

## Physical properties of Alkanes

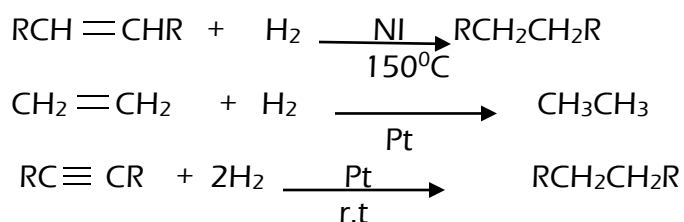
1. Lower alkanes (C<sub>1</sub> – C<sub>4</sub>) are colourless odourless gases. C<sub>5</sub> – C<sub>17</sub> are colourless odourless liquids. The higher alkanes are colourless odourless solids.
2. Alkanes are non – polar molecules and hence are insoluble in polar solvents like water but soluble in non – polar solvents like benzene, ether e.t.c
3. Physical constants like M.pt and B.pt increase with increase in molecular mass. With increase in surface area, the strength of Van der Waal's forces between molecules increase, therefore more energy or a higher temperature is required to separate the molecules and produce boiling.

**N.B** Branched alkanes have lower boiling points than the corresponding straight chain counterparts with the same formula mass. This is because increased branching tends to give the molecule a more spherical shape leading to a reduction in the degree of contact between neighbouring molecules thereby reducing the strength of intermolecular forces of attraction.

## Methods of Preparation of Alkanes

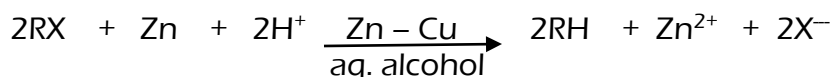
### 1. Hydrogenation of Alkenes and Alkynes

A mixture of hydrogen and the alkene or alkyne is passed over a finely divided catalyst to give the alkane. With platinum, the reaction takes place at room temperature and with Nickel at a temperature of 150°C.



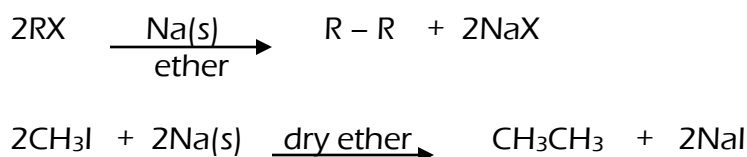
### 2. Reduction of Alkyl halides

An alkyl halide can be hydrogenated using Zinc – Copper couple in the presence of an alcohol and a halogen acid.



### 3. The Wurtz Reaction

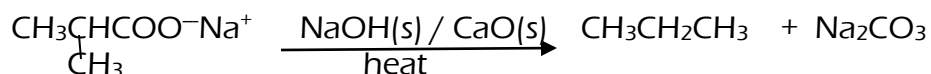
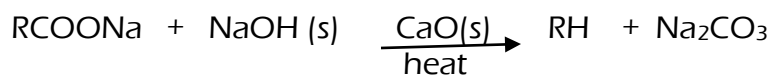
In this reaction, the alkyl halide is reacted with sodium metal in the presence of dry ether to form an alkane which has twice the number of carbon atoms as the starting material.



The above reaction is important in increasing the chain length.

#### 4. Decarboxylation

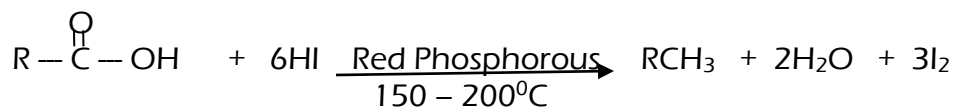
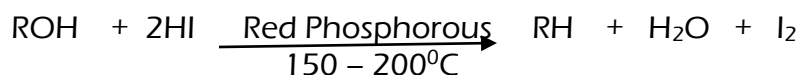
This is the removal of the elements of carbon dioxide from a compound. The reaction is carried out by heating a carboxylic acid or a carboxylic acid salt with soda lime (a mixture of calcium oxide and sodium hydroxide).



The alkane formed is one carbon atom less than the starting material implying that the reaction facilitates reduction of the carbon chain length.

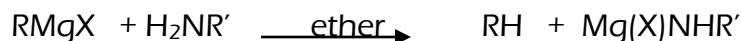
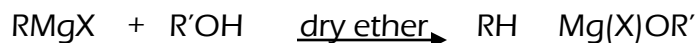
#### 5. From alcohols, Ketones and Carboxylic acids

When alcohols, ketones and carboxylic acids are reduced with hot hydroiodic acid and red phosphorous (150 – 200°C) in a sealed tube, alkanes are formed.



#### 6. From Grignard's reagent

Grignard's reagent is prepared by reacting an alkyl halide with metallic Magnesium in the presence of dry ether. Grignard's reagent when treated with compounds containing active hydrogen, like water, alcohols or amines, yield pure alkanes.

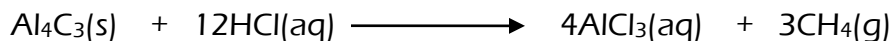
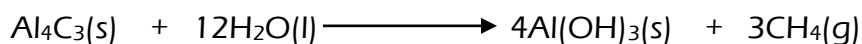


Where X is Cl, Br, or I

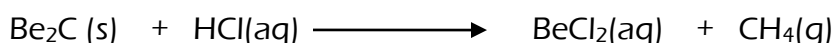
## Methods specific to methane

In addition to the above general methods of preparation, methane may be prepared by:

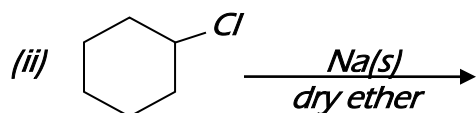
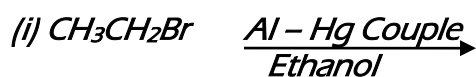
### (i) Treating Aluminium carbide with hot water or dilute acid



Similarly



*Complete each of the following organic reactions and name the main organic product.*

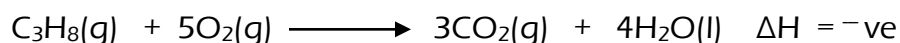
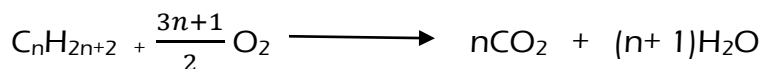


## CHEMICAL PROPERTIES OF ALKANES

Alkanes are dominated by carbon – carbon and carbon – hydrogen bonds which are very strong. In addition, the carbon – hydrogen bonds are non – polar because carbon and hydrogen have almost the same electronegativities. This implies that alkanes are relatively inert. However, they undergo some reactions at a fairly high temperature or in presence of ultra violet light. These reactions include:

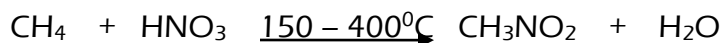
### 1. Oxidation

Alkanes burn in air (oxygen) giving off carbon dioxide and water in an exothermic reaction.



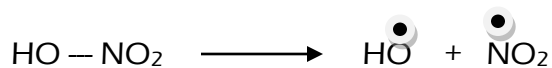
### 2. Nitration

This is the replacement of a hydrogen atom of the alkane by a nitro ( $-\text{NO}_2$ ) group. It is carried out by using concentrated nitric acid vapour at temperatures of about  $150 - 400^\circ\text{C}$ . The reaction goes by free radical mechanism.

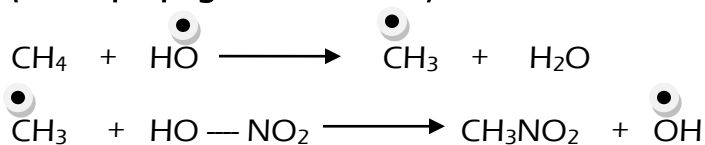


## Mechanism

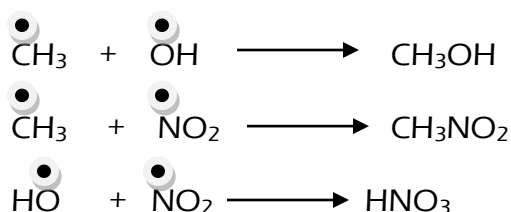
### Step 1 (Initiation step)



### Step 2 (Chain propagation reactions)



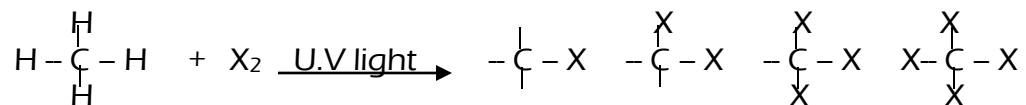
### Step 3 (Chain termination steps)



Since the reaction follows free radical mechanism, a mixture of products is formed.

## 3. Halogenation

Alkanes react with the first three members of the halogen family: Fluorine, Chlorine and Bromine in the presence of ultra violet light. With methane, the reaction produces a mixture of halo methanes.



e.g Chlorination of methane



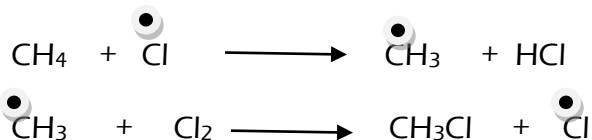
### Mechanism

Halogenation of alkanes follows a free radical mechanism and therefore the reaction can be referred to a *free radical substitution reaction*. This reaction / mechanism involves three stages:

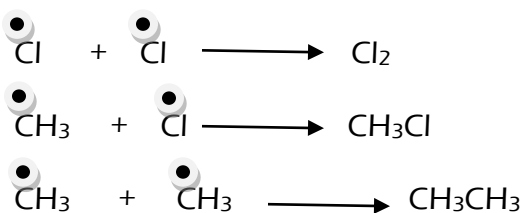
#### 1. Chain initiation step – homolysis of the Cl – Cl bond



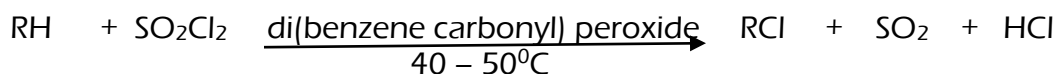
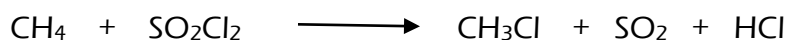
#### 2. Chain Propagation stage



### 3. Termination steps



N.B Chlorination can also be brought about by reacting the alkane with Sulphur dichloride dioxide,  $\text{SO}_2\text{Cl}_2$  in the presence of a catalyst (e.g benzoyl chloride) at 40 to 50°C.

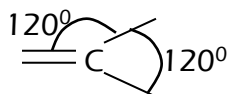


## ALKENES

These are unsaturated hydrocarbons whose molecules consist of at least a double bond between adjacent carbon atoms. Open chain alkenes are represented by the general formula  $\text{C}_n\text{H}_{2n}$ .

N.B (i) The functional group in alkenes is the carbon – carbon double bond.

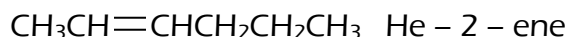
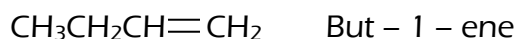
(ii) The carbon atoms in the double bond are  $sp^2$  hybridised and the bond angle is  $120^\circ$ .



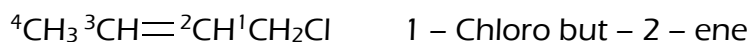
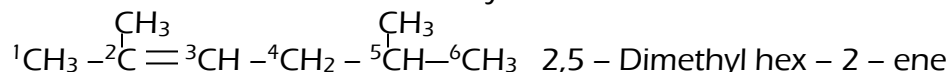
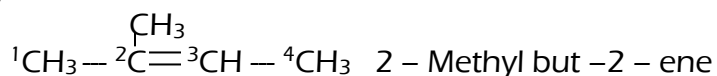
### Nomenclature of Alkenes

The IUPAC rules for naming alkenes are similar in many respects to those for naming alkanes.

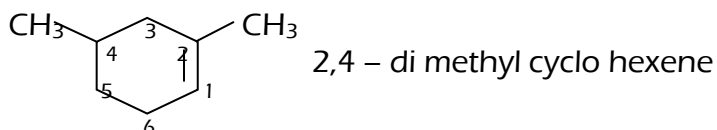
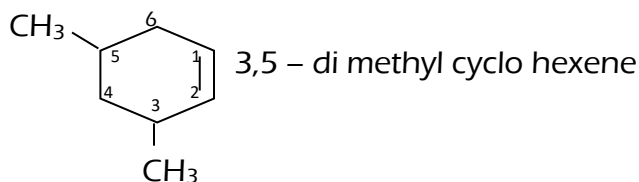
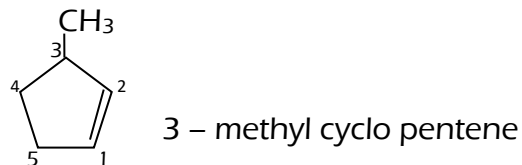
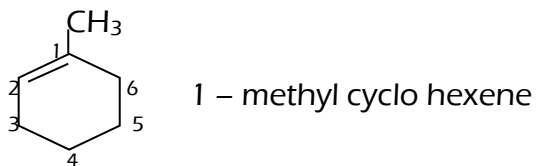
1. Alkenes are named by replacing the suffix “ – ane” in alkanes with the suffix “–ene”.
2. Determine the base (or parent) name by selecting the longest chain that contains the double bond. Number the carbon atoms in such a way as to give the carbon atom before the double bond the lowest possible number. Designate the position of the double bond by inserting this number between the stem and the ending “–ene”.



3. Indicate the locations of any substituent groups by the number of the carbon atoms to which they are attached.



N.B With cyclo alkenes, it is not necessary to specify the location of the double bond since the chain is numbered to give the carbon atoms of the double bond the 1 and 2 positions.



### General Physical Properties of Alkenes

1. The first three members ( $C_2 - C_4$ ) of alkenes are gases at room temperature.  $C_5 - C_{15}$  are liquids while the rest are solids.

2. Alkenes are insoluble in water but unlike alkanes, some of them are soluble in polar organic solvents e.g alcohols, because of their pi ( $\pi$ ) electrons.

3. Alkenes are less volatile than alkanes i.e their melting and boiling points are higher than those of corresponding alkanes.

The boiling points of alkenes increase with increase in molecular mass since increase in molecular mass increases the strength of intermolecular forces of attraction.

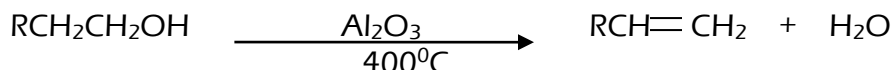
Cis – alkenes have higher melting and boiling points than the Trans – isomers because of their polarity.

## LABORATORY PREPARATION OF ALKENES

### 1. Catalytic dehydration of alcohols

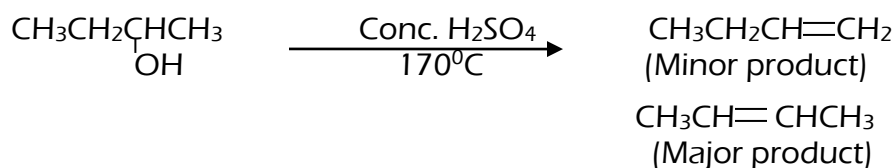
Alcohols can be dehydrated in the presence of a catalyst. The catalysts usually used are Conc.  $\text{H}_2\text{SO}_4$  or Conc.  $\text{H}_3\text{PO}_4$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{P}_2\text{O}_3$

General equation



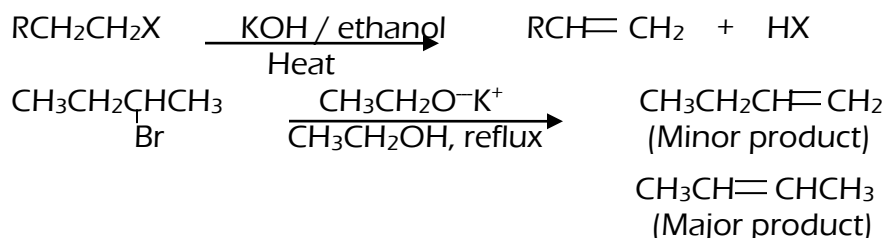
The ease of dehydration is in the order  $3^\circ$  alcohols  $>$   $2^\circ$  alcohols  $>$   $1^\circ$  alcohols. This is because dehydration of alcohols goes by formation of a "carbocation" as an intermediate and the order of stability of the carbocations is  $3^\circ > 2^\circ > 1^\circ$ .

*In dehydration of secondary and tertiary alcohols where there is a possibility of formation of two products, the product preferred is where the hydrogen is removed from the carbon atom with the least number of hydrogen atoms. This is Markownikoff's rule.*



### 2. Dehydrohalogenation of alkyl halides using hot ethanolic KOH or NaOH

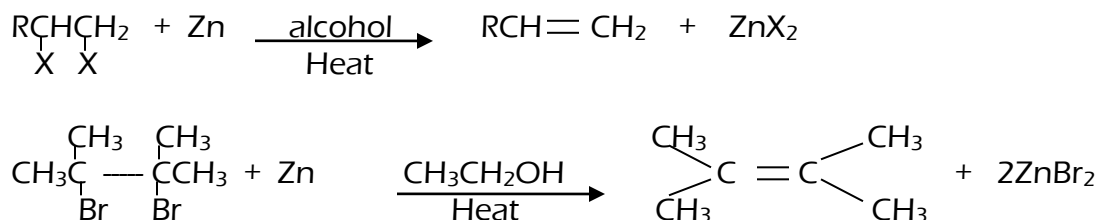
When alkyl halides are heated with an alcoholic solution of potassium hydroxide or sodium hydroxide, a hydrogen halide (HX) molecule is eliminated.



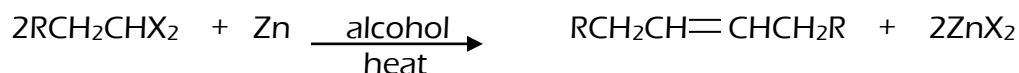
The ease of dehydrohalogenation is in the order  $3^\circ > 2^\circ > 1^\circ$  and the ease of removal of different halides is  $\text{I} > \text{Br} > \text{Cl}$ .

### 3. Dehalogenation of Vicinal dihalides

Vicinal (Vic —) dihalides are dihalide compounds in which the halogens are situated on adjacent carbon atoms. The Vic — dihalide is heated with zinc powder in the presence of an alcohol.



With Geminal (Gem —) dihalides (where halogens are attached on the same carbon atom)

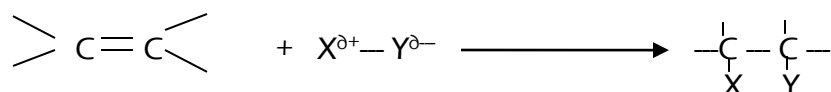


## CHEMICAL CHARACTERISTICS OF ALKENES

### Nature of the double bond

The two unsaturated carbon atoms in the C = C bond are joined by a sigma bond and also a Pi bond. The cloud of electrons which forms the Pi bond lies above and below the plane of the unsaturated carbon atoms. The Pi bond therefore provides a region of high electron density and is therefore susceptible to attack by electrophilic reagents.

Alkenes generally undergo electrophilic addition reactions. These can be generally written as;

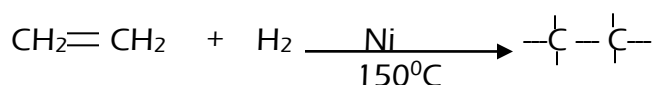


**Definition:** An electrophilic addition reaction is one in which an unsaturated organic compound such as an alkene combines with an electron deficient species (electrophile) to form a single product which is normally saturated.

## REACTIONS OF ALKENES

### 1. Hydrogenation

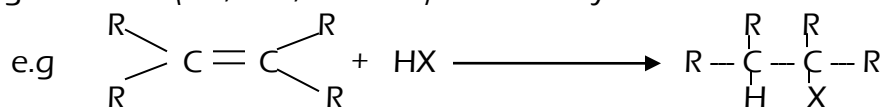
Alkenes react with hydrogen when heated and passed over a catalyst to form alkanes.



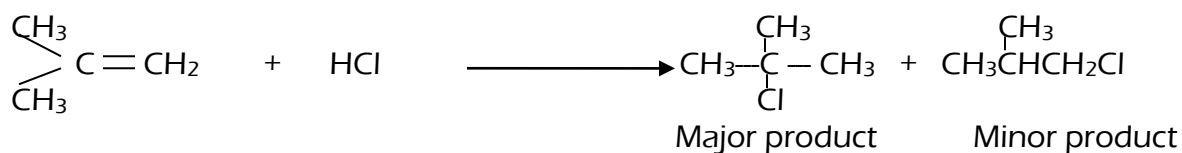
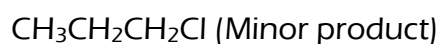
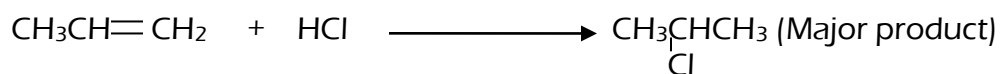
Using finely divided Pt or Pd, hydrogenation takes place at room temperature.

### 2. Addition of HX to alkenes

Hydrogen halides (HF, HBr, and HCl) add directly to the double bond of alkenes



The addition reaction to an unsaturated alkene (where the carbon atoms in the double bond have an unequal number of hydrogen atoms) could occur in two ways. However, in practice, one product usually predominates.

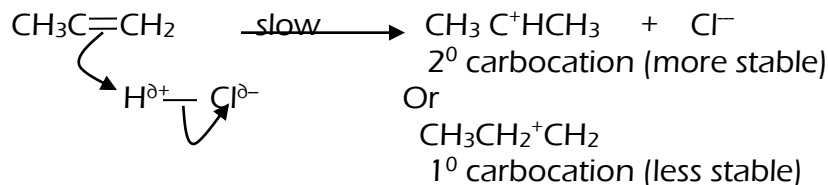




*"In electrophilic addition to unsymmetrical alkenes, the electrophile e.g the hydrogen of the HX molecule, adds to the carbon atom in the double bond which bears the greater number of hydrogen atoms."* This is *Markownikoff's rule*.

This is explained in terms of the order of stability of the carbocation formed i.e  $3^{\circ} > 2^{\circ} > 1^{\circ}$ .

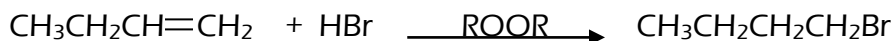
### Mechanism



Markownikoff's rule can be restated as: *"In the ionic addition to unsymmetrical alkenes, the positive portion of the adding reagent attaches itself to a carbon atom of the double bond so as to yield a more stable carbocation as the intermediate."*

### 3. Anti Markownikoff's addition of HBr to alkenes

It occurs in the presence of a peroxide.

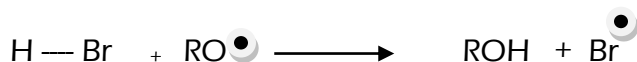


### Mechanism

The first step is the decomposition of the peroxide into free radicals via homolytic cleavage either by heat or light.



The free radicals formed attack the hydrogen bromide molecule to form a bromine free radical.



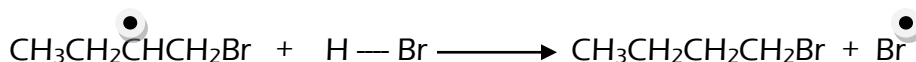
### Chain propagation steps

In the first propagation step, bromine radical adds to the alkene double bond to form an alkyl free radical



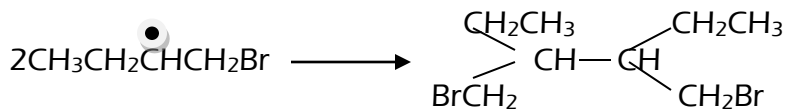
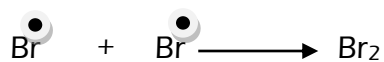
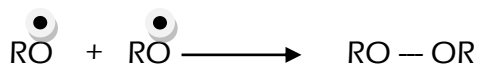
The more stable  $2^{\circ}$  free radical is the one that is formed as compared to the less stable  $1^{\circ}$  free radical.

In the second propagation step, the alkyl free radical attacks another HBr molecule to give a bromo alkane and another bromine free radical which recycles back into the first propagation step and carry on a chain reaction.



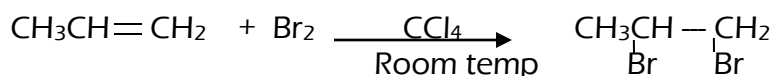
The product formed is anti Markownikoff's rule.

### Chain termination steps

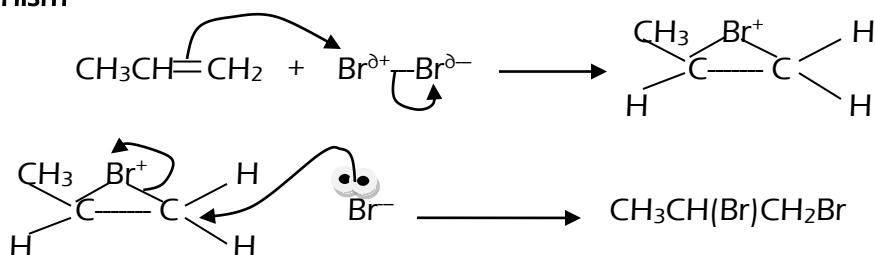


### 4. Halogenation – Addition of halogens in $\text{CCl}_4$

Halogens react with alkenes in  $\text{CCl}_4$  as solvent to form dihalide derivatives.



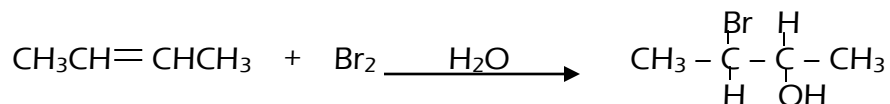
#### Mechanism



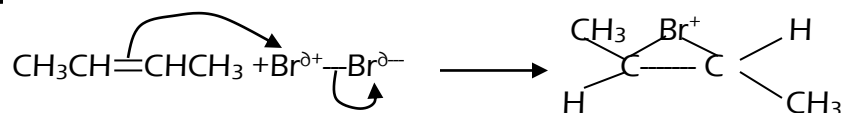
NOTE: The true intermediate in this reaction is a cyclic bromonium ion and not a true carbocation. Using its lone pair of electrons, the bromo substituent forms a three membered ring bromonium ion with the carbon atoms in the double bond.

### 5. Addition of $\text{X}_2 / \text{H}_2\text{O}$

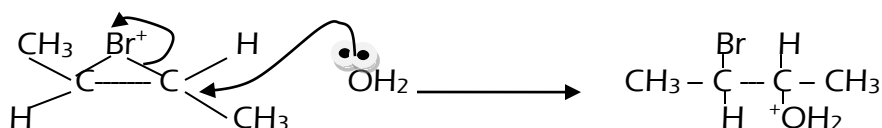
If halogenations of an alkene is carried out in aqueous solution (rather than  $\text{CCl}_4$  as solvent) the major product is not a vicinal dihalide but rather a halo alcohol, In this case, the molecules of the solvent become reactants too.



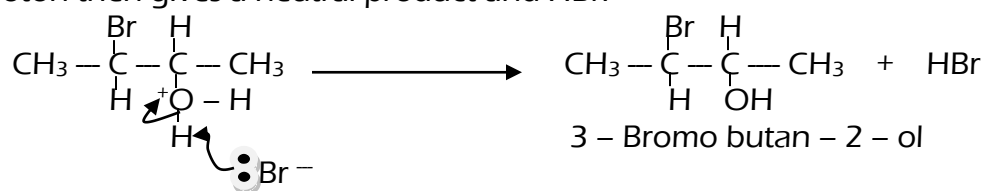
#### Mechanism



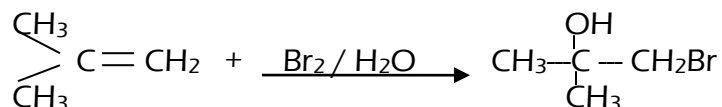
Then  $\text{H}_2\text{O}$  acts as a nucleophile and attacks the bromonium ion. This is because water molecules as solvent outnumber the  $\text{Br}^-$  ions.



Loss of a proton then gives a neutral product and HBr.

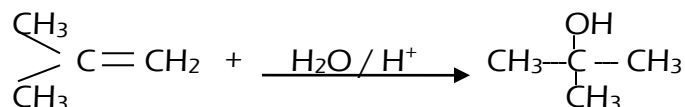


**Note:** If the alkene is unsymmetrical, the halogen ends up on the carbon atom with a greater number of hydrogen atoms.



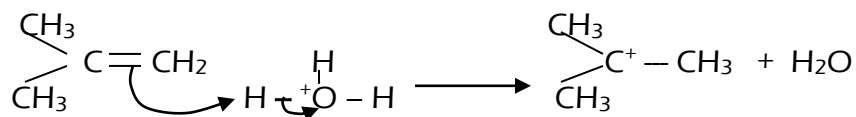
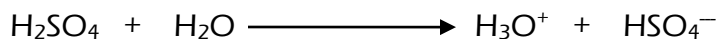
## 6. Acid catalysed hydration of alkenes

Alkenes react with acidified water to form an alcohol. The acids most commonly used to catalyse the hydration of alkenes are  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$ . The addition of water to the double bond follows Markownikoff's rule.



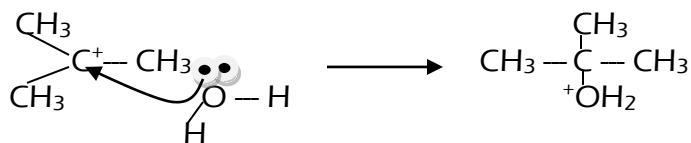
### Mechanism

The first step is the electrophilic attack by the proton from the acid on the double bond to form a carbocation.



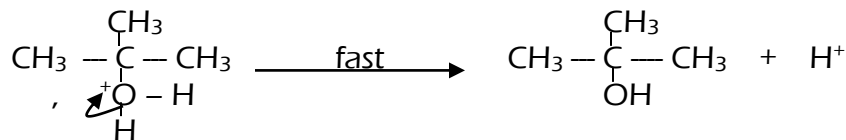
### Step 2

Since water is in large amounts than the acid, the next step is the nucleophilic attack by water molecules on the carbocation to give a protonated alcohol.

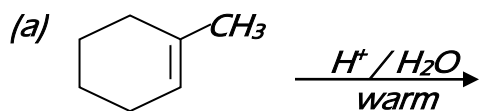


### Step 3

The protonated alcohol then eliminates a proton

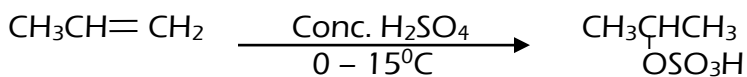


Qn. Complete the following equations and in each case suggest a mechanism for the reaction

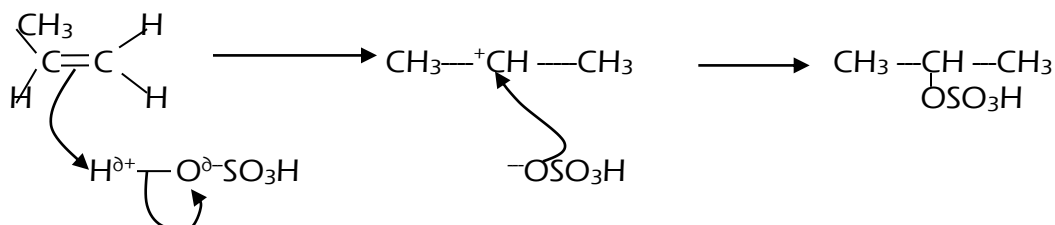


### 7. Addition of concentrated sulphuric acid

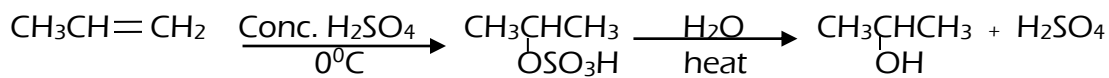
Alkenes react with cold (0 – 15°C) concentrated sulphuric acid to form compounds known as alkyl hydrogen sulphates.



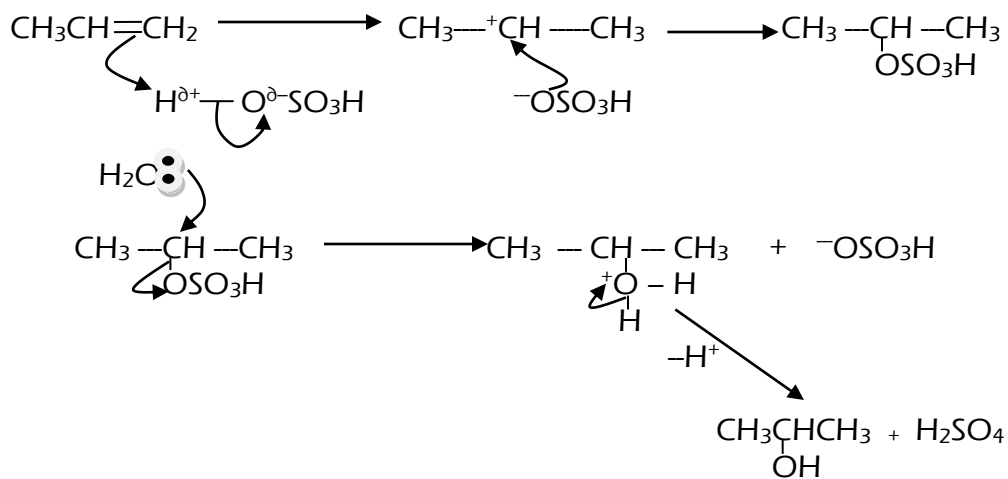
#### Mechanism



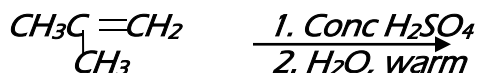
Alkyl hydrogen sulphates can be easily hydrolysed to alcohols by heating with water



#### Mechanism

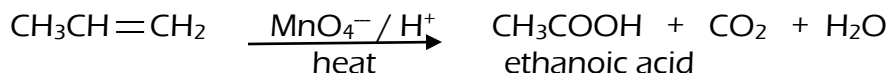


Complete the following equation and write an acceptable mechanism for the reaction.

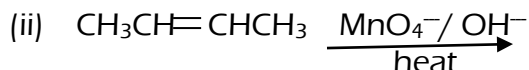
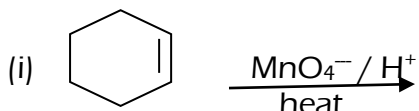


### 8. Oxidative cleavage of alkenes

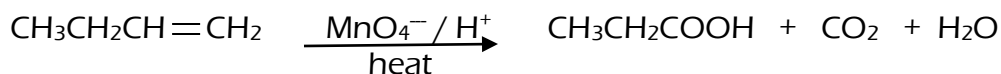
An alkene which does not have a branch on the carbon atoms of the double bond is oxidized to carboxylic acids when heated strongly with acidified or alkaline potassium permanganate.



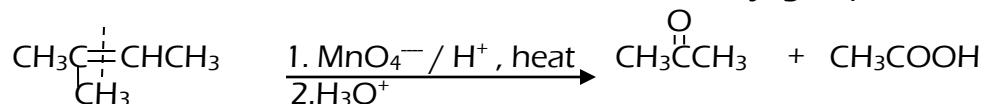
Complete the following reactions



**Note:** The terminal  $-\text{CH}_2$  group of a 1-alkene is completely oxidized to carbon dioxide and water by hot permanganate solutions.

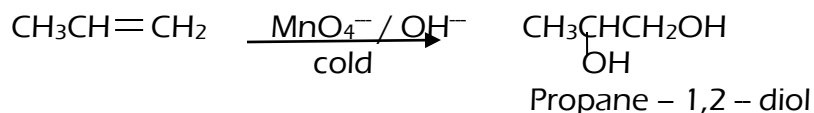


A branched carbon atom of the double bond becomes a carbonyl group i.e. ketone.



### 9. Reaction with cold alkaline $\text{KMnO}_4$

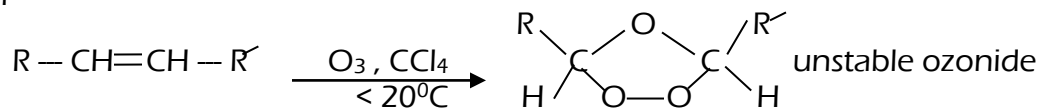
Alkenes react with acidified or alkaline potassium manganate (VII) solution to form diols. This reaction is also known as hydroxylation. The purple colour of the manganate (VII) solution turns to colourless implying that this reaction is useful in testing for unsaturation.



The first step of the mechanism involves formation of a cyclic intermediate ester which is unstable.

## 10. Ozonolysis of alkenes

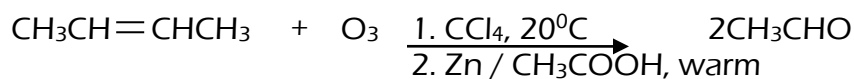
Ozone is usually bubbled through a solution of an alkene in the presence of an organic solvent. The reaction is performed below  $20^{\circ}\text{C}$  since the ozonide formed is an explosive compound.



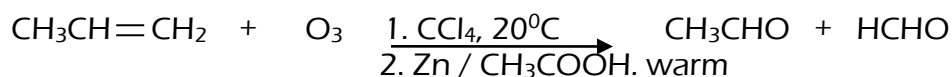
On reducing the ozonide with a mixture of Zinc and water or Zinc and aqueous ethanoic acid, the ozonide breaks to give carbonyl compounds.



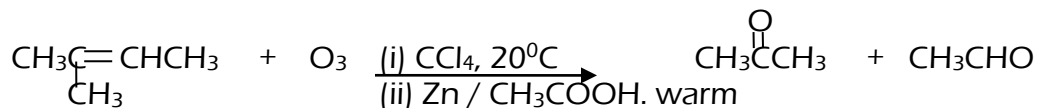
**Note 1:** Ozonolysis followed by reduction can be used to locate / identify the position of the double bond in an alkene.



**Note 2:** Alkenes without branches on the carbon atoms of the double bond react to give aldehydes.

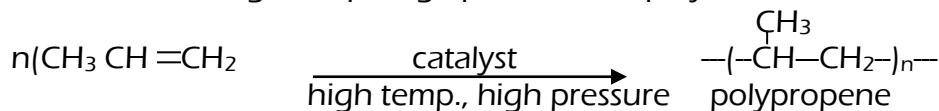
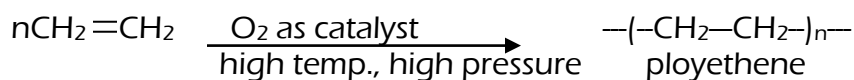


Alkenes with branches on the carbon atoms of the double bond react to form ketones as one of the products.

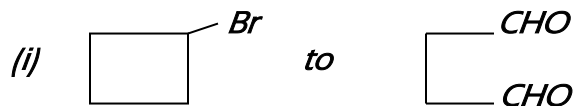


## 11. Polymerisation of alkenes

Polymerisation is the aggregation of many small molecules called monomers to form one large molecule called a polymer.



Qn. Write equations, indicating the conditions, to show how the following conversions can be effected.



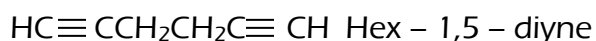
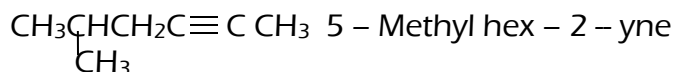
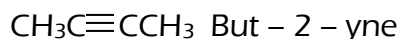
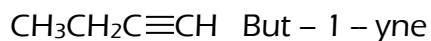
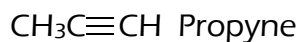
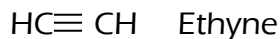
## ALKYNES

Straight chain alkynes can be represented by the general formula  $\text{C}_n\text{H}_{2n-2}$ .

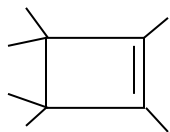
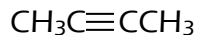
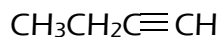
They have at least a triple bond between carbon atoms.

### NOMECLATURE OF ALKYNES

The ending *-ane* of the corresponding alkane is replaced by *-yne* in the alkyne. If the triple bond can take up more than one position in the molecule, then the carbon chain is numbered in such a way as to assign a minimum number to the carbon atom preceding the triple bond.



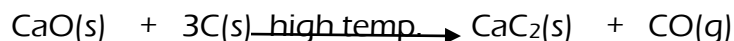
N.B Alkynes are isomeric to cyclic alkenes and are also isomeric to dienes. e.g  $\text{C}_4\text{H}_6$  has the following isomers



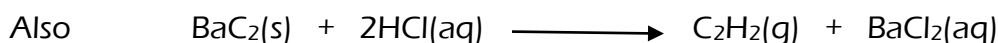
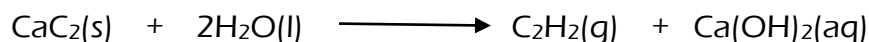
## General methods of preparation of alkynes

### 1. Preparation of ethyne

The first member of the alkynes, ethyne, is prepared by reacting Calcium carbide with water. Calcium carbide is prepared by heating Calcium oxide with Carbon (Coke) at very high temperature.

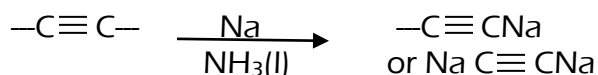


Calcium carbide then reacts with water to give ethyne.



### 2. Alkylation of Sodium alkynides

This reaction is important in producing higher alkynes by increasing the carbon chain length. Ethyne is first converted to a mono- or di- Sodium alkynide ( $\text{HC}\equiv\text{CNa}$  or  $\text{NaC}\equiv\text{CNa}$ ) by treating with Sodium metal in liquid ammonia.

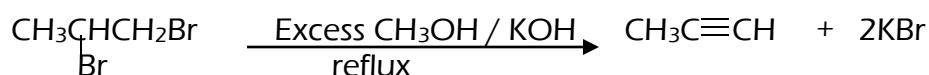


The alkynide is then treated with an alkyl halide to give a higher alkyne.



### 3. Dehydrohalogenation of dihalo alkanes

When dihalo alkanes are treated with hot alcoholic potassium hydroxide, alkynes are obtained by elimination of two hydrogen halide molecules. The dihalides may be vic- or gem- dihalides.



*Qn. Use equations to show how the following conversion can be effected.*

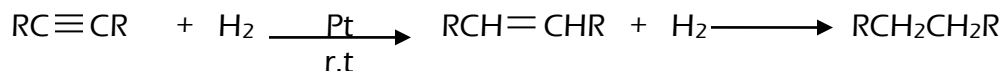




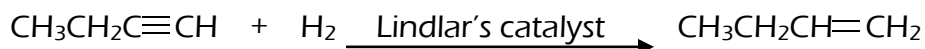
## REACTIONS OF ALKYNES

### 1. Addition of hydrogen

Alkynes when heated with hydrogen in the presence of finely divided Pt, Pd or Ni catalyst; they are reduced to alkanes, the reduction being too difficult to stop in order to isolate alkenes. Pt and Pd operate at ordinary temperatures but Ni requires heating.

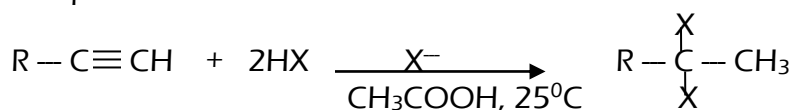


In the reduction of certain higher alkynes, the intermediate alkene can be isolated using a poisoned catalyst (Lindlar catalyst) e.g Pd / CaCO<sub>3</sub> + quinoline.



### 2. Addition of HX to alkynes (hydrohalogenation)

The reaction in unsymmetrical (usually terminal) alkynes occurs according to Markownikoff's rule if there is no peroxide.

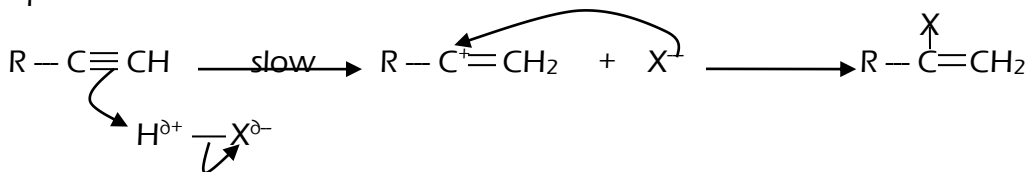


#### Mechanism

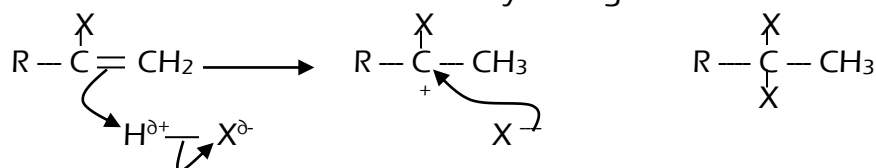
It involves formation of an intermediate carbocation which subsequently reacts with a halide ion to produce a halo alkene.

#### Mechanism

It involves formation of an intermediate carbocation which subsequently reacts with a halide ion to produce a halo alkene.

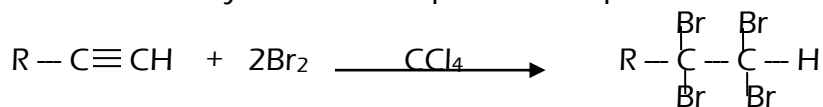


The halo alkene then reacts further to yield a gem - dihalide.

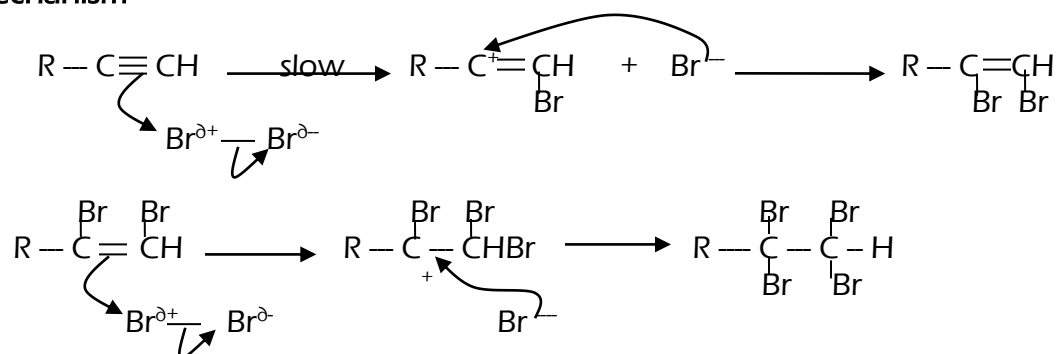


### 3. Reaction with halogens

Chlorine and Bromine readily add to the triple bond to produce tetra halides.



## Mechanism



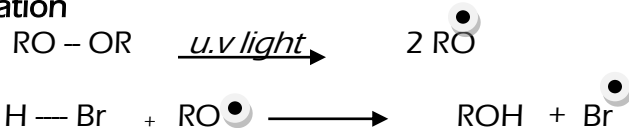
## 4. Anti Markownikoff's addition of HX

Anti Markownikoff's addition of HBr to alkynes occurs in the presence of peroxides. The reactions take place through a free radical mechanism.

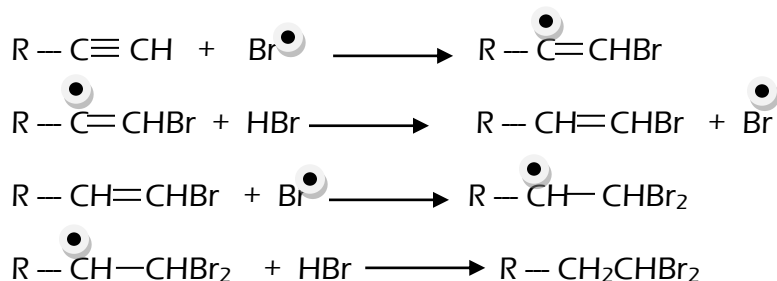


## Mechanism

### Chain initiation

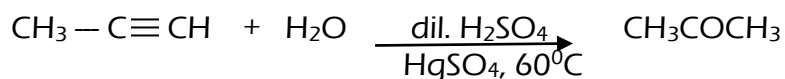
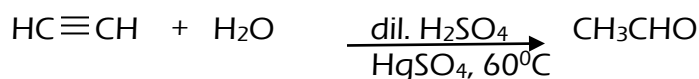


### Chain propagation

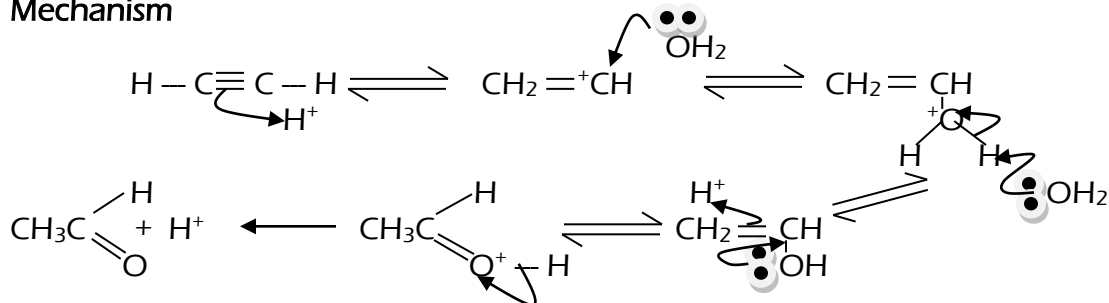


## 5. Reaction with water in the presence of sulphuric acid

Alkynes react with water in the presence of dilute sulphuric acid and a little Mercury (II) sulphate as a catalyst. Ethyne yields ethanal while higher alkynes yield ketones.

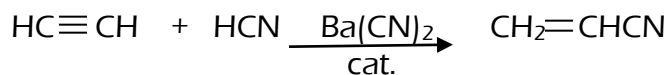


## Mechanism



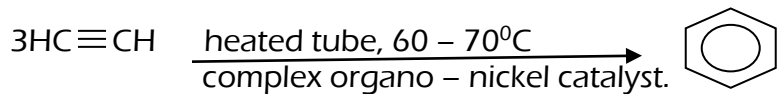
## 6. Addition of hydrogen cyanide

Alkynes react with hydrogen cyanide (HCN) to give a cyano nitrile, a useful starting material for manufacture of polymers.

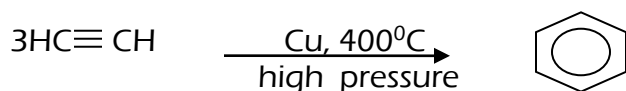


## 7. Polymerisation of alkynes

Ethyne polymerises to benzene when passed through a heated tube containing complex organo – nickel catalyst.

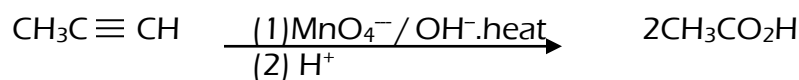
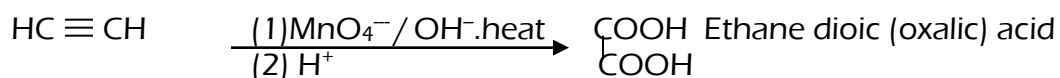
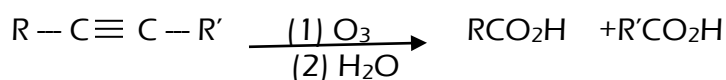


Or



## 8. Oxidative cleavage of alkynes

Treating alkynes with ozone or with basic potassium manganate (VII) leads to cleavage at the carbon – carbon triple bond. The products are carboxylic acids.



## Chemical tests for alkenes and alkynes

### (a) Bromine in carbon tetra chloride

Alkenes and alkynes both react with bromine at room temperature in the absence of light. Thus the rapid decolourisation of bromine in  $\text{CCl}_4$  at room temperature indicates the presence of carbon – carbon double bond or carbon – carbon triple bond.

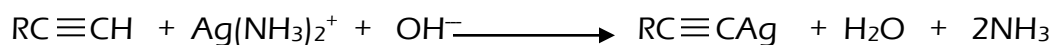
### (b) Cold dilute potassium manganate (VII) solution

Alkenes and alkynes are oxidized by cold dilute potassium manganate (VII) solutions. If the alkene or alkyne is present in excess, the purple colour of potassium permanganate solution turns colourless and is replaced by a brown colour of the precipitated manganese dioxide.

## Reactions of alkynes with a terminal triple bond

### (1) Reaction with ammoniacal Silver nitrate

Silver nitrate reacts with aqueous ammonia to give a solution containing the complex  $\text{Ag}(\text{NH}_3)_2^+$ . This reacts with terminal alkynes to form a white precipitate of Silver alkynide.



Non terminal alkynes do not form a white precipitate.

## 2. Reaction with ammoniacal Copper (I) chloride

A reddish – brown precipitate of Copper (I) alkynide is formed with terminal alkynes.



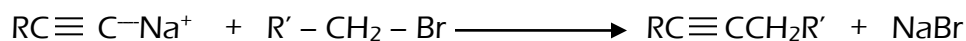
Non terminal alkynes do not form a precipitate.

## 3. Reaction with sodium amide

Treating terminal alkynes with sodium amide in liquid ammonia yield sodium alkynide.



Treating the Sodium alkynide with a  $1^\circ$  alkyl halide yields a higher alkyne.

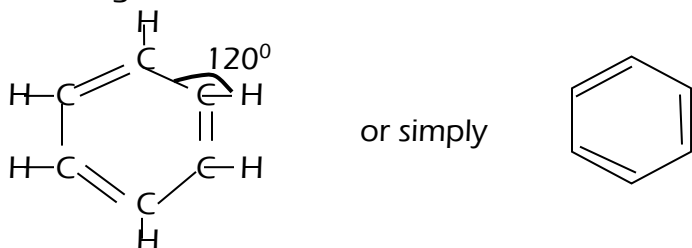


## AROMATIC COMPOUNDS

Benzene and its derivatives form a group of compounds known as aromatic compounds. Benzene is the simplest of the aromatic compounds.

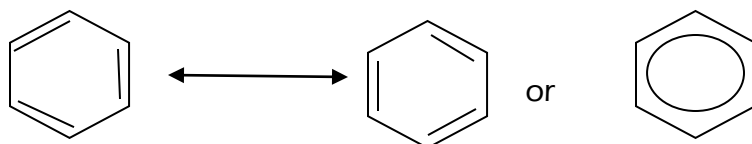
### Structure of Benzene

The molecular formula  $C_6H_6$  indicates that benzene is highly unsaturated. The benzene molecule will be represented by the Kekule structure (1865). Benzene is a planar cyclic compound in which each carbon atom is covalently bonded to three other carbon atoms and the bond angles are  $120^\circ$ . In the structure, double and single bonds alternate positions.



### Comments

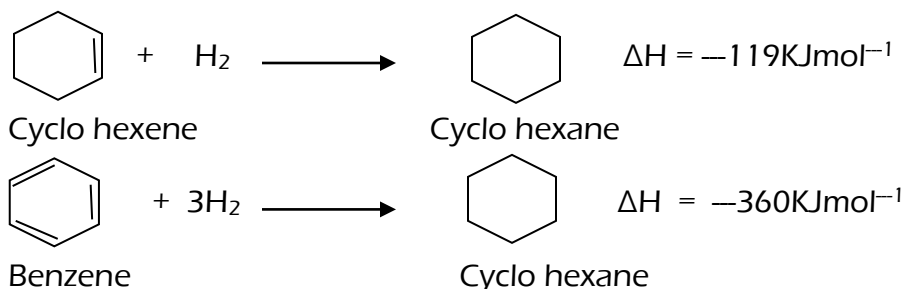
1. From bond length measurements, all carbon – carbon bonds in benzene are of the same length ( i.e 0.139nm). i.e what appears as a double or single bond between carbon atoms are not true double or single bonds but are intermediate between the two. The molecule of benzene is therefore sometimes written as a resonance hybrid of two structures. These two structures are known as *Canonical forms*.



N.B In chemical reactions, any of the three structures may be used.

2. From studies of enthalpy changes, the enthalpy of formation of benzene is  $82 \text{ KJmol}^{-1}$  and yet the expected value if benzene was "cyclo hexa triene" is  $252 \text{ KJmol}^{-1}$ . Therefore benzene is stable by  $170 \text{ KJmol}^{-1}$  ( $252 - 82$ ).

3. From heats of hydrogenation (amount of heat evolved when one mole of hydrogen is added to an unsaturated compound), the enthalpy of hydrogenation of cyclo hexene is  $-120 \text{ KJmol}^{-1}$  whereas that of benzene is  $-200 \text{ KJmol}^{-1}$  yet the expected value would be  $-360 \text{ KJmol}^{-1}$  (i.e  $120 \times 3$ ).



N.B The enthalpy of hydrogenation of benzene is not three times that of cyclo hexane. This shows that benzene is more stable than when looked at as to contain three double bonds.

Benzene is stabilized by delocalization of the Pi electrons and hence the ability to undergo resonance and exist as hybrid structures or canonical forms. Any structure in which delocalization occurs tends to be stabilised.

*Qn. Explain the following observations*

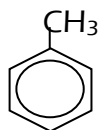
*(i) The enthalpy of hydrogenation of cyclohexene to cyclohexane is  $-120\text{KJmol}^{-1}$  while that of benzene to cyclohexane is  $-200\text{KJmol}^{-1}$ .*

*(ii) Although ethene and benzene are both unsaturated compounds, ethene undergoes electrophilic addition reactions whereas benzene undergoes electrophilic substitution reactions.*

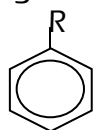
### Nomenclature of Aromatic compounds

Benzene is the simplest aromatic compound. Other aromatic compounds are obtained when one or more hydrogen atoms in benzene are replaced by another atom or groups of atoms.

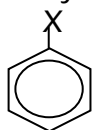
**(i)** Two systems are used in naming mono substituted benzenes. In certain compounds, the name of the substituent is given first followed by the word benzene as the parent name.



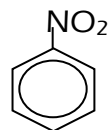
Methyl benzene



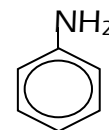
Alkyl benzene



Halo benzene

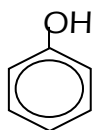


Nitro benzene

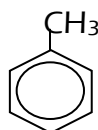


Aminobenzene  
(Phenyl amine)

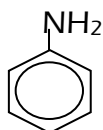
For other compounds, the substituent and the benzene ring are taken together to form the parent name.



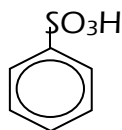
Phenol



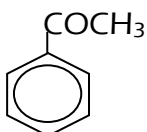
Toluene



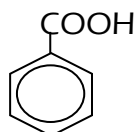
Aniline



Benzene sulphonamic acid

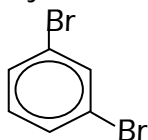


Acetophenone

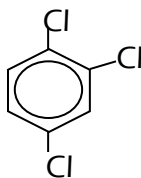


Benzoic acid

**(ii)** If there are two or more substituents in the benzene ring, since all the carbon atoms are identical, any carbon atom can be number one. But, for the sake of uniformity, the top carbon atom is usually taken as number one.

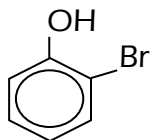


1,3 – Dibromo benzene

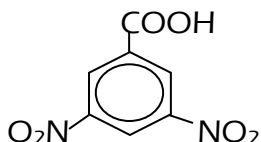


1,2,4 – Trichloro benzene

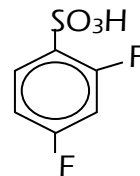
(iii) If one of the groups / substituents is such that it gives a special name to the compound, then it is assumed to be in position one.



2 – Bromo phenol

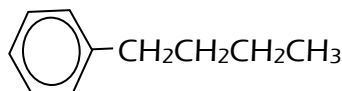


3,5 – Dinitro benzoic acid

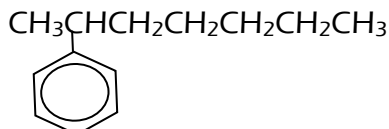


2,4 – difluoro benzene–  
Sulphonic acid

(iv) a hydrocarbon composed of one saturated side chain and one benzene ring is usually named as a derivative of the larger structural unit.

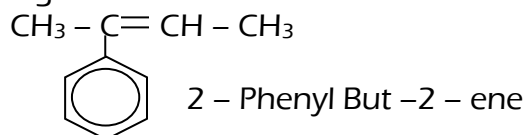


Butyl benzene



2 – Phenyl heptane

If the side chain is unsaturated, the compound may be named as a derivative of that chain, regardless of the ring size.

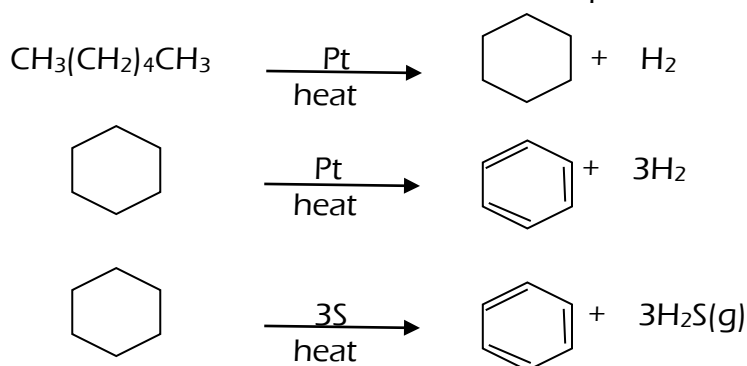


## PREPARATION OF BENZENE

### Industrial Preparation of Benzene

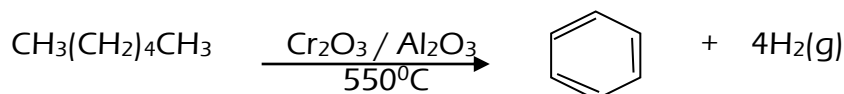
#### 1. Dehydrogenation of cyclo hexane

Cyclo hexane can be obtained from normal hexane and undergoes dehydrogenation in the presence of heated Palladium or Platinum or Sulphur to form benzene.



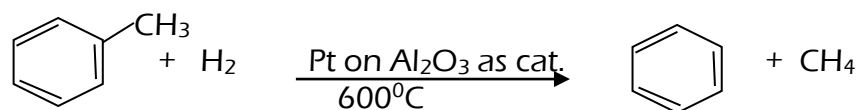
#### 2. Catalytic reformation of Petroleum

This involves catalytic dehydrogenation of hexane obtained from petroleum. This is effected at a temperature of about 550°C in the presence of Chromium (III) oxide and Aluminium oxide.



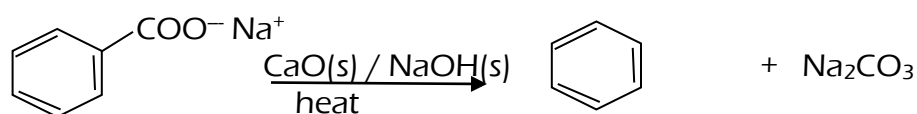
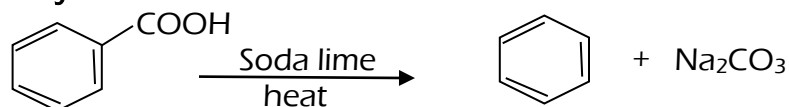
### 3. Hydro dealkylation (addition of a hydrogen and removal of an alkyl group)

This is achieved in the presence of Platinum catalyst or Aluminium oxide at temperatures about 600°C.

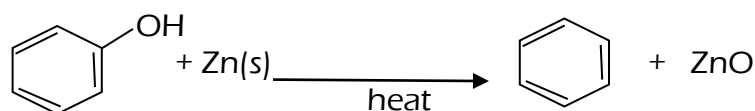


### Laboratory preparation of Benzene

#### 1. By decarboxylation of benzoic acid or benzoates

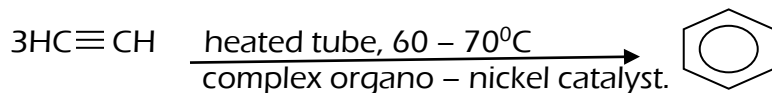


#### 2. From Phenol vapour – Pass Phenol vapour over heated Zinc dust.

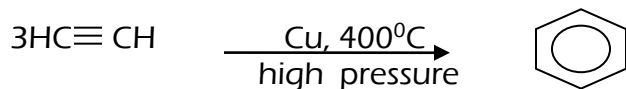


### 3. Polymerisation of ethyne

Ethyne is heated to 60 – 70°C in the presence of a complex organo – Nickel catalyst.



Or



### Physical Properties of Benzene

1. Colourless liquid with a characteristic odour
2. It is insoluble in water but soluble in organic solvents and it is itself a good solvent for organic compounds.
3. It burns with a sooty and luminous flame.
4. It freezes at 5°C and boils at 80°C.
5. It is highly toxic / poisonous



## CHEMICAL PROPERTIES OF BENZENE

Although highly unsaturated, benzene does not undergo addition reactions (in most of its reactions, the benzene ring is not destroyed) except in hydrogenation and chlorination in the presence of U.V light.

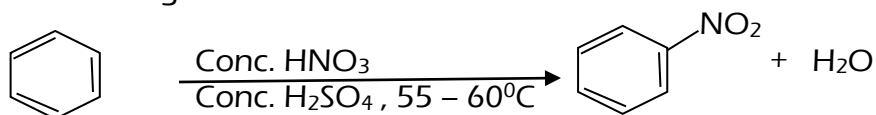
The availability of the Pi ( $\pi$ ) electrons in benzene serves as a source of electrons and its reactions are characterized by electrophilic substitution in the ring.

*Electrophilic substitution reaction is a reaction in which one or more hydrogen atoms in the aromatic ring are replaced by another atom or group of atoms which is usually electro deficient.*

### 1. NITRATION OF BENZENE

This involves replacement of a hydrogen atom in the benzene ring with a nitro – ( $-\text{NO}_2$ ) group.

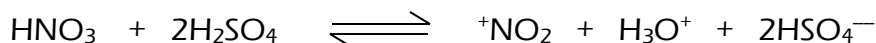
Benzene if refluxed with an equimolar mixture of Conc. Nitric and Conc. Sulphuric acid at about  $55 - 60^\circ\text{C}$  to give nitro benzene.



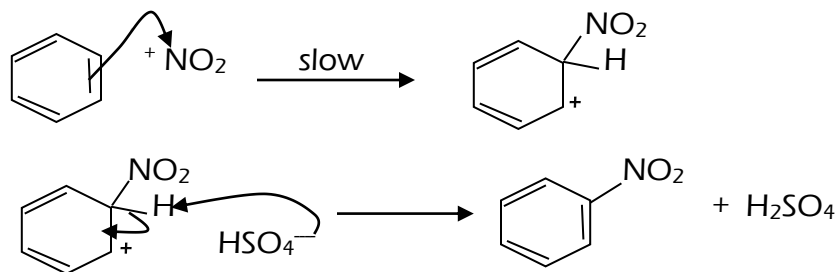
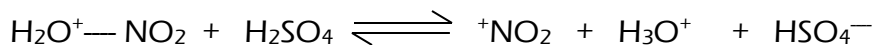
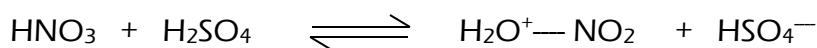
#### Mechanism

Conc. Sulphuric acid acts as a catalyst by donating a proton to Conc.  $\text{HNO}_3$  so as to facilitate the formation of the electrophile (nitronium ion)

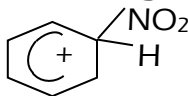
#### Overall equation



#### Half equations



The positive charge is delocalized in the ring and the intermediate may also be represented as



N.B. Nitro benzene can be converted to phenyl amine by treating with Conc. HCl and tin..