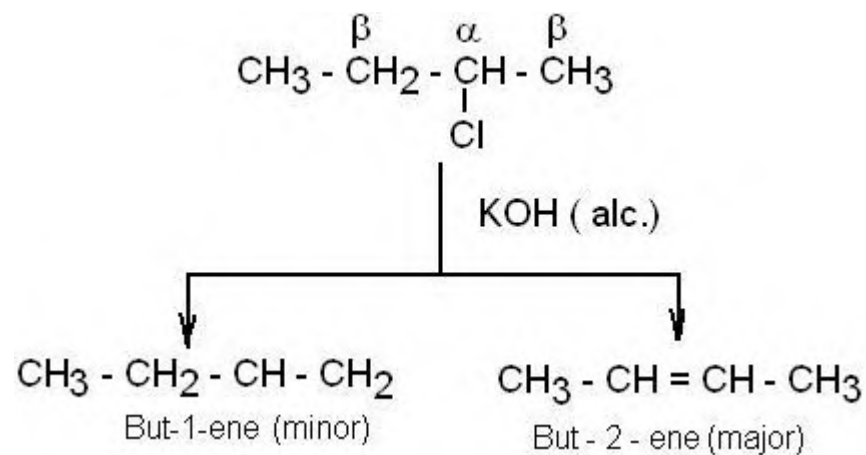


## 2. Dehydrohalogenation of alkyl halides

It involves removal of halogen atom along with  $\beta$ -hydrogen atom on heating with alcoholic solution of potassium hydroxide

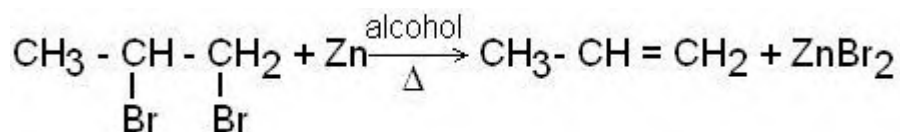


Reactivity order of different alkyl halides

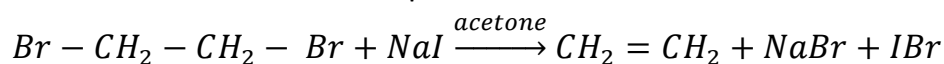


It follows Saytzeff's rule

## 3. Dehalogenation of vicinal dihalides

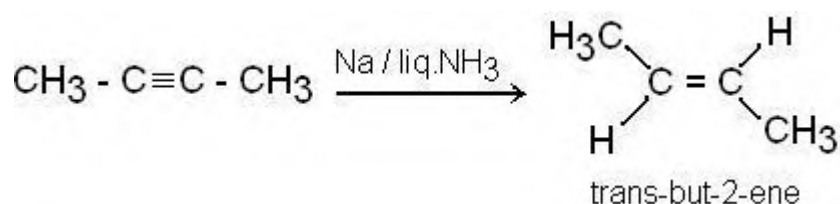


NaI in acetone can also be used in place of Zinc

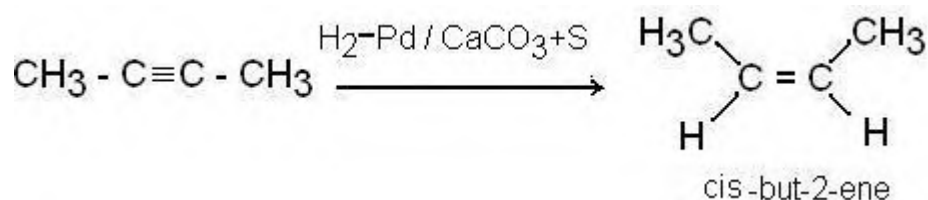


## 4. Partial reduction of alkynes

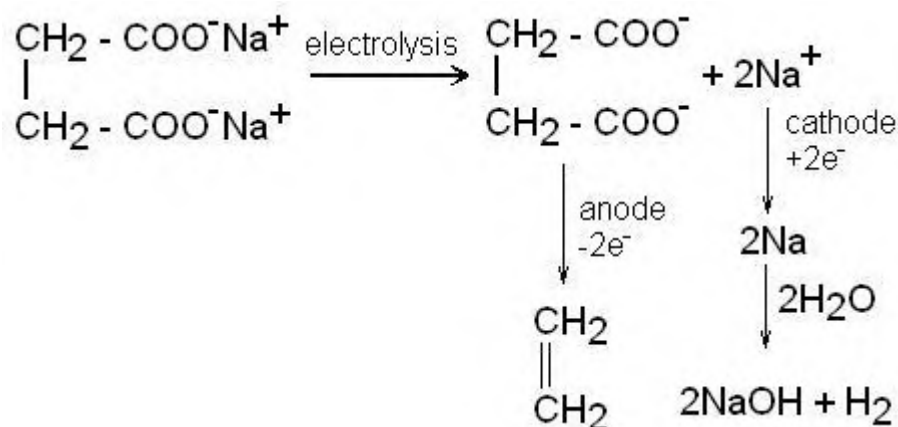
(i) Birch reduction



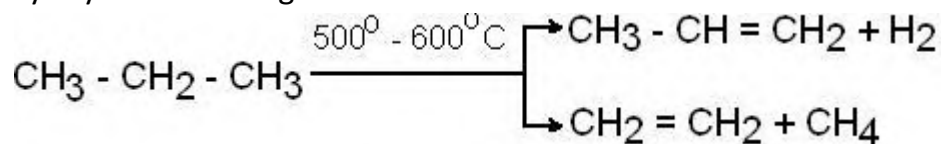
(ii) Lindlar's catalyst



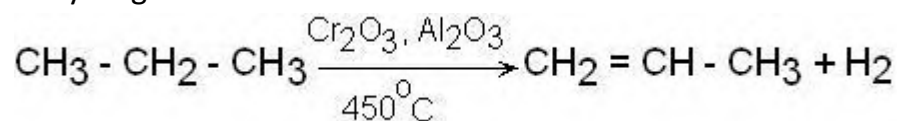
## 5. Kolbe's electrolytic method



## 6. Pyrolysis or cracking



## 7. Dehydrogenation of alkanes

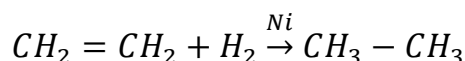


## PHYSICAL PROPERTIES OF ALKENES

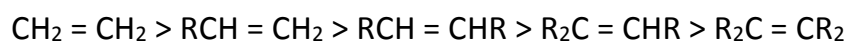
- Physical state  
C<sub>2</sub> – C<sub>4</sub> are colourless gases, next fourteen members (C<sub>5</sub> – C<sub>18</sub>) are liquids and next higher members are solid at room temperature
- Melting point  
Melting point increases with increase in molecular mass.
- Boiling point  
Boiling point also increases with increase in molecular mass  
Like alkanes, branching in alkenes lower the boiling point
- Solubility  
Alkenes are insoluble in water but soluble in non-polar solvents like CCl<sub>4</sub>, benzene, ether, etc.
- Density  
Alkenes are lighter than water
- Dipole moment  
Alkenes are generally non-polar but certain unsymmetrical alkenes are slightly polar.

## CHEMICAL PROPERTIES OF ALKENES

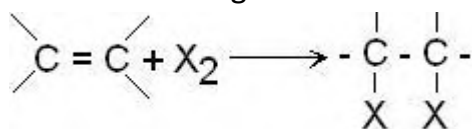
- Addition of dihydrogen (H<sub>2</sub>) [ Hydrogenation]



The order of reactivity of various alkenes towards catalytic hydrogenation is



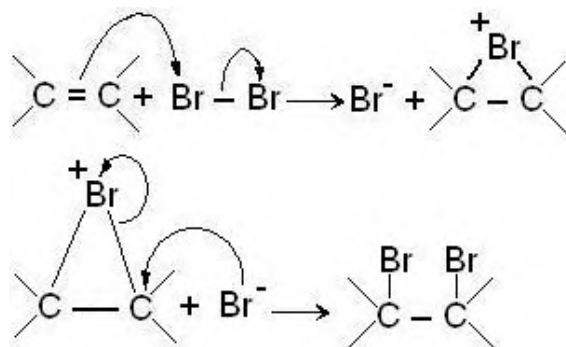
- Addition of halogens



The order of reactivity of halogens is

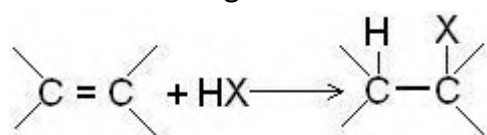
Fluorine > Chlorine > Bromine > Iodine

Mechanism





## 3. Addition of halogen acids

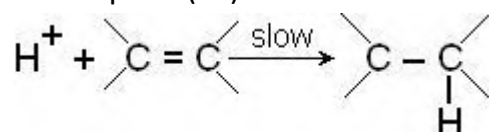


Mechanism

Step I

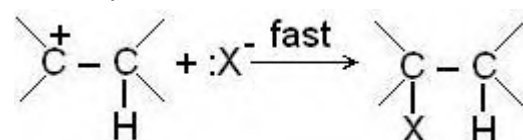


Step II

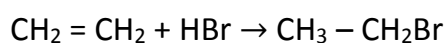
Electrophile ( $\text{H}^+$ ) attacks the double bond to form carbocation

Step III

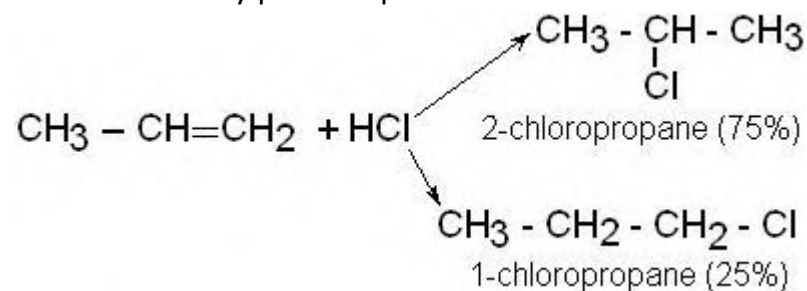
Nucleophile attacks the carbocation to form the alkyl halide



In case of unsymmetrical alkene having group on either side of double bond, two theoretically possible product is obtained



In case of unsymmetrical alkenes having groups on either side of double bond, two theoretically possible products are obtained.



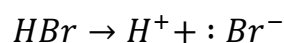
This can be explained by Markownikoff's rule

Markownikoff's rule

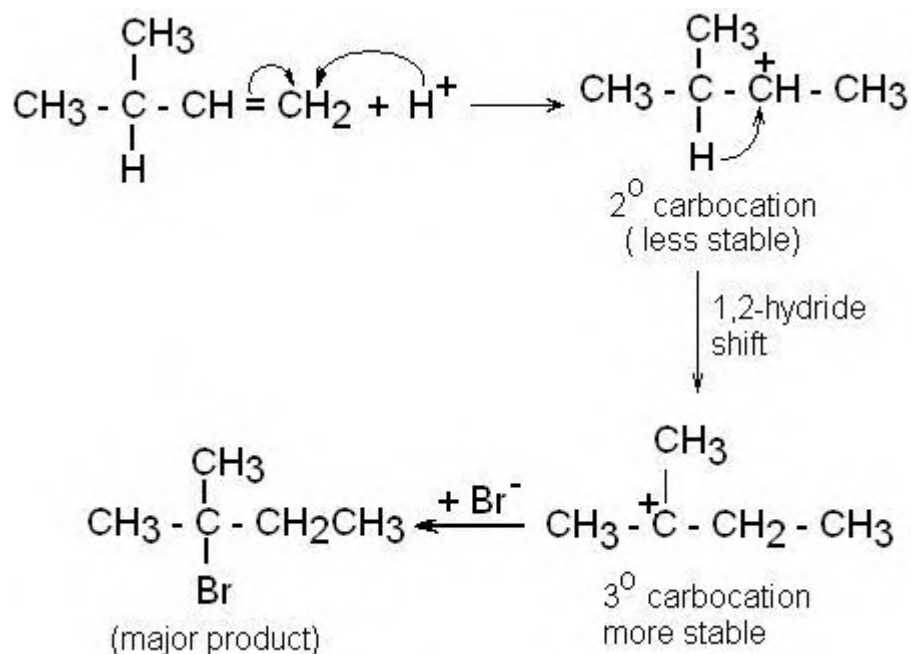
The rule states that negative part of the addendum ( adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms

Mechanism

Step I



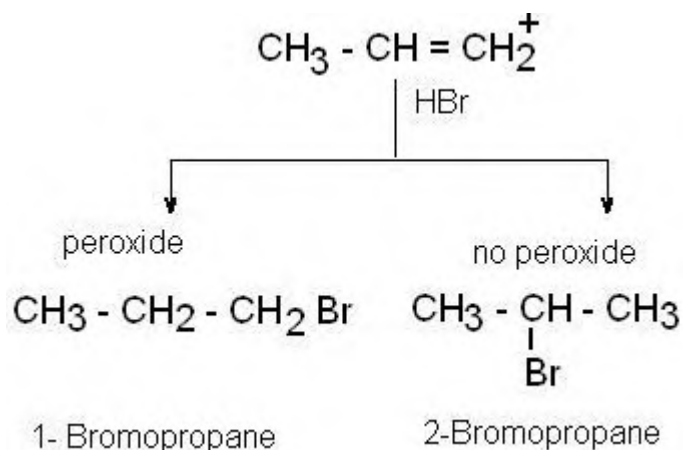
Step II



Since tertiary carbocation is more stable than secondary carbocation, therefore, the former predominates because it is formed at faster rate.

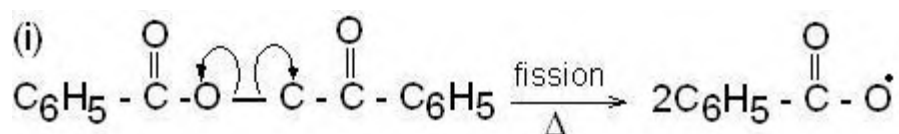
Peroxide effect or Kharasch effect

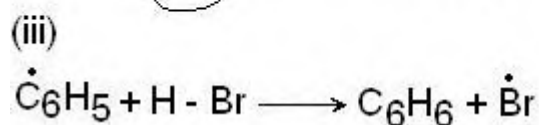
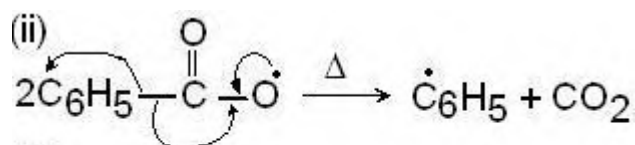
Addition of HBr to an unsymmetrical alkene in the presence of peroxides gives the product contrary to Markownikoff's rule. It is also known as anti-markonikoff addition.



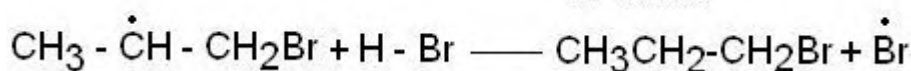
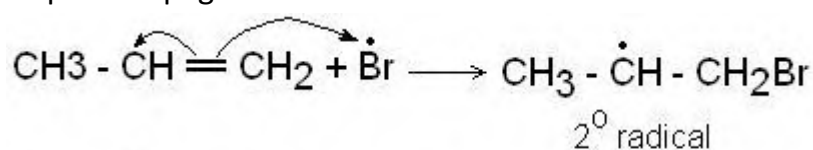
Free radical mechanism

Step I : Peroxide ( like benzoyl peroxide undergoes hemolytic fission to give free radicals

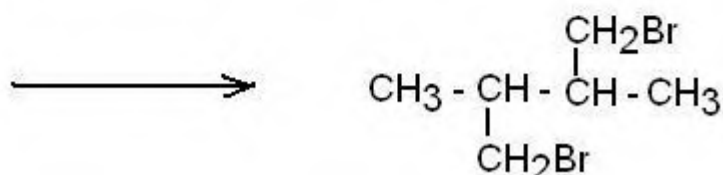
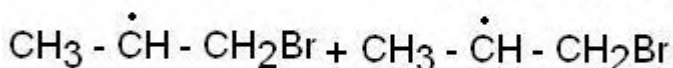
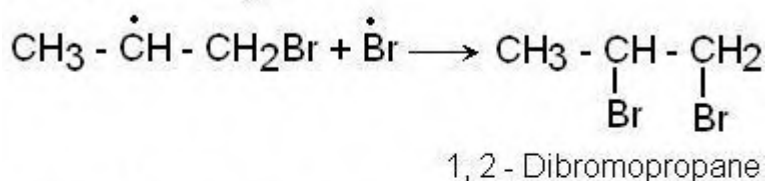
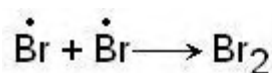




Step II : Propagation



Step III : Termination

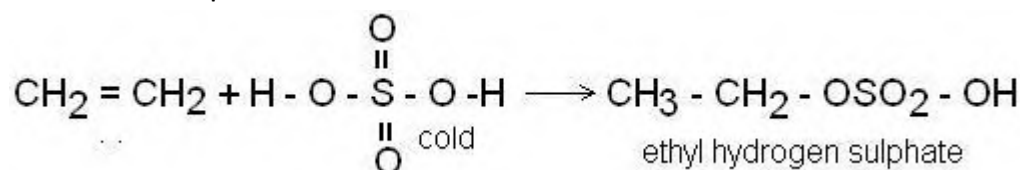


Peroxide effect is observed only in case of HBr and not in HCl and HI

This may be due to the fact that the H-Cl bond being stronger than H-Br bond, is not cleaved by the free radical.

Whereas the H-I bond is weaker and iodine free radicals combine to form iodine molecules instead of adding to the double bond

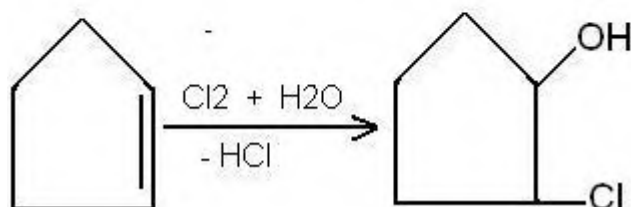
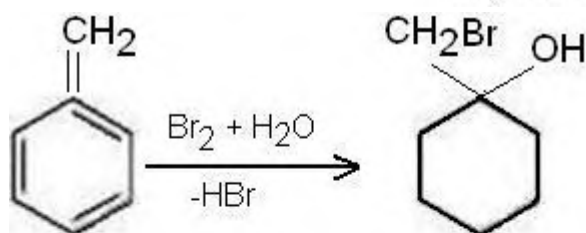
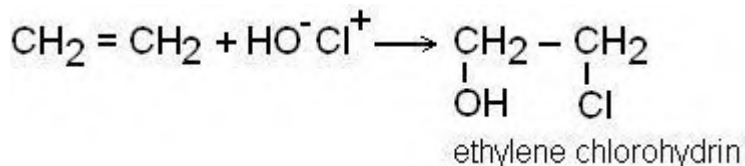
#### 4. Addition of sulphuric acid



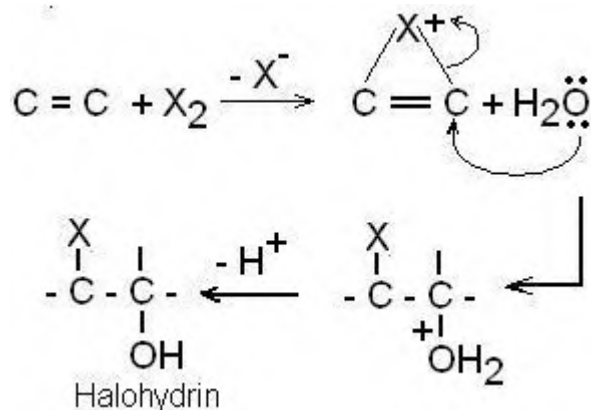
Since alkenes are soluble in cold concentrated acid, this method can be used for separating them from insoluble compounds like alkanes and alkylhalides.

## 5. Addition of hypohalous acid

Hypohalous acid (HOX) [Chlorine or bromine + H<sub>2</sub>O] readily added on alkenes to form corresponding halohydrins



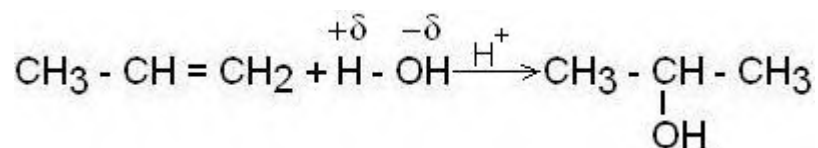
## Mechanism



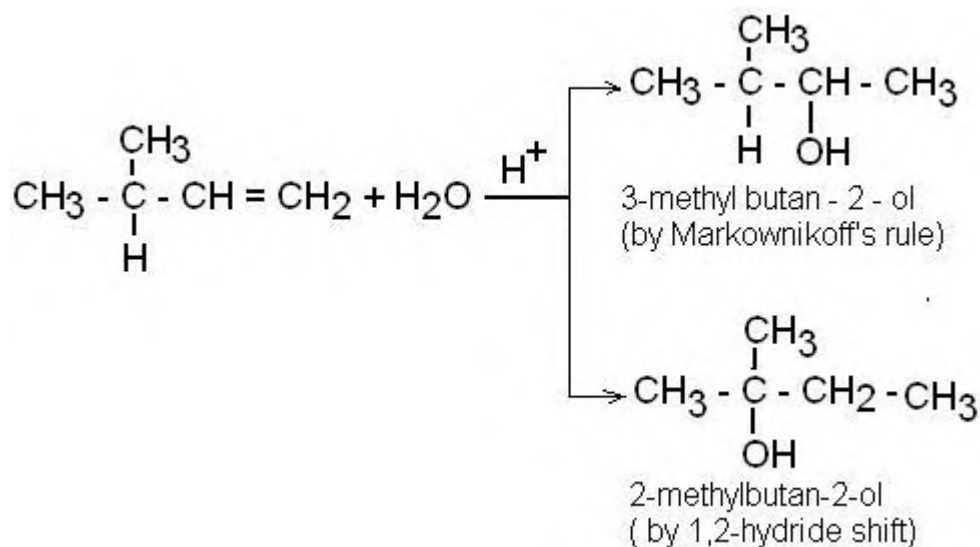
The order of reactivity HOX is



## 6. Addition of water

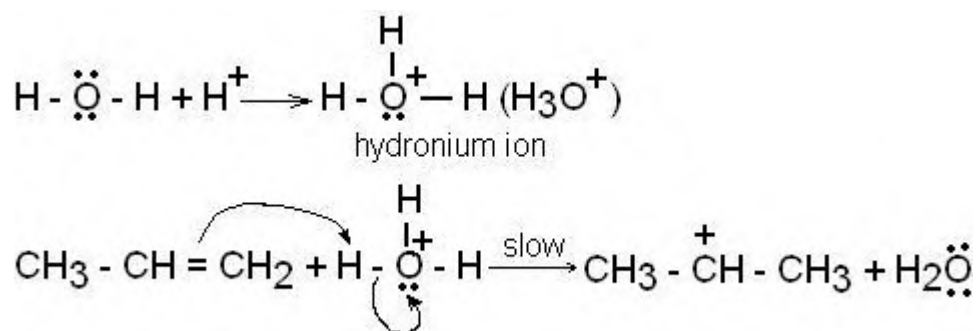


This reaction involves formation of carbocation intermediate that may result into some unexpected product due to carbocation rearrangement

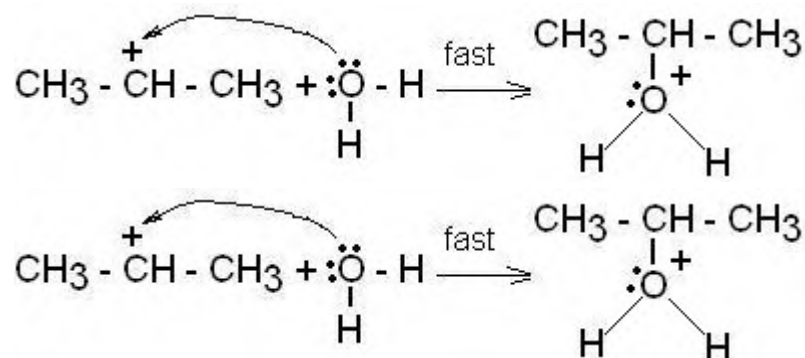


## Mechanism

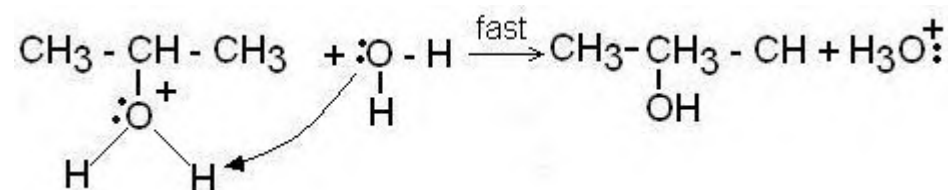
Step I : Electrophilic attack by hydronium ion ( $\text{H}_3\text{O}^+$ ) on alkene gives an intermediate carbocation.



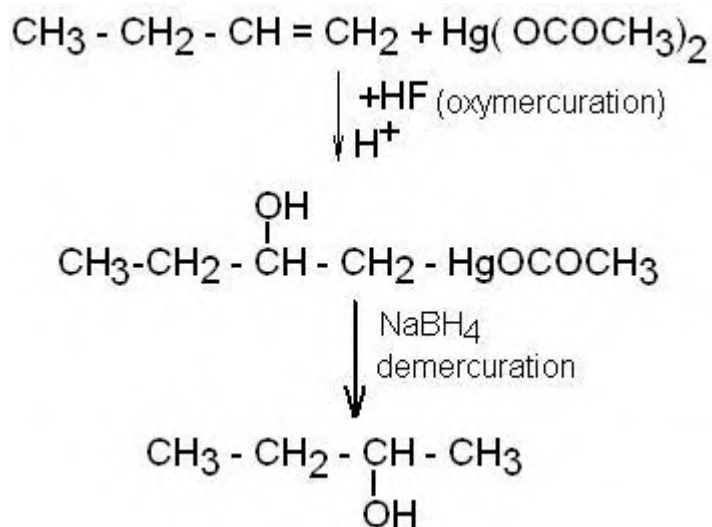
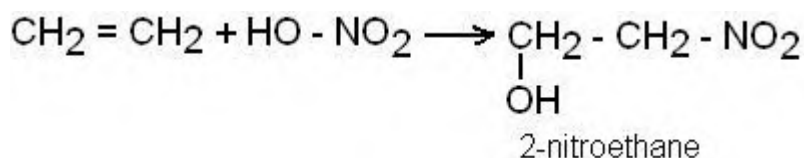
Step II : Nucleophilic attack by water on carbocation to yield protonated alcohol



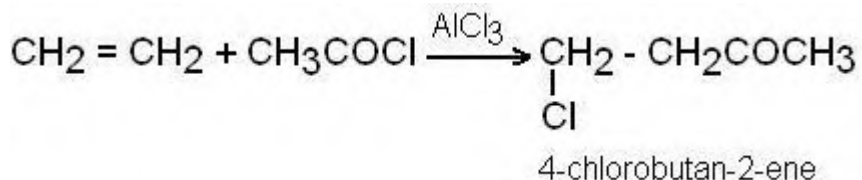
Step III: Deprotonation to form alcohol



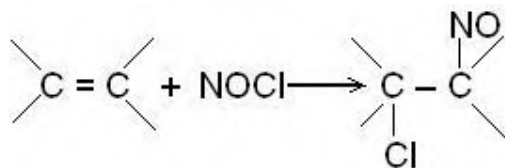
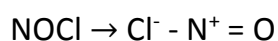
## 7. Oxymercuration – demercuration

8. Addition of  $\text{HNO}_3$ 

## 9. Addition of acetyl chloride

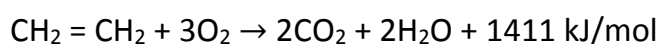


## 10. Addition of nitrosyl chloride (Tilden's Reagent)



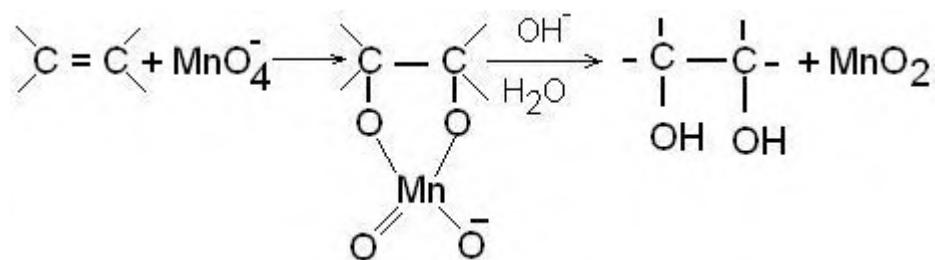
## 11. Oxidation

(i) Complete combustion



(ii) Oxidation with potassium permanganate

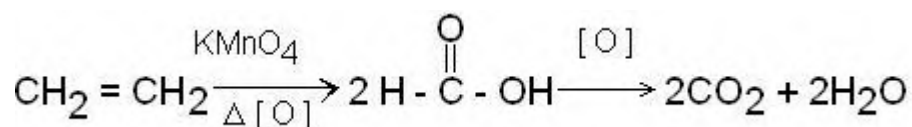
(a) Oxidation with cold dilute neutral or alkaline  $\text{KMnO}_4$  cold alkaline $\text{KMnO}_4$  is known as Baeyer's reagent



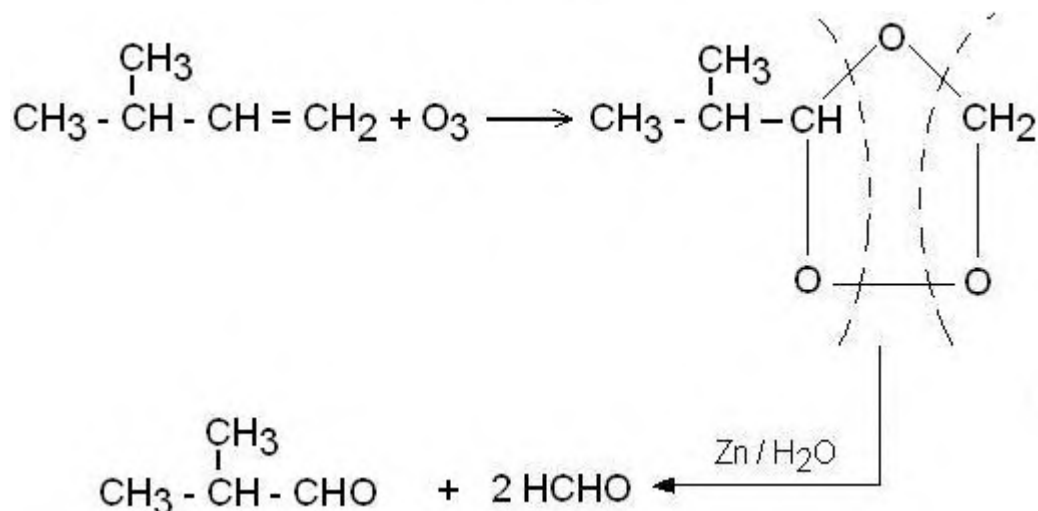
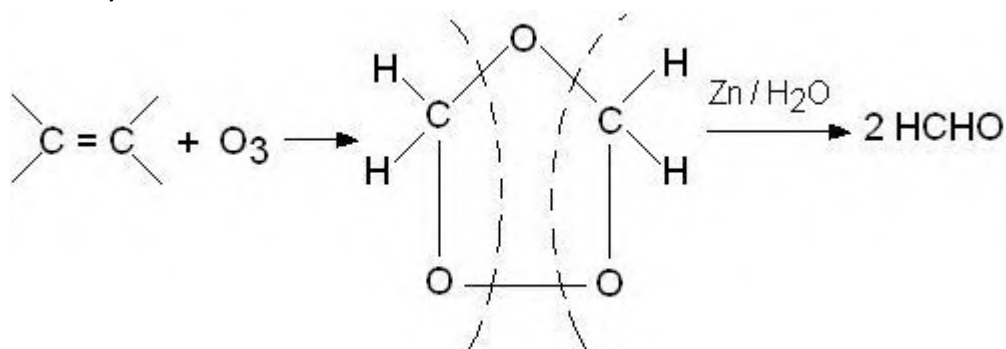
This reaction is used for testing presence of unsaturation

As soon as  $\text{KMnO}_4$  reacts with alkene its pink colour gets discharged and brown precipitate of  $\text{MnO}_2$  is obtained

(b) Oxidation with hot  $\text{KMnO}_4$

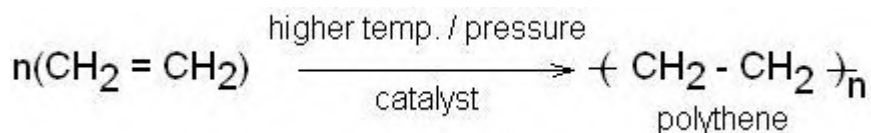


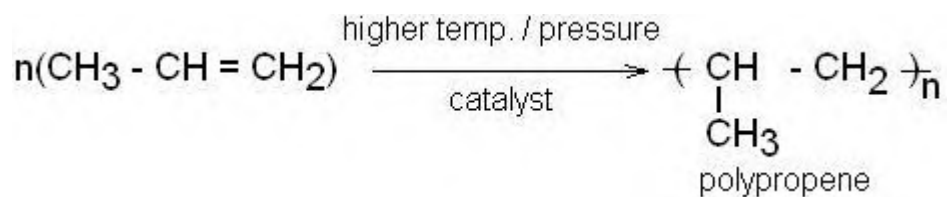
### 12. Ozonolysis



### 13. Polymerisation

Two or more molecules of an alkene link together to form a new bigger molecule of higher molecular mass. This process is called polymerization





Polymers are used for manufacture of plastic bags, toys, pipe, etc

Uses of alkenes

Ethene is used:

- (i) For the manufacture of polythene – a plastic material
- (ii) For artificial ripening of fruits
- (iii) As a general anaesthetic.
- (iv) As a starting material for a large number of compounds such as glycol, ethyl alcohol etc
- (v) For making poisonous mustard gas ( war gas)
- (vi) For making ethylene – oxygen flame for cutting and welding metals