

CHAPTER 13

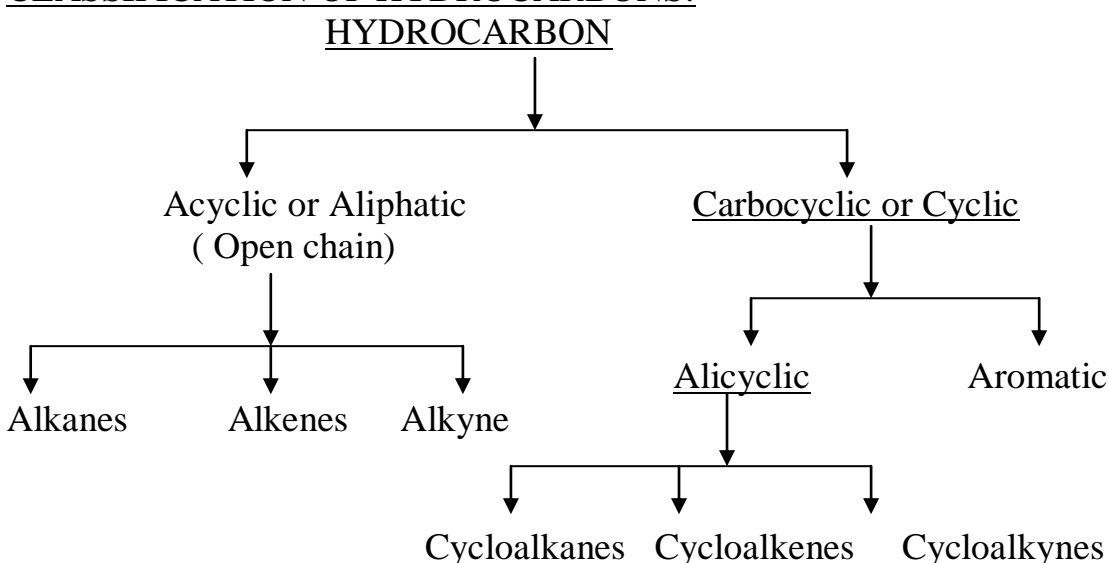
HYDROCARBON

- Hydrocarbons are composed of Carbon and hydrogen.
- The important fuels like Petrol, kerosene, coal gas, CNG, LPG etc. are all hydrocarbons or their mixture.

Sources:

Petroleum and natural gas are the major sources of aliphatic hydrocarbon while coal is an important source of aromatic hydrocarbons. The oil trapped inside the rocks is known as petroleum. PETRA – ROCK, OLEUM – OIL. The oil in the petroleum field is covered with a gaseous mixture known as natural gas. The main constituents of the natural gas are methane, ethane, propane and butane.

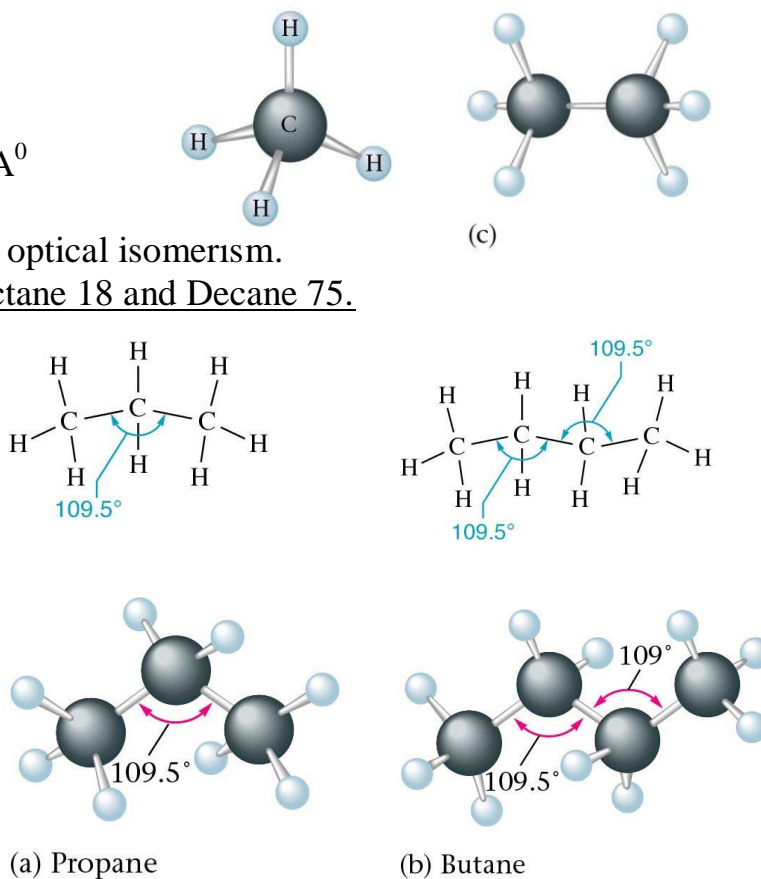
CLASSIFICATION OF HYDROCARBONS:



Alkanes:-

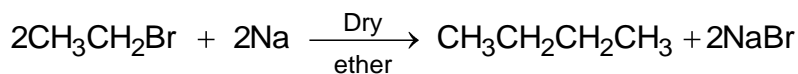
- Paraffins
- General formula C_nH_{2n+2}
- sp^3 hybridisation
- C–C bond length 1.54 \AA
- Chemically unreactive
- Show chain, position and optical isomerism.
- Heptane has 9 isomer, Octane 18 and Decane 75.

Nomenclature:



Preparation:-

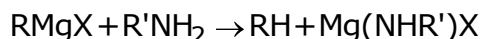
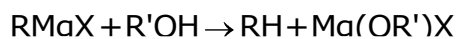
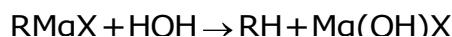
① Wurtz reaction:-



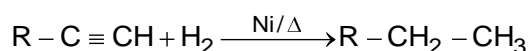
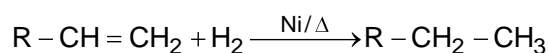
- Follow mainly free radical mechanism
 - Useful in preparing an alkane containing even number of carbon atoms
 - Stepping up reaction
- Frankland reaction



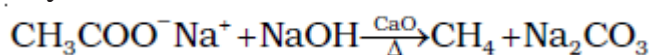
② From Grignard reagent (RMgX)



③ From unsaturated hydrocarbons:- Sabatier-Senderens reduction

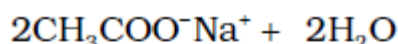


4. From carboxylic acids- Decarboxylation.-



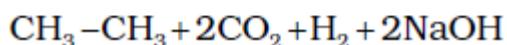
Sodium ethanoate

Kolbe's electrolytic method-



Sodium acetate

↓ Electrolysis



❖ Physical Properties:-

- (1) Nature:- Non-Polar due to covalent nature of C—C bond and C—H bond. C—C bond energy = 83 kJ/mole and C—H bond energy = 99 kJ/mole.
C₁—C₄ = gases, C₅—C₁₇ = colourless odourless liquid and > C₁₇ = Solid.
- (2) Solubility:- Like dissolve like
Viz, Polar compounds dissolve in polar solvent and Non-Polar compound dissolve in non polar solvent.
- (3) Boiling point:- Low boiling point due to non polar in nature.

The molecules are held together only by weak Van der Waals' forces.

Since we know that the magnitude of Van der Waals' forces is directly proportional to the molecular size. Therefore, the boiling point increases with increase the molecular size i.e. with increase in number of carbon atoms.

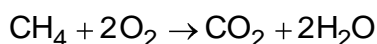
Noted:- the boiling points of the branched chain Alkanes are less than the straight chain isomers.

This is due to the fact that branching of the chain makes the molecule more compact and thereby decreases the surface area and consequently, the magnitudes of Van der Waals' forces also decrease.

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	$\begin{array}{c} \text{H}_3\text{C}-\text{CH}-\text{CH}_2\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$
n-pentane	iso-pentane	neo-pentane
(boiling point = 309 K)	(boiling point = 301 K)	(boiling point = 282.5 K)
regular variation with increase in number of carbon atoms having higher melting point a immediately next lower and immediately next higher odd number of carbon atoms.		

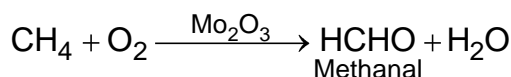
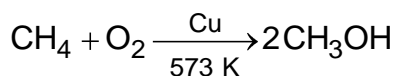
❖ Chemical properties

① Combustion:-



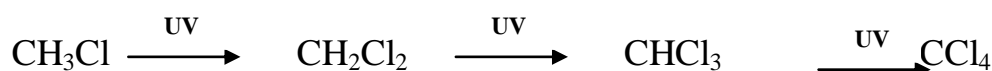
$$\Delta H = -217.0 \text{ K cal/mole}$$

② Oxidation:-

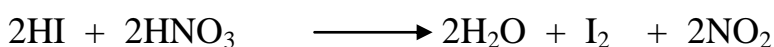
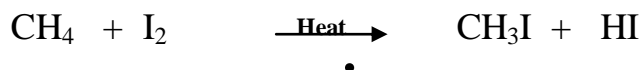


③ Substitution:-

① Halogenation:-



Noted:- Iodination is a reversible reaction. So it is carried out by heating alkane in the presence of some oxidizing agent like iodic acid (HIO_3) or nitric acid (HNO_3) or mercuric oxide (HgO) which oxidizes HI formed during the reaction.

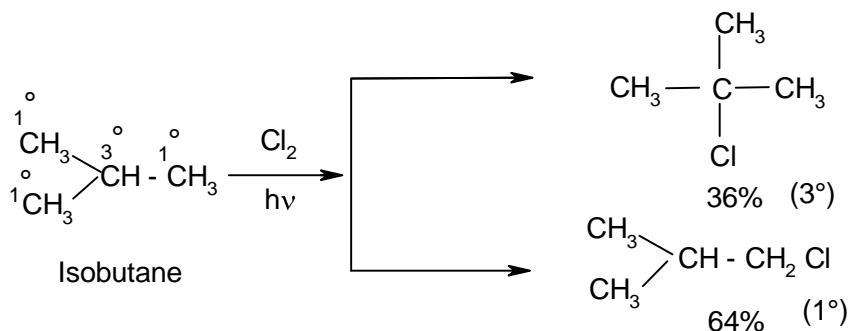
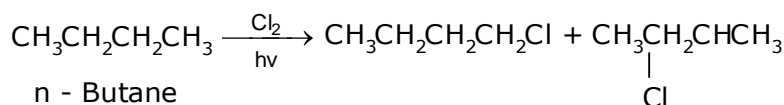


Noted:- Fluorination of alkane takes place explosively resulting even in the rupture of C—C bond in higher alkanes.

• Features of Halogenations:-

(i) The reactivity of Halogens:- $F_2 > Cl_2 > Br_2 > I_2$.

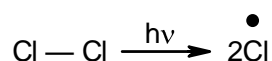
(ii) The rate of replacement of Hydrogens of alkanes is:
 $3^\circ > 2^\circ > 1^\circ$



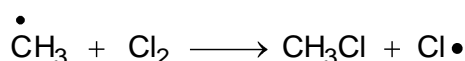
Mechanism:- halogenations reaction take place by free radical mechanism. The reaction proceeds in the following steps:

Initiation

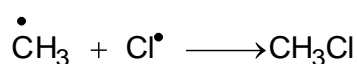
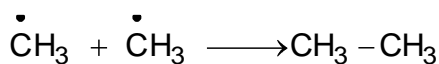
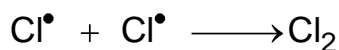
(i) Chain initiation step:-



(ii) Chain Propagation step:-



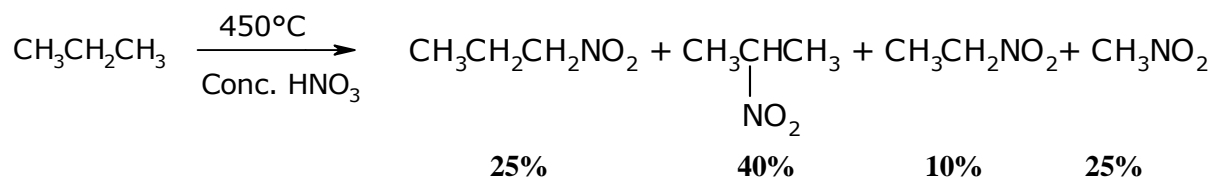
(iii) Chain Termination step:-



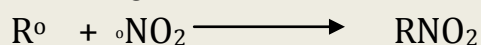
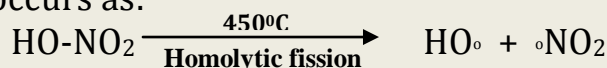
② Nitration:-

☞ The reaction takes places by free radicals mechanism at high temp (450°C).

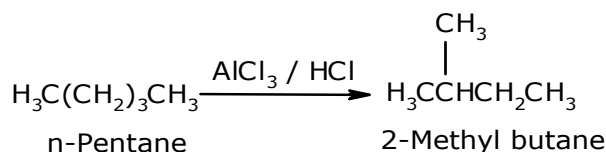
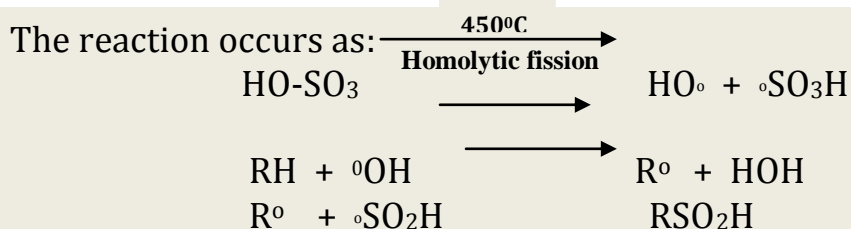
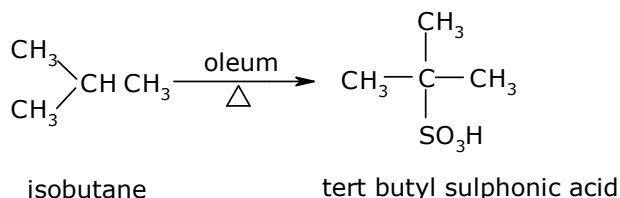
☞ At high temp C—C bond is also broken so that mixture of nitroalkanes is obtained.



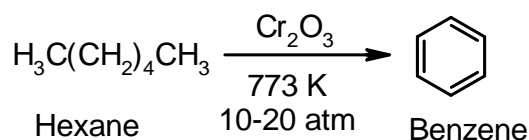
The reaction occurs as:



③ Sulphonation:- replacement of hydrogen atom of alkane by $-\text{SO}_3\text{H}$ group.



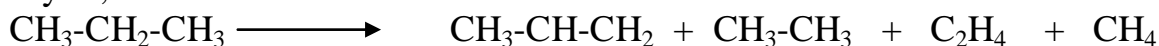
⑤ Aromatization:-



This method is also called dehydrogenation or hydroforming

Similarly, heptane gives toluene, n-Octane give o-xylene and 2, methyl heptane give m-xylene.

⑥ Thermal decomposition or Pyrolysis or cracking or Fragmentation: - when higher alkanes are heated at high temp (about 700-800K) in the presence of alumina or silica catalysts, the alkanes break down to lower alkanes and alkenes.

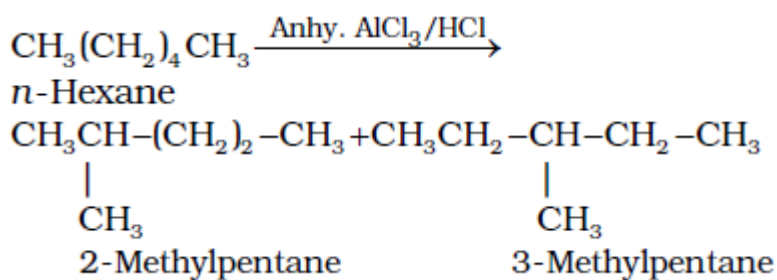


⑦ Action of steam:- catalyst: nickel, alumina Al_2O_3
1000 $^\circ\text{C}$



This reaction is used for the industrial preparation of hydrogen from natural gas.

8. Isomerisation:-

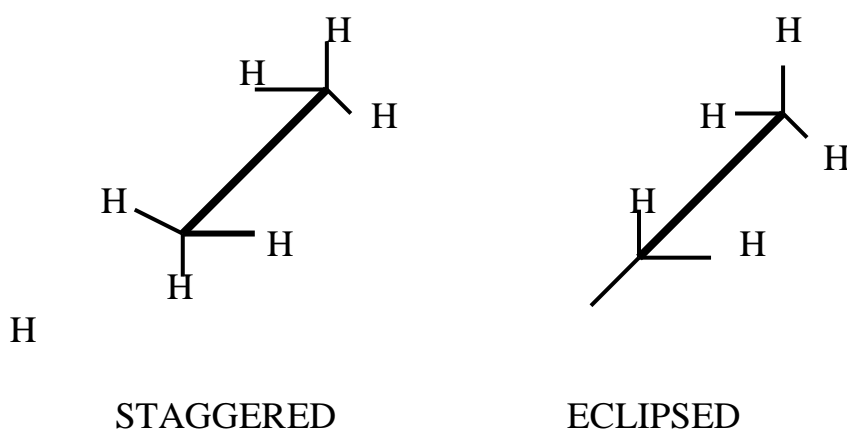


❖ CONFORMATIONAL ISOMERISM:

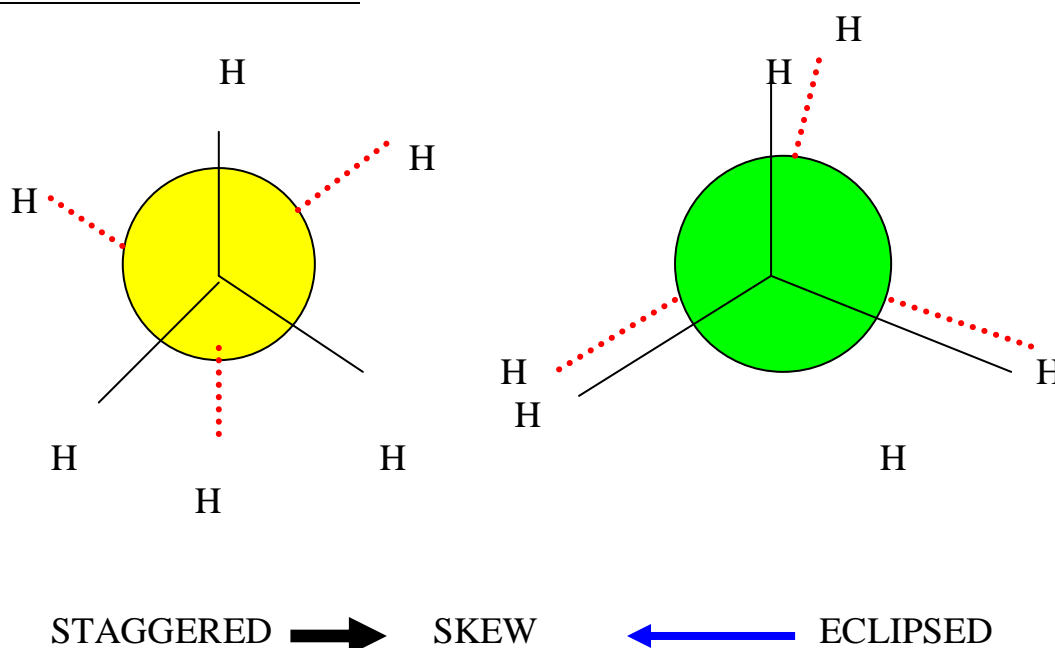
The different molecular arrangements arising as a result of rotation around carbon carbon single bonds are called conformational isomers or rotational isomers and the phenomenon is called conformational isomerism.

Numerous possible arrangements of ethane are possible. Two extreme conformations are known. These are eclipsed conformation and staggered conformation.

SAWHORSE REPRESENTATION

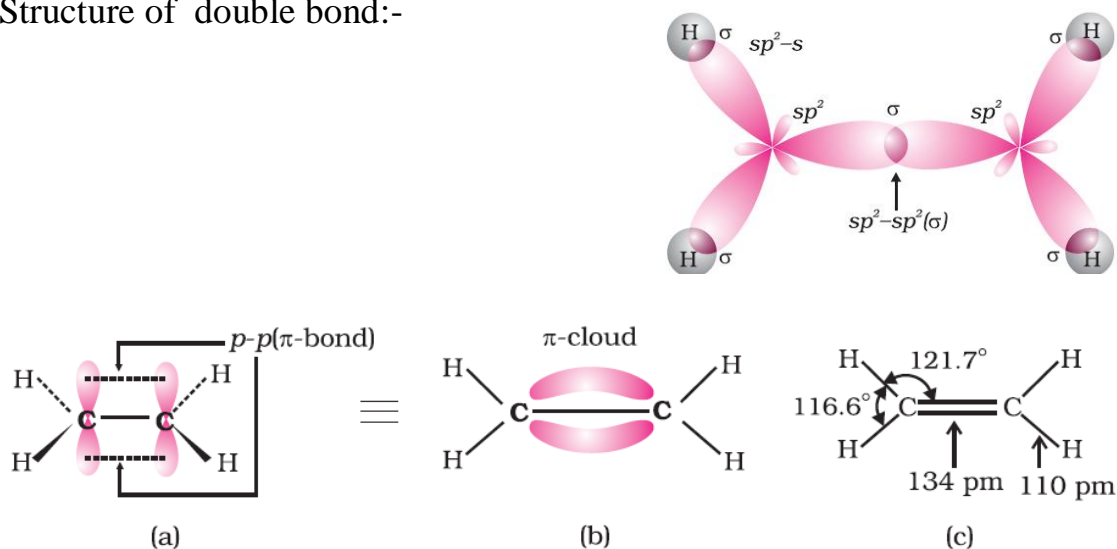


NEWMAN PROJECTION



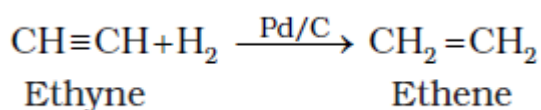
Alkenes

- ☞ Unsaturated hydrocarbon which have double bond.
- ☞ General molecular formula C_nH_{2n}
- ☞ C-C bond hybridization 1.34 \AA^0
- ☞ sp^2 hybridization
- ☞ When we treated Alkene with chlorine, oily products are obtained. So Alkenes are also known as Olefins. (Greek olefiant meaning oil forming).
- ☞ Show chain, positional and geometrical isomerism
- ❖ Structure of double bond:-

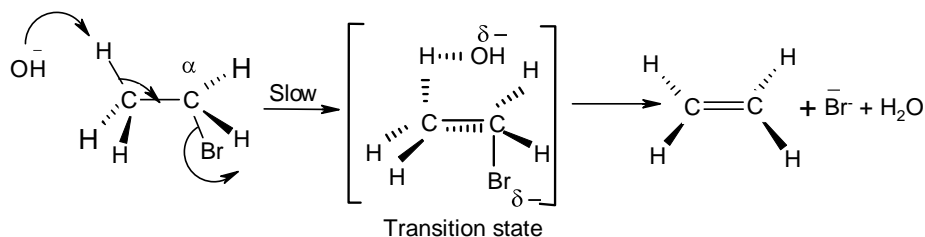
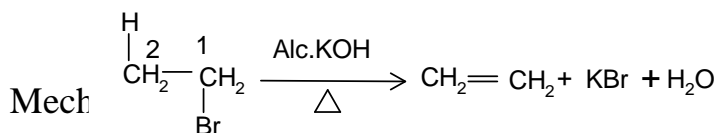


❖ Preparation:-

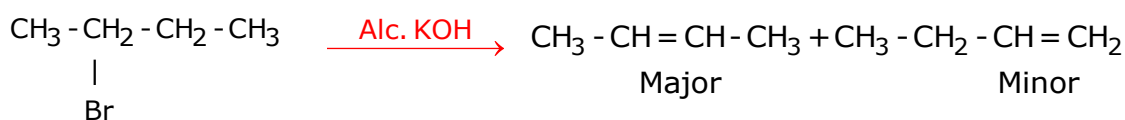
- From Alkynes:- Alkynes on partial reduction with Partially deactivated palladised charcoal known as *Lindlar's catalyst* give alkenes.



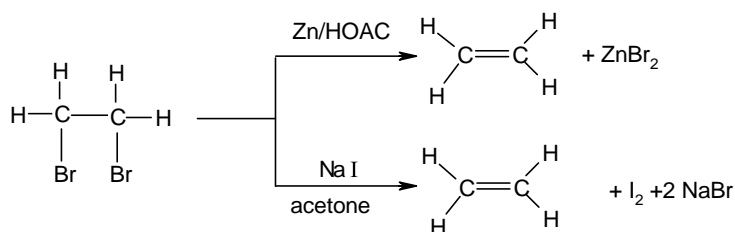
- From Haloalkanes: - dehydrohalogenation
(E_2 or 1,2-elimination or Bita-elimination)



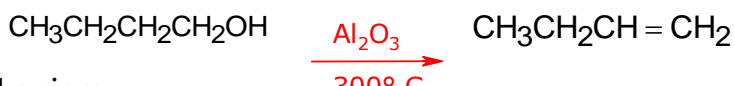
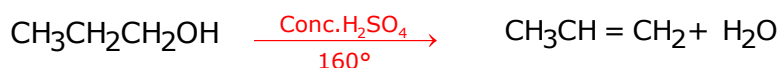
- predominant formation of a substituted alkene is formed according to Saytzeff's rule



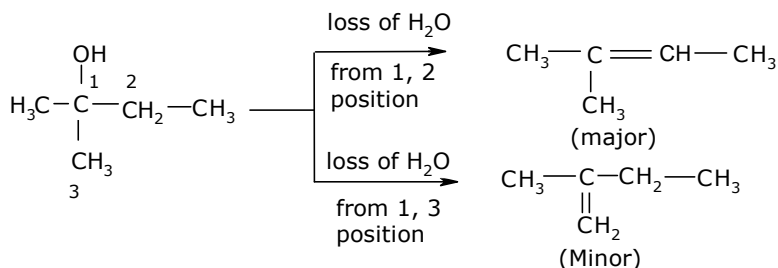
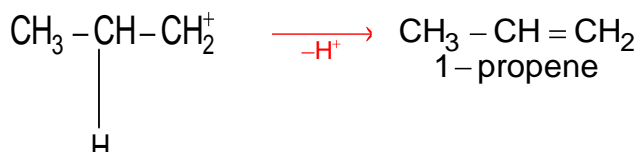
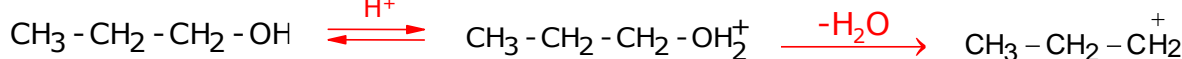
3. From Dihaloalkanes: - dehalogenation



4. From Alcohols:- Dehydration (E1 - elimination)



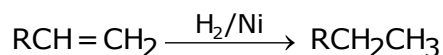
Mechanism



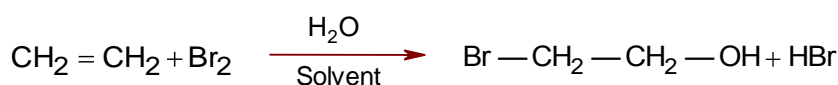
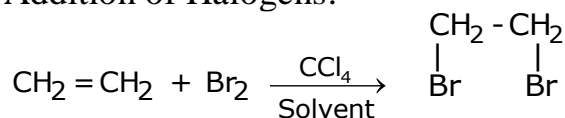
❖ Chemical Properties:-

① Addition Reaction:- Alkene show electrophilic addition reaction.

1. Addition of Hydrogen:-



2. Addition of Halogens:-

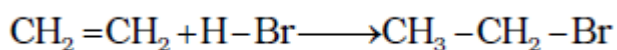


(Brown colour)

(Colourless)

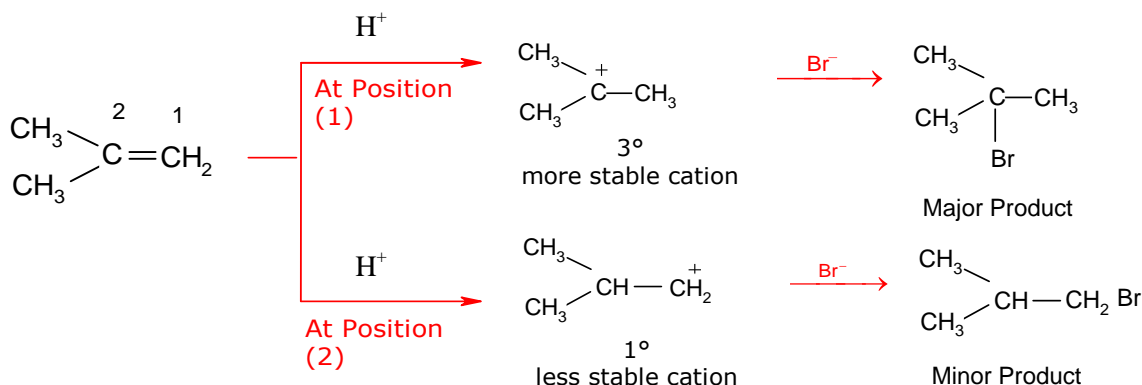
3. Addition of hydrogen halides-

Addition reaction of HBr to symmetrical alkenes

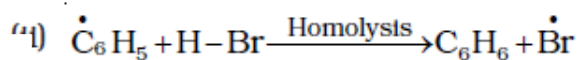
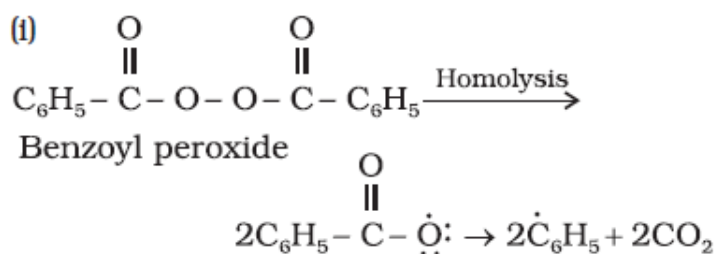
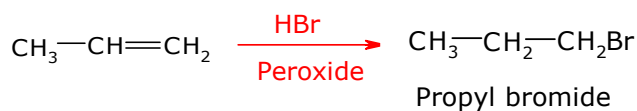


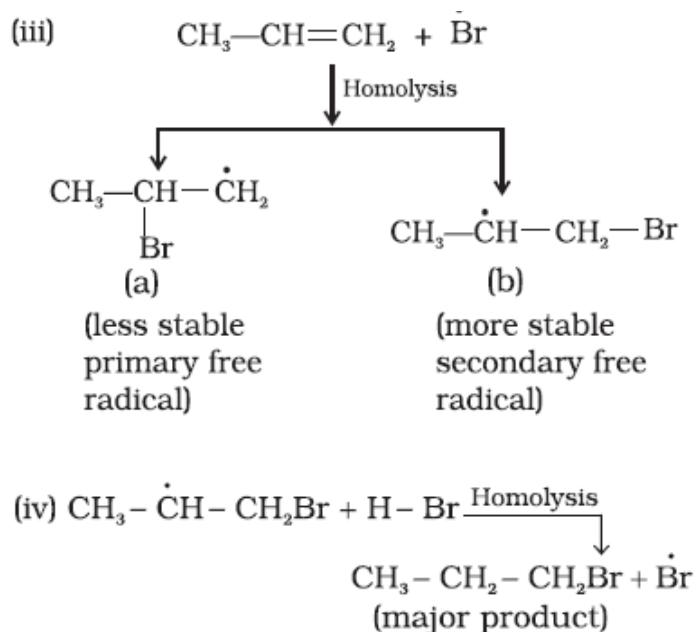
Addition reaction of HBr to unsymmetrical alkenes takes place according to Markovnikov Rule

Markovnikov rule:- negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms. e.g



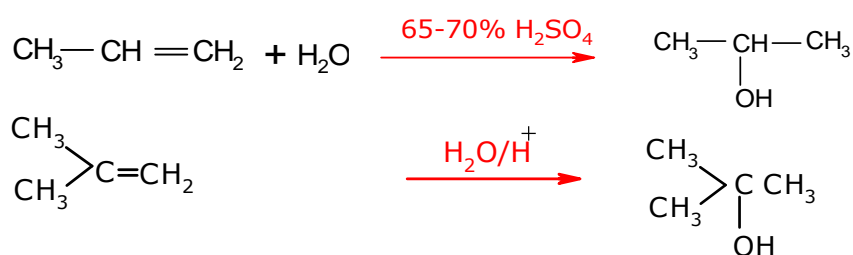
Peroxide effect or Kharasch (Anti Markownikoff's addition):- In 1933 Kharasch and Mayo observed that when HBr is added to an unsymmetrical double bond in the presence of organic peroxide, the reaction takes place opposite to the Markovnikov rule.





Noted:- peroxide effect is applicable only to HBr and not to HF, HCl and HI. Addition of HF, HCl and HI takes place according to Markovnikov's rule even in the presence of peroxide.

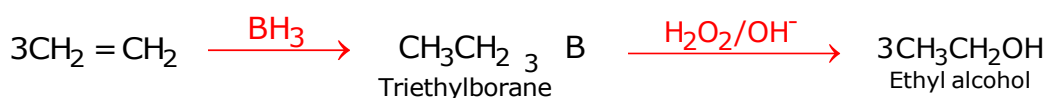
4. Addition of water (Hydration):- Acid catalyzed addition of water



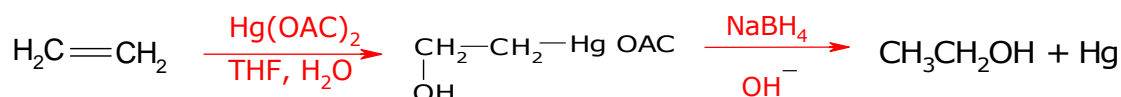
② Oxidation:-

① Combustion:- $\text{CO}_2 + \text{H}_2\text{O}$

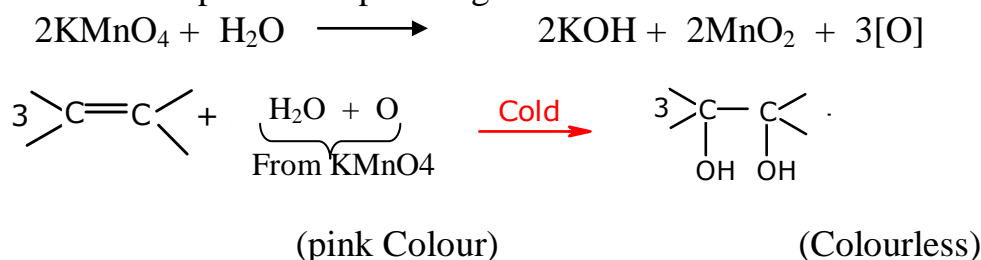
② Hydroboration-oxidation:- Alkanes react with diborane to form trialkyl boranes which on oxidation with alkaline H_2O_2 give alcohols.



③ Oxymercuration-demercuration:-

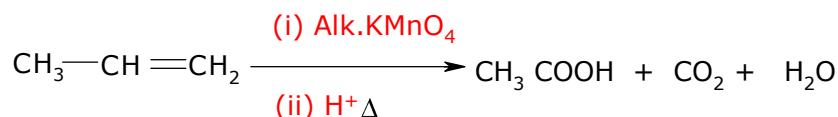


④ Oxidation with potassium permanganate:-

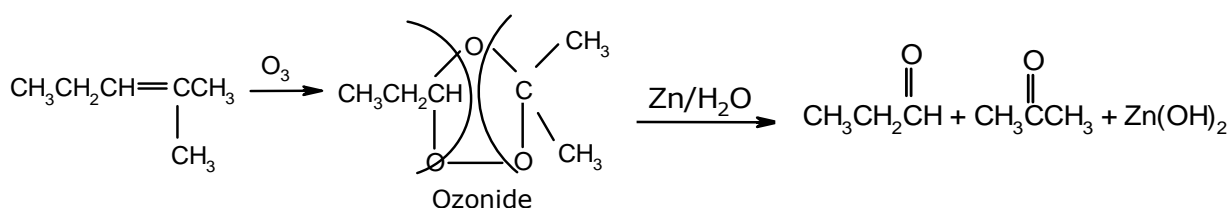


- This reaction is also called *Hydroxylation*
- *Cis product I.e. cis-diol* is obtained.

Noted:- The alkaline potassium permanganate solution is known as Baeyer's reagent. It has bright pink colour. It oxidizes alkenes to glycols which is colourless. This reaction is used as a test for the presence of double bond in a molecule. This is also known as Baeyer test.



☺ Oxidation with Ozone:- Ozonolysis – give carbonyls compounds



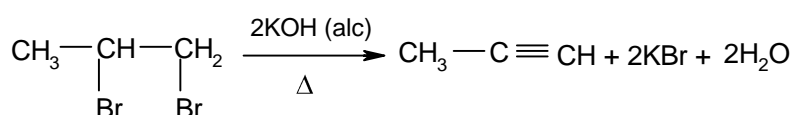
Noted:- Bromine water test and Baeyer's test are used to detect the presence of double bond while ozonolysis is used to detect the position of double bond.

Alkynes

- ☞ Unsaturated hydrocarbon which have triple bond.
- ☞ General molecular formula $\text{C}_n\text{H}_{2n-2}$
- ☞ sp hybridization
- ☞ Shows chain, positional and functional isomerism

❖ Preparation:-

From vicinal dihalides: - dehalogenation

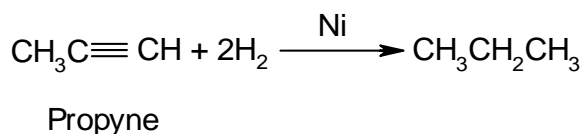


By the action of water on calcium carbide:-



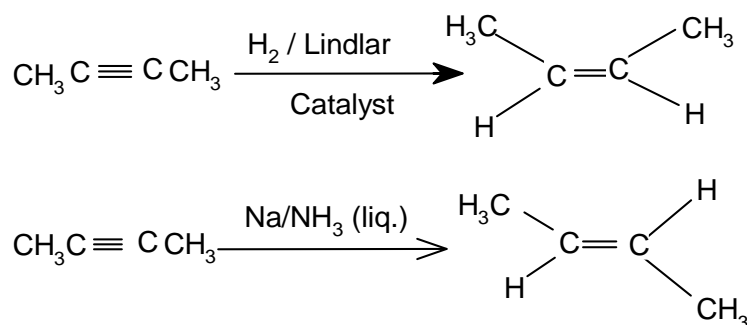
❖ Chemical Properties:-

- ❶ Addition Reaction:- Alkyne show electrophilic addition reaction.
- ① Addition of Hydrogen:- Hydrogenation.

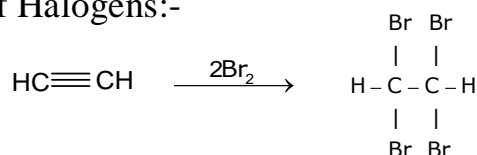


Noted:- It may be noted that the hydrogenation can be controlled at the alkene stage only. This is possible by using a *Lindlar's catalysts* or *sodium in liquid NH₃* at 200k temp..

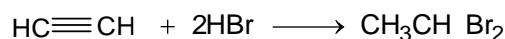
Noted:- It may be again noted that the catalytic reduction of alkynes in the presence of Lindlar's catalyst gives cis-alkenes while in the presence of sodium in liquid NH₃ (Birch reduction) gives trans-alkenes.



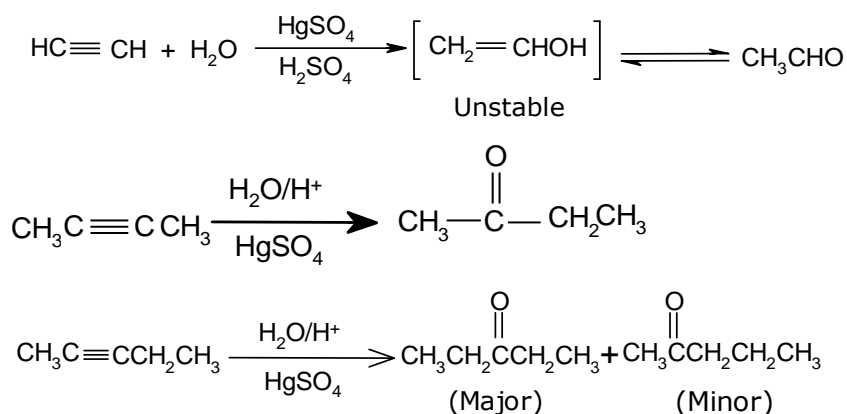
② Addition of Halogens:-



③ Addition of hydrogen halides:-

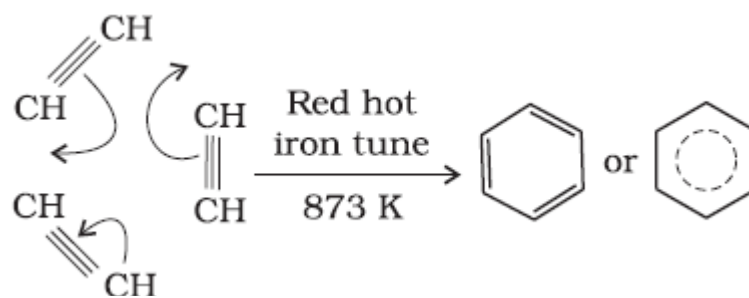


④ Addition of water (Hydration):- Acid catalyzed addition of water

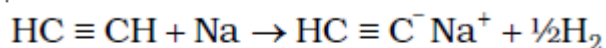


5. Polymerisation-

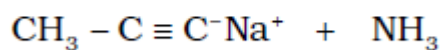
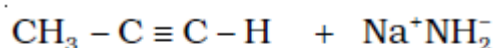
- Linear polymerisation:** of ethyne gives polyacetylene or polyethyne which is a high molecular weight polyene containing repeating units of (CH = CH – CH = CH) and can be represented as —(CH = CH – CH = CH)_n—
- Cyclic polymerization- results in the formation of aromatic compound.



Acidity of Alkynes- Terminal alkynes are acidic in nature.



Monosodium
ethynide



Sodium propynide

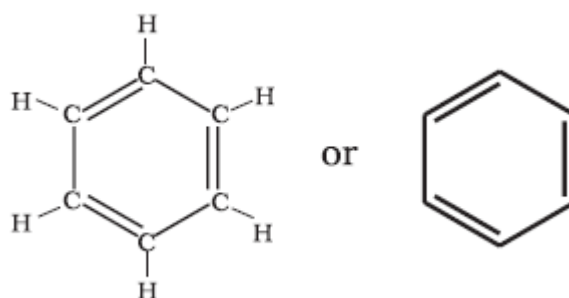
Alkanes, alkenes and alkynes follow the following trend in their acidic behaviour :

- i) $\text{HC} \equiv \text{CH} > \text{H}_2\text{C} = \text{CH}_2 > \text{CH}_3 - \text{CH}_3$
- ii) $\text{HC} \equiv \text{CH} > \text{CH}_3 - \text{C} \equiv \text{CH} > \text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3$

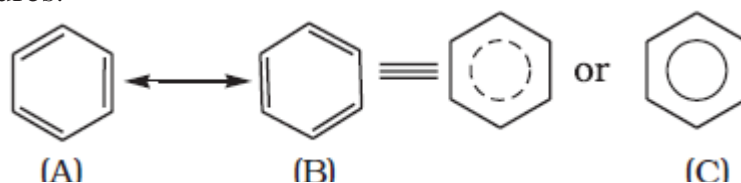
AROMATIC HYDROCARBON

Aromatic compounds containing benzene ring are known as **benzenoids** and those not containing a benzene ring are known as **non-benzenoids**.

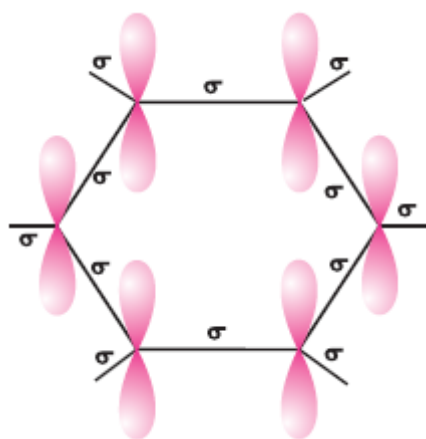
Structure of Benzene- Kekulé structure



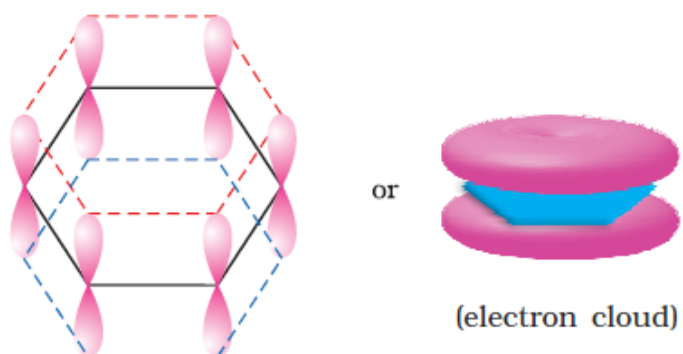
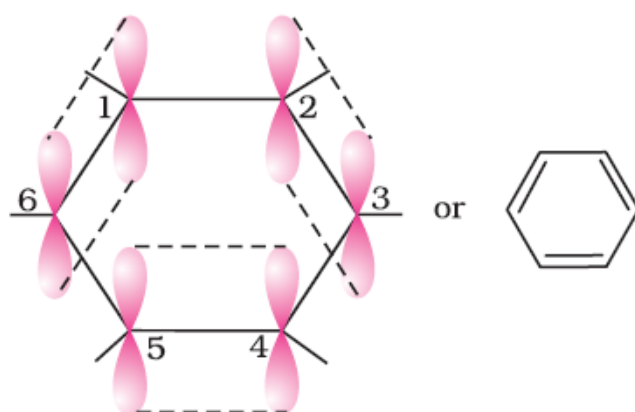
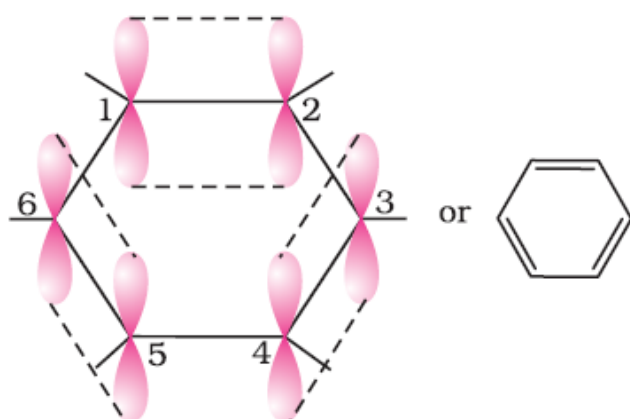
Resonance and stability of benzene- Benzene is a hybrid of various resonating structures.



The orbital overlapping picture benzene- All the six carbon atoms in benzene are sp^2 hybridized and these hybrid orbitals form sigma bonds.



The unhybridised p orbital of carbon atoms are close enough to form a π bond by lateral overlap.



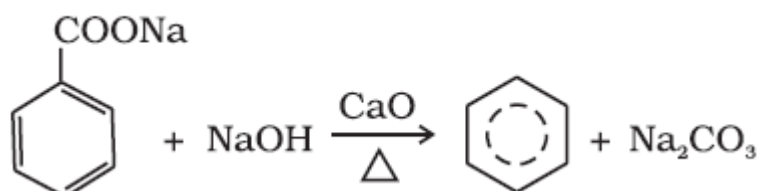
The six π electrons are thus delocalised and can move freely about the six carbon nuclei. The delocalised π electron cloud is attracted more strongly by the nuclei of the carbon atoms than the electron cloud localized between two carbon atoms. Therefore, presence of delocalised π electrons in benzene makes it more stable.

Aromaticity:- The compounds that follow the following features are to be considered aromatic.

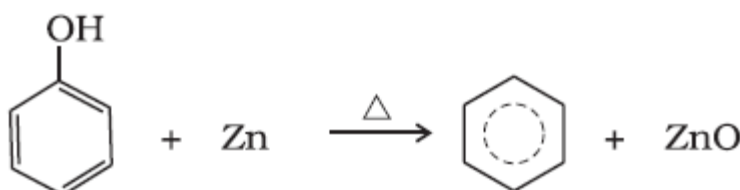
- (i) Planarity
- (ii) Complete delocalisation of the π electrons in the ring
- (iii) Presence of $(4n + 2)$ π electrons in the ring where n is an integer ($n = 0, 1, 2, \dots$). This is often referred to as **Hückel Rule**.

Preparation of Benzene:

- (i) Cyclic polymerisation of ethyne:
- (ii) Decarboxylation of aromatic acids:



(iii) *Reduction of phenol:* Phenol is reduced to benzene by passing its vapours over heated zinc dust



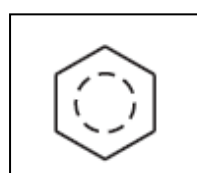
Physical properties:

1. Aromatic hydrocarbons are non-polar molecules and are usually colourless liquids or solids with a characteristic aroma.
2. Aromatic hydrocarbons are immiscible with water but are readily miscible with organic solvents.
3. They burn with sooty flame.

Chemical properties

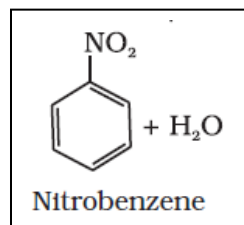
Arenes are characterised by electrophilic substitution reactions proceed via the following three steps:

- (a) Generation of the electrophile
- (b) Formation of carbocation intermediate
- (c) Removal of proton from the carbocation intermediate



Nitration

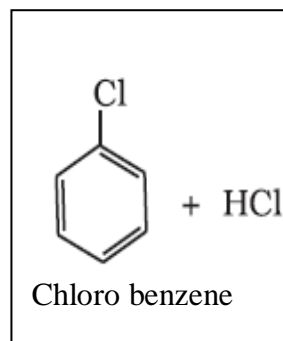
Conc. HNO_3 + Conc. H_2SO_4



Halogenation

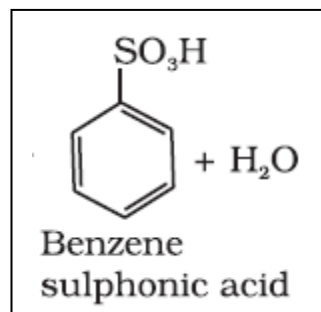
+ Cl_2

Anhyd. AlCl_3



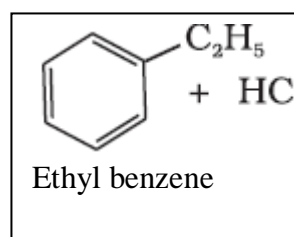
Sulphonation

Fuming sulphuric acid
 $\text{H}_2\text{SO}_4(\text{SO}_3)$



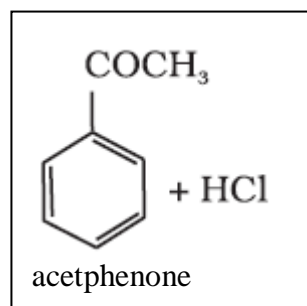
Friedel-Crafts alkylation

+ $\text{C}_2\text{H}_5\text{Cl}$
Anhyd. AlCl_3

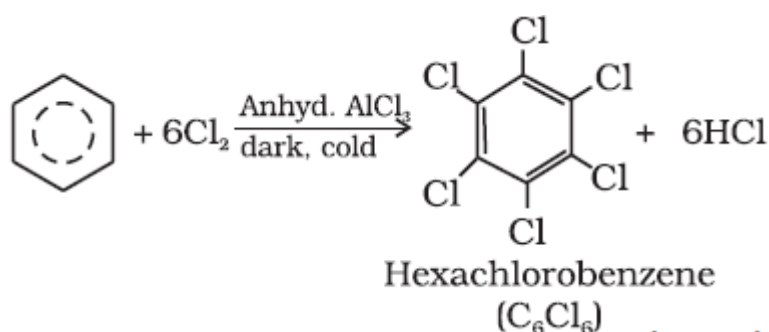


Friedel-Crafts acylation

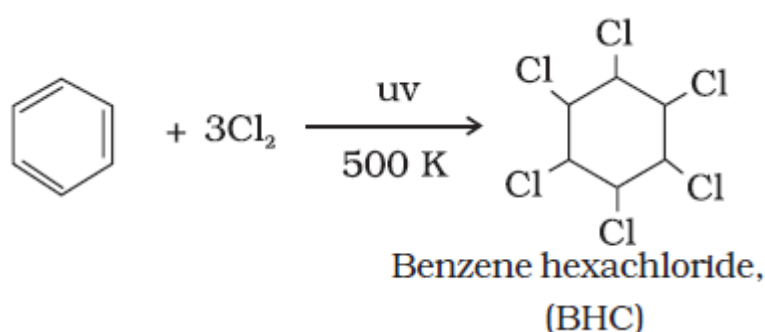
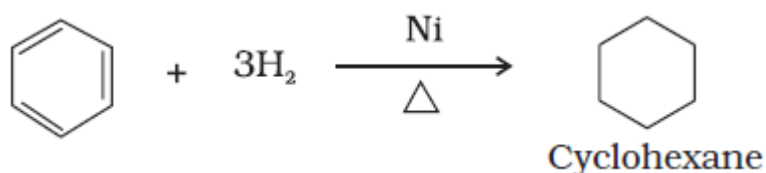
+ CH_3COCl
Anhyd. AlCl_3



benzene on treatment with excess of chlorine in the presence of anhydrous AlCl_3 in dark yields hexachlorobenzene (C_6Cl_6)

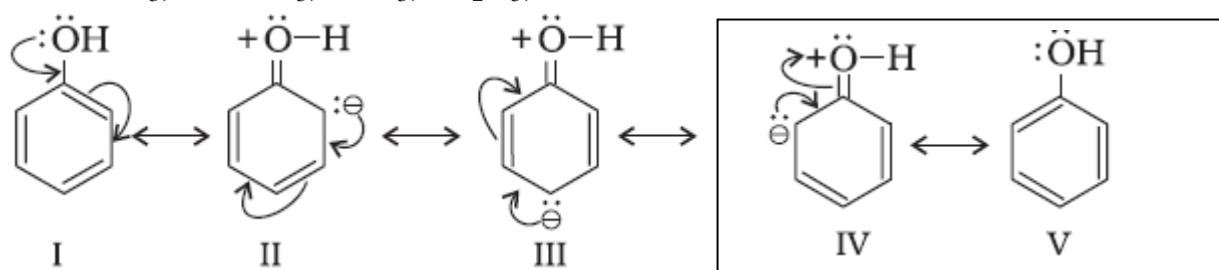


Addition reactions of benzene-

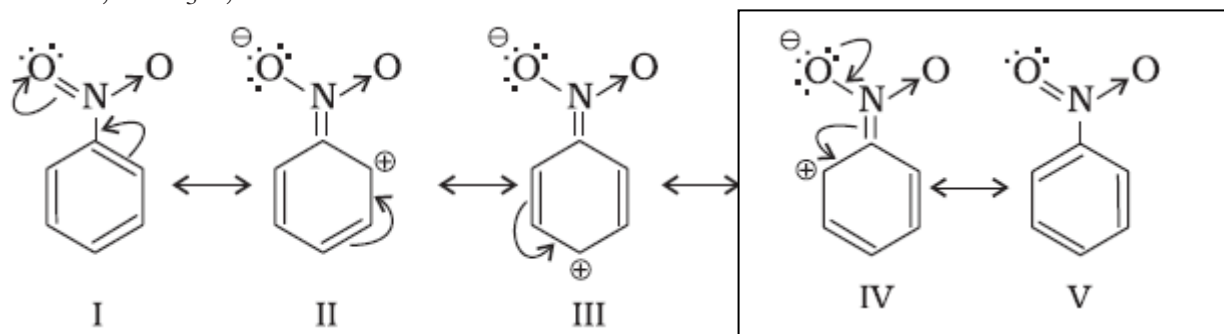


Directive influence of a functional group in monosubstituted benzene:-

1. Ortho and para directing groups and activating- -OH, -NH₂, -NHR, -NHCOCH₃, -OCH₃, -CH₃, -C₂H₅, etc.



2. Meta directing group and deactivating:-NO₂, -CN, -CHO, -COR, -COOH, -COOR, -SO₃H, etc.



3. Ortho and para directing groups and deactivating- Halogens because of their strong - I effect, overall electron density on benzene ring decreases. However,

due to resonance the electron density on *o*- and *p*- positions is greater than that at the *m*-position. Hence, they are also *o*- and *p*- directing groups.

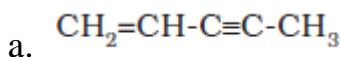
CARCINOGENICITY AND TOXICITY-Benzene and polynuclear hydrocarbons containing more than two benzene rings fused together are toxic and said to possess cancer producing (carcinogenic) property.

ONE MARK QUESTIONS

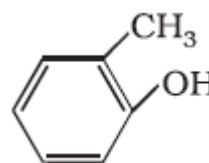
- What are hydrocarbons?
Ans. Compounds of hydrogen and carbon.
- What is the general formula of alkanes?
Ans. C_nH_{2n+2}
- Write the general formula of alkenes.
Ans. C_nH_{2n}
- What is the general formula of alkynes?
Ans. C_nH_{2n-2}
- Give the IUPAC name of lowest molecular weight alkane that contains a quaternary carbon.
Ans. 2,2dimethylpropane.
- Arrange the following in the increasing order of C-C bond length-
 C_2H_6 C_2H_4 C_2H_2
Ans. $C_2H_2 < C_2H_4 < C_2H_6$
- Out of ethylene and acetylene which is more acidic and why?
Ans. Acetylene, due to greater electronegativity of the *sp* hybrid carbon.
- Name two reagents which can be used to distinguish between ethene and ethyne.
Ans. Tollen's reagent and ammonical $CuCl$ solution.
- Arrange the following in order of decreasing reactivity towards alkanes.
 HCl , HBr , HI , HF
Ans. $HI > HBr > HCl > HF$
- How will you detect the presence of unsaturation in an organic compound?
Ans. Generally Unsaturated organic compound decolourise Bayer's reagent and Bromine water.
- What is Grignard reagent?
Ans. Alkyl magnesium halides

TWO MARKS QUESTIONS

- Write the IUPAC names of the following-

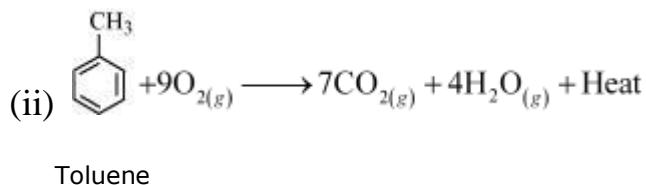
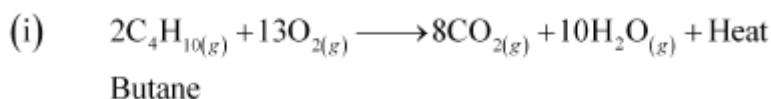


Ans. a. Pent-en-3-yne



b. 2-methylphenol

2. Write chemical equations for combustion reaction of (i) Butane (ii) Toluene
Ans.



3. What are the necessary conditions for any system to be aromatic?

Ans. A compound is said to be aromatic if it satisfies the following three conditions: (i) It should have a planar structure.

(ii) The π -electrons of the compound are completely delocalized in the ring.

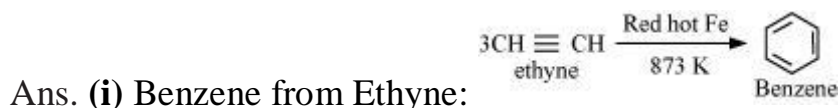
(iii) The total number of π -electrons present in the ring should be equal to $(4n + 2)$, where $n = 0, 1, 2 \dots$ etc. This is known as Huckel's rule.

4. What effect does branching of an alkane chain has on its boiling point?

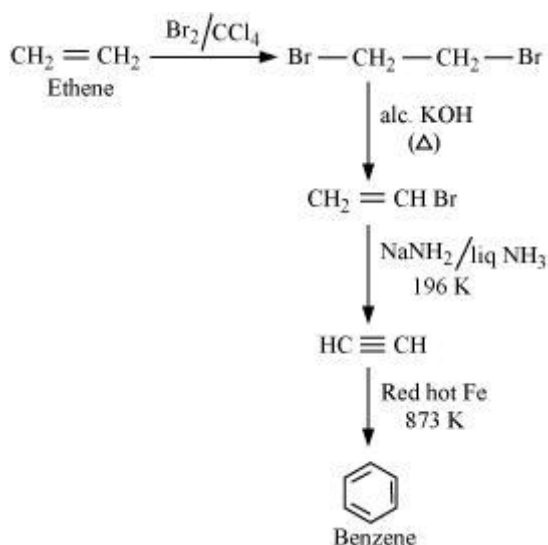
Ans. As branching increases, the surface area of the molecule decreases which results in a small area of contact. As a result, the Van der Waals force also decreases which can be overcome at a relatively lower temperature. Hence, the boiling point of an alkane chain decreases with an increase in branching.

5. How would you convert the following compounds into benzene?

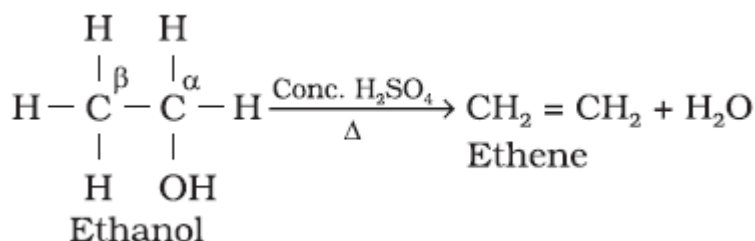
(i) Ethyne (ii) Ethene



(ii) Benzene from Ethene:



6. Suggest the name of Lewis acids other than anhydrous aluminium chloride which can be used during ethylation of benzene.
Ans. anhydrous FeCl_3 , SnCl_4 , BF_3 etc.
7. Write the name of all the possible isomers of $\text{C}_2\text{H}_2\text{Cl}_2$ and indicate which of them is non-polar.
Ans. (i) cis-1,2-dichloroethene (ii) trans-1,2-dichloroethene (iii) 1,1-dichloroethene. trans-1,2-dichloroethene is non-polar.
8. Although benzene is highly unsaturated, it does not undergo addition reactions, why?
Ans. Because of extra stability due to delocalization of π -electrons.
9. What are alkanes? Why are they called paraffins?
Ans. Those hydrocarbons which contain single bond between carbon- carbon are called alkanes. They are called paraffins because they are very less reactive (Latin- Parum= little, affins = affinity)
10. How can ethene be prepared from (i) ethanol (ii) ethyl bromide?
Ans. (i) Ethene from ethanol- by acidic dehydration of alcohols

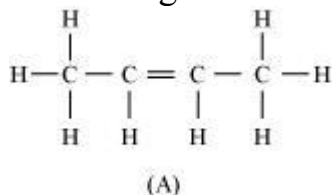


- (ii) Ethene from ethyl bromide- by dehydrohalogenation of ethyl bromide
 $\text{CH}_3\text{CH}_2\text{Br} + \text{KOH (alc)} \rightarrow \text{H}_2\text{C} = \text{CH}_2 + \text{KBr} + \text{H}_2\text{O}$

THREE MARKS QUESTIONS

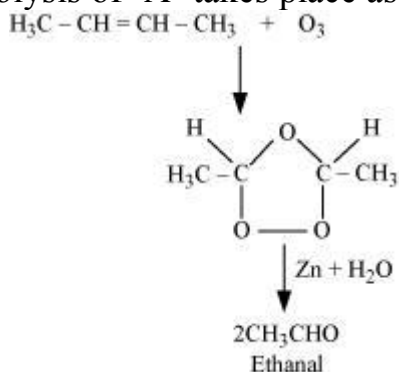
1. What is Wurtz reaction? How can it be used to prepare butane?
 Ans- When alkyl halides is treated with metallic Na in presence of dry ether, alkanes are formed. This reaction is called Wurtz reaction.
 Butane is prepared by the reaction of bromoethane with metallic Na in presence of dry ether
- $$\begin{array}{ccc}
 \text{C}_2\text{H}_5\text{Br} + 2\text{Na} + \text{BrC}_2\text{H}_5 & \xrightarrow{\text{dry ether}} & \text{C}_2\text{H}_5 - \text{C}_2\text{H}_5 \\
 \text{Bromoethane} & & \text{n-Butane}
 \end{array}$$
2. An alkene 'A' contains three C – C, eight C – H σ bonds and one C – C π bond. 'A' on ozonolysis gives two moles of an aldehyde of molar mass 44 u. Deduce IUPAC name of 'A'.
 Ans.. The formation of two moles of an aldehyde indicates the presence of identical structural units on both sides of the double bond containing carbon atoms. Hence, the structure of 'A' can be represented as:
 $\text{XC} = \text{CX}$
 There are eight C–H σ bonds. Hence, there are 8 hydrogen atoms in 'A'. Also, there are three C–C bonds. Hence, there are four carbon atoms present in the structure of 'A'.

Combining the inferences, the structure of 'A' can be represented as:



the IUPAC name of 'A' is But-2-ene.

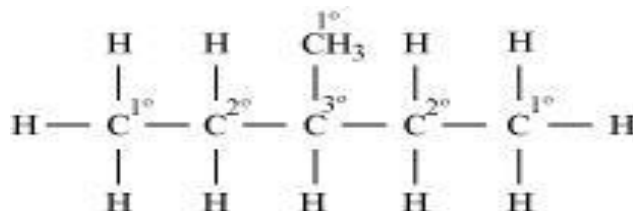
Ozonolysis of 'A' takes place as:



The final product is ethanal with molecular mass

$$\begin{aligned}
 &= [(2 \times 12) + (4 \times 1) + (1 \times 16)] \\
 &= 44 \text{ u}
 \end{aligned}$$

3. In the alkane $\text{H}_3\text{C} - \text{CH}_2 - \text{C}(\text{CH}_3)_2 - \text{CH}_2 - \text{CH}(\text{CH}_3)_2$, identify $1^\circ, 2^\circ, 3^\circ$ carbon atoms and give the number of H atoms bonded to each one of these.
Ans.



The given structure has five 1° carbon atoms and fifteen hydrogen atoms attached to it.

The given structure has two 2° carbon atoms and four hydrogen atoms attached to it.

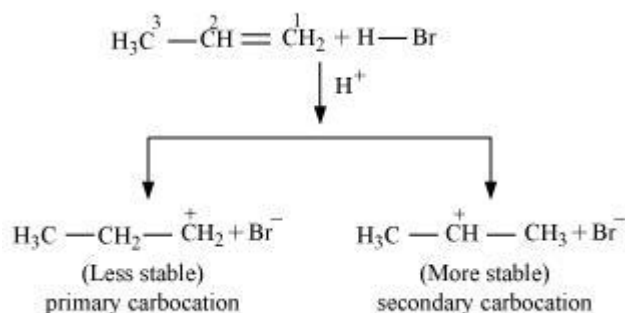
The given structure has one 3° carbon atom and only one hydrogen atom is attached to it

FIVE MARKS QUESTIONS

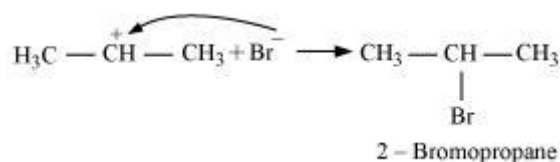
4. Addition of HBr to propene yields 2-bromopropane, while in the presence of benzoyl peroxide, the same reaction yields 1-bromopropane. Explain and give mechanism

Ans. Addition of HBr to propene is an example of an electrophilic substitution reaction.

Hydrogen bromide provides an electrophile, H^+ . This electrophile attacks the double bond to form 1° and 2° carbocations as shown:

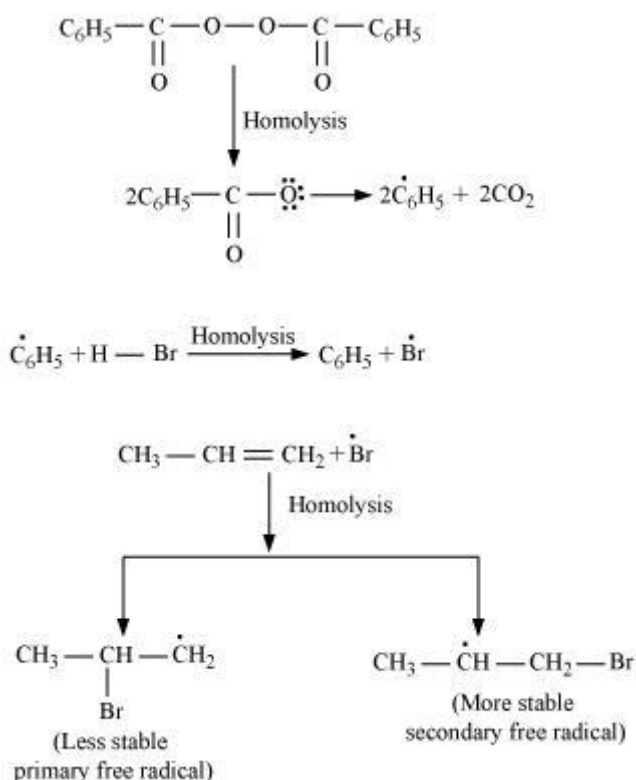


Secondary carbocations are more stable than primary carbocations. Hence, the former predominates since it will form at a faster rate. Thus, in the next step, Br^- attacks the carbocation to form 2-bromopropane as the major product.

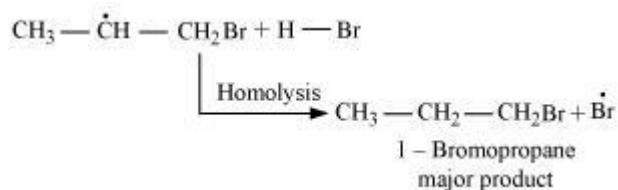


This reaction follows Markovnikov's rule

In the presence of benzoyl peroxide, an addition reaction takes place anti to Markovnikov's rule. The reaction follows a free radical chain mechanism as:



Secondary free radicals are more stable than primary radicals. Hence, the former predominates since it forms at a faster rate. Thus, 1 – bromopropane is obtained as the major product.



HOTS QUESTIONS

- How will you demonstrate that double bonds of benzene are somewhat different from that of olefins?
Ans. The double bonds of olefins decolourize bromine water and discharge the pink colour of Bayer's reagent while those of benzene not
- How will you separate propene from propyne?
Ans. By passing the mixture through ammonical silver nitrate solution when propyne reacts while propene passes over.
- Write the structure of the alkene which on reductive ozonolysis gives butanone and ethanol,
Ans. $-\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)=\text{CHCH}_3$