unit - 13

HYDROCARBONS

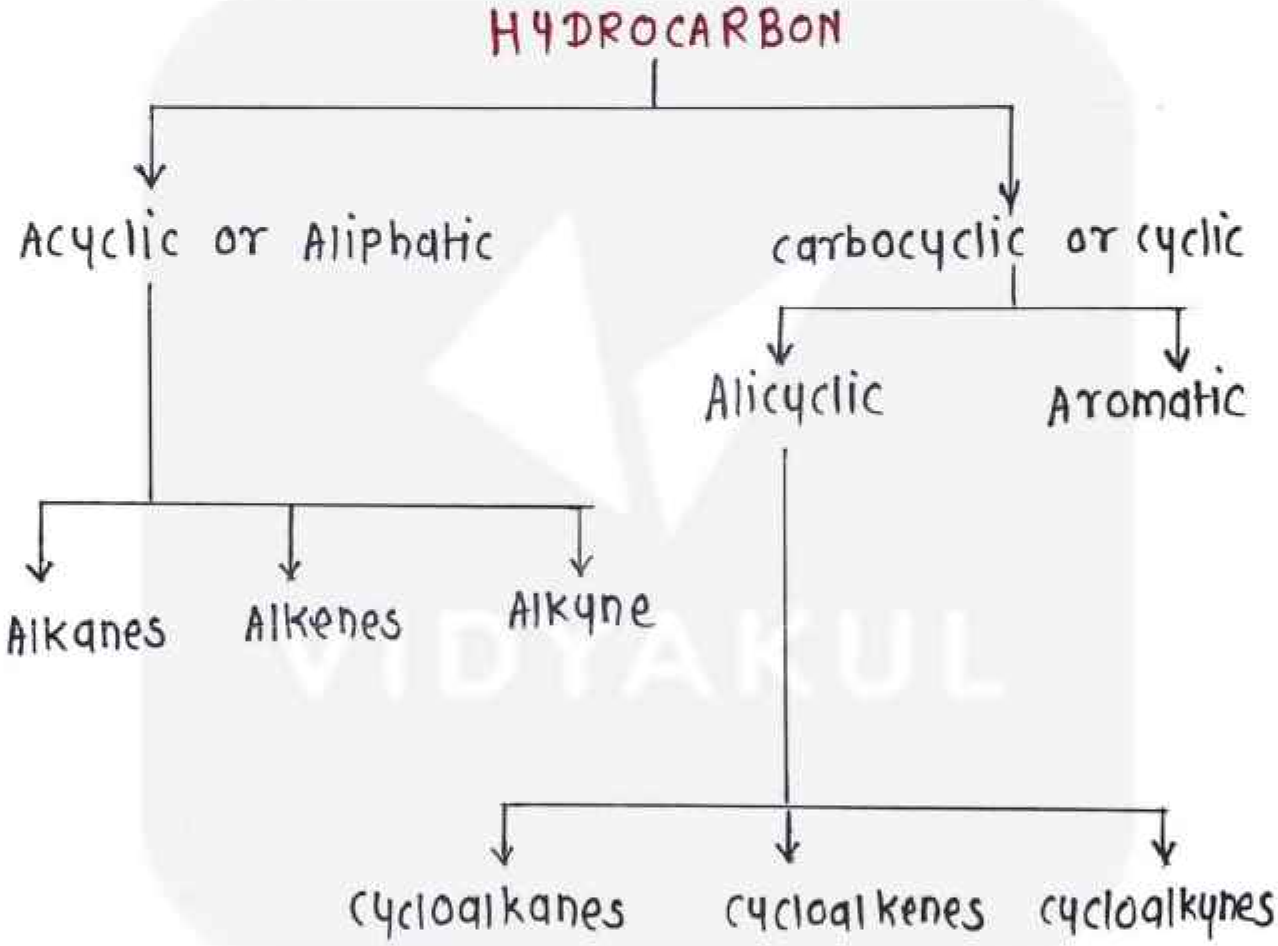
- Hydrocarbons are composed of carbon and hydrogen. The important fuels like petrol, kerosene, Coal gas, CNG, LPG etc. are all hydrocarbons or their mixture.

- 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.

Classification of Hydrocarbons



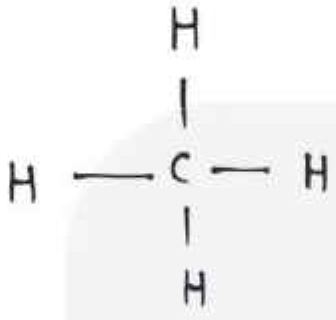
Alkanes

- Alkanes are the simplest organic compounds made of carbon and hydrogen only. They have the general formula C_nHC_{2n+2} (Where, n = 1, 2, 3.. etc)

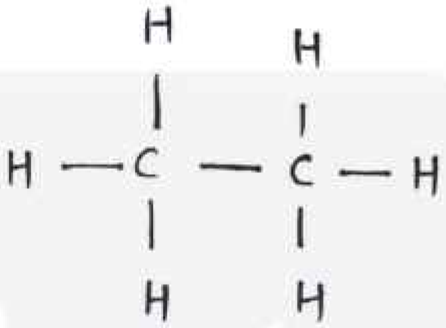
- The carbon atoms in their molecules are bonded to each other by single covalent bond. since the carbon skeleton is fully saturated here with hydrogen They are also called as saturated hydrocarbons.

- Alkanes contain strong C-C and C-H bonds. therefore this class of hydrocarbons are relatively chemically inert. Hence they are sometimes reffered as Paraffins.

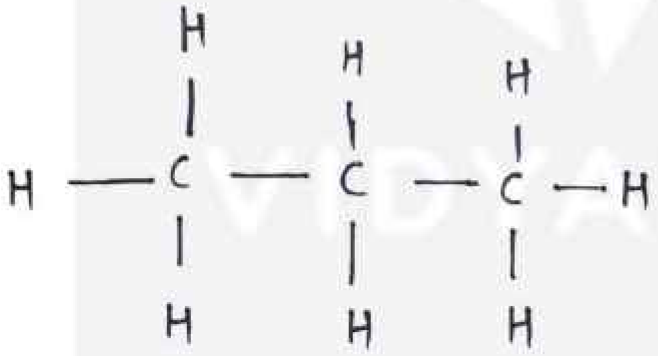
- First three members of this class can be represented as :



(a) methane



(b) Ethane

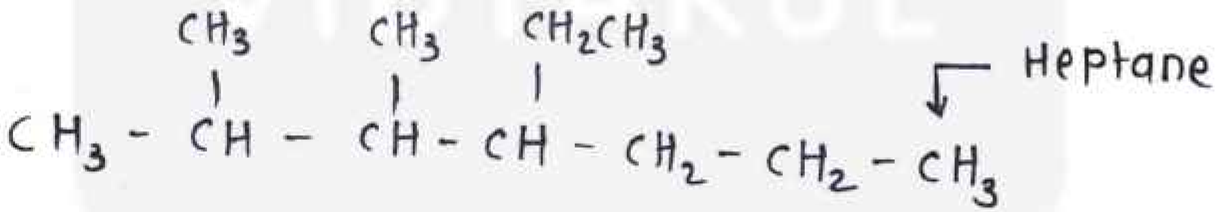


(c) Propane .

- In methane carbon forms single bonds with four hydrogen atoms. All H-C-H bond angles are of 109.5°. Methane has a tetrahedral structure C-C and C-H bonds are formed by head-on overlapping of sp^3 hybrid orbitals of carbon and 1s orbitals of hydrogen atom.

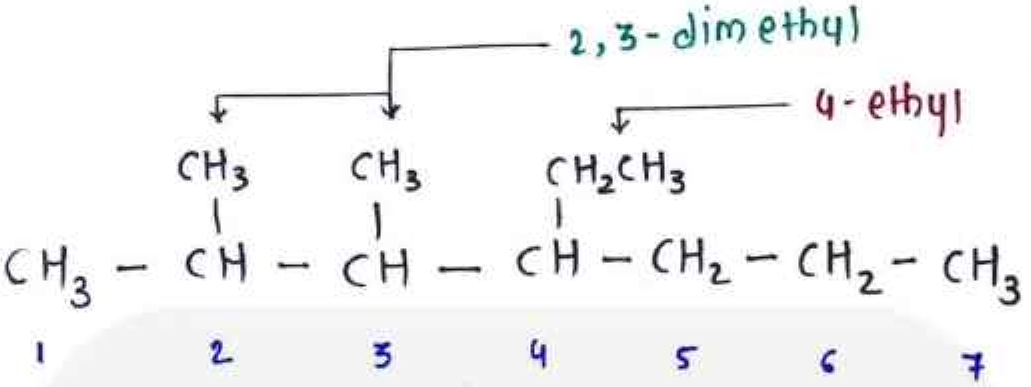
Nomenclature and Isomerism

Use the following step-by-step procedure to write the IUPAC names from the structural formulas.



$$CH_3-\overset{CH_3}{\overset{|}{C}}H-\overset{CH_3}{\overset{|}{C}}H-\overset{CH_2CH_3}{\overset{|}{C}}H-CH_2-CH_2-CH_3$$

Step 1 - Identify the longest chain; In the given example, longest chain has seven carbons. The seven carbon chain is Heptane.



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

step 2 - Number the chain: The chain is numbered from left to right. This gives lowest number to the attached alkyl group.

step 3 - Identify the alkyl group:

There are two methyl group at C-2 and C-3, there is one ethyl group of C-4

step 4 - Write the IUPAC name: In this case The IUPAC name is

4-Ethyl-2,3-dimethyl heptane.

Preparation

1) From unsaturated hydrocarbons

- Dihydrogen gas adds to alkenes and alkynes in the presence of finely divided catalysts like platinum, palladium or nickel to form alkanes. This process is called hydrogenation.

- These metals absorb hydrogen gas on their surfaces and activate H-H bond.

- $CH_2 = CH_2 + H_2 \xrightarrow{Pt/Pd/Ni} CH_3 - CH_3$

  Ethene Ethane

- $CH_3 - C \equiv C - H + 2H_2 \xrightarrow{Pt/Pd/Ni} CH_3 - CH_2 - CH_3$

  Propyne Propane

2) From alkyl halides

i) Alkyl halides on reduction with zinc and dilute hydrochloric acid gives alkanes.

$$CH_3-Cl + H_2 \xrightarrow{Zn,\ H^+} CH_4 + HCl$$

chloromethane

methane

$$C_2H_5-Cl + H_2 \xrightarrow{Zn,\ H^+} C_2H_6 + HCl$$

chlorethane

Ethane

ii) Alkyl halides on treatment with sodium metal in dry ethereal solution gives higher alkanes. This reaction is known as Wurtz reaction.

$$CH_3Br + 2Na + BrCH_3 \longrightarrow CH_3-CH_3 + 2NaBr$$

Bromomethane

Ethane

3) From carboxylic acids

i) sodium salts of carboxylic acid on heating with soda lime give alkanes containing one carbon atom less than the carboxylic acid. This process is known as decarboxylation.

$$CH_3COO^-Na^+ + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

sodium ethanoate

ii) kolbe's electrolytic method : An aqueous solution of sodium or potassium salt of a carboxylic acid on electrolysis gives alkane containing even number of carbon atoms at the anode.

$$2CH_3COO^-Na^+ + 2H_2O \xrightarrow{Electrolysis} CH_3-CH_3 + 2CO_2 + H_2 + 2NaOH$$

sodium acetate

Physical properties

- Alkanes are almost non-polar due to covalent nature of C-C and C-H bonds.
- They are colourless and odourless. It is generally observed that they are like dissolves like.
- They have low Boiling points due to non-polar in nature and there is a steady increase in boiling point with increase in molecular mass.
- The molecules are held together only by weak van der waals forces.
- The boiling points of the branched chain Alkanes are less than the straight chain isomers. This is due to the branching of the chain makes the molecules more compact and thereby decreases the surface area.

Chemical Properties

1) **combustion :** Alkanes on heating in the presence of air or dioxygen are completly oxidized to carbon dioxide and water with the evolution of large amount of heat.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

$$\therefore \Delta H = -217.0 \, K\,cal/mole.$$

2) **controlled oxidation :** Alkanes on heating with a regulated supply of dioxygen or air at high pressure and in the presence of suitable catalysts gives a variety of oxidation products.

i) $CH_4 + O_2 \xrightarrow[523K]{Cu/100atm} 2CH_3OH$

methanol

ii) $CH_4 + O_2 \xrightarrow{Mo_2O_3} HCHO + H_2O$

Methanal

3) **substitution** : one or more hydrogen can be replaced by halogens, nitro group and sulphonic acid group.

i) **Halogenation** takes place either at higher temperature or in the presence of diffused sunlight or ultraviolet light.

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl$$

chloromethane

$$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$$

Dichloromethane

ii) **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.

$$CH_4 + I_2 \rightleftharpoons CH_3I + HI$$

$$HIO_3 + 5HI \longrightarrow 3I_2 + 3H_2O$$

- Fluorination of alkane takes place exposively resulting even in the rupture of C-C bond in higher alkanes.

mechanism : Halogenations reaction takes place by free radical mechanism. The reaction proceeds in the following steps :

i) Initiation : The reaction is Initiated by homolysis of chlorine molecule in the presence of light or heat.

$$Cl - Cl \xrightarrow[\text{homolysis}]{h\nu} \dot{Cl} + \dot{Cl}$$

chlorine free radicals

ii) Propagation : chlorine free radicals attacks the methane molecules and takes the reaction forward direction by breaking the C-H bond to generate methyl free radical with the formation of H-Cl.

(a) $CH_4 + \dot{Cl} \xrightarrow{h\nu} \dot{C}H_3 + H-Cl$

The methyl radical thus obtained attacks the second molecule of chloride to form

CH_3-Cl with the liberation of another chlorine free radical by homolysis of chlorine molecule.

(b) $\dot{C}H_3 + Cl-Cl \longrightarrow CH_3-Cl + \dot{Cl}$

chlorine
free
radical

iii) Termination : The reaction stops after some time due to consumption of reactants and /or due to following side reactions:

The possible chain termination steps are:

a) $\dot{Cl} + \dot{Cl} \longrightarrow Cl-Cl$

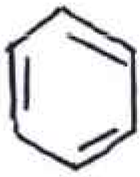
b) $H_3\dot{C} + \dot{C}H_3 \longrightarrow H_3C-CH_3$

c) $H_3\dot{C} + \dot{Cl} \longrightarrow H_3C-Cl$

4) **Isomerisation** : n-Alkanes on heating in the presence of anhydrous aluminium chloride and hydrogen chloride gas isomerise to branched chain alkanes.

5) **Aromatization** : n-Alkanes having six or more carbon atoms on heating to 773 K at 10-20 atmospheric pressure in the presence of oxides of vanadium, molybdenum or chromium supported over alumina get dehydrogenated and cyclised to benzene and its homologues. This reaction is known as aromatization or reforming.

$H_3C(CH_2)_4CH_3 \xrightarrow[773K]{Cr_2O_3}$



Hexane

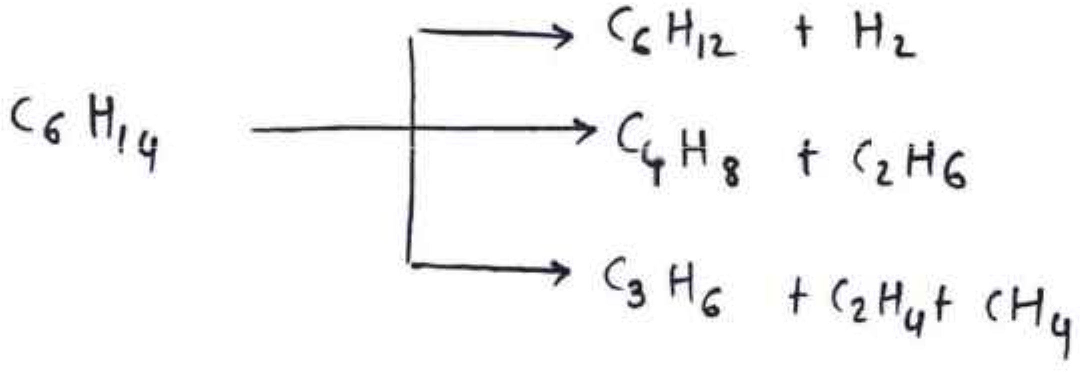
10-20 atm

Benzene

6) <u>Reaction with steam</u> : methane reacts with steam at 1273 K in the presence of nickel catalyst to form carbon monoxide and dihydrogen.

$$CH_4 + H_2O \xrightarrow[\Delta]{Ni} CO + 3H_2$$

7) <u>pyrolysis</u> : Higher alkanes on heating to higher temperature decompose into lower alkanes, alkenes etc. such a decomposition reaction into smaller fragments by the application of heat is called pyrolysis.



Conformational Isomerism

- The different molecular arrangements arising as a result of rotation around carbon- carbon single bonds are called as conformational isomerism.

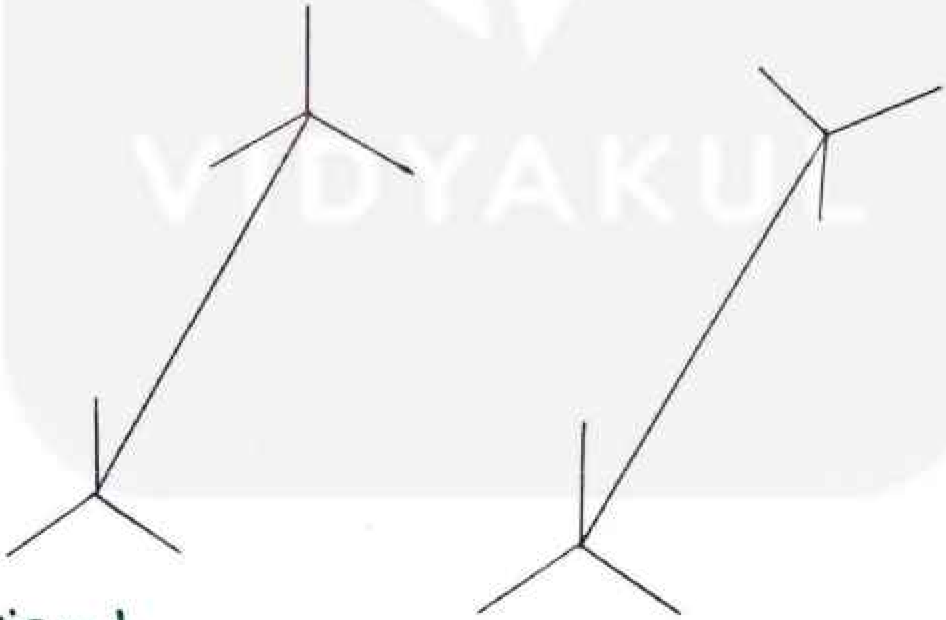
- There are infinite number of conformations of ethane are possible. However, there are two extreme cases.

- one such conformation in which H-atoms attached to two carbons are closed together as possible is called eclipsed conformation.

- Other one, in which hydrogens are as far apart as possible is known as the staggered conformation.

sawhorse projections

The molecule is viewed along the molecular axis. It is then projected on paper by drawing the central c-c bond as a somewhat longer straight line. The front carbon is shown at the lower end of the line and the rear carbon is shown at the upper end of the line.

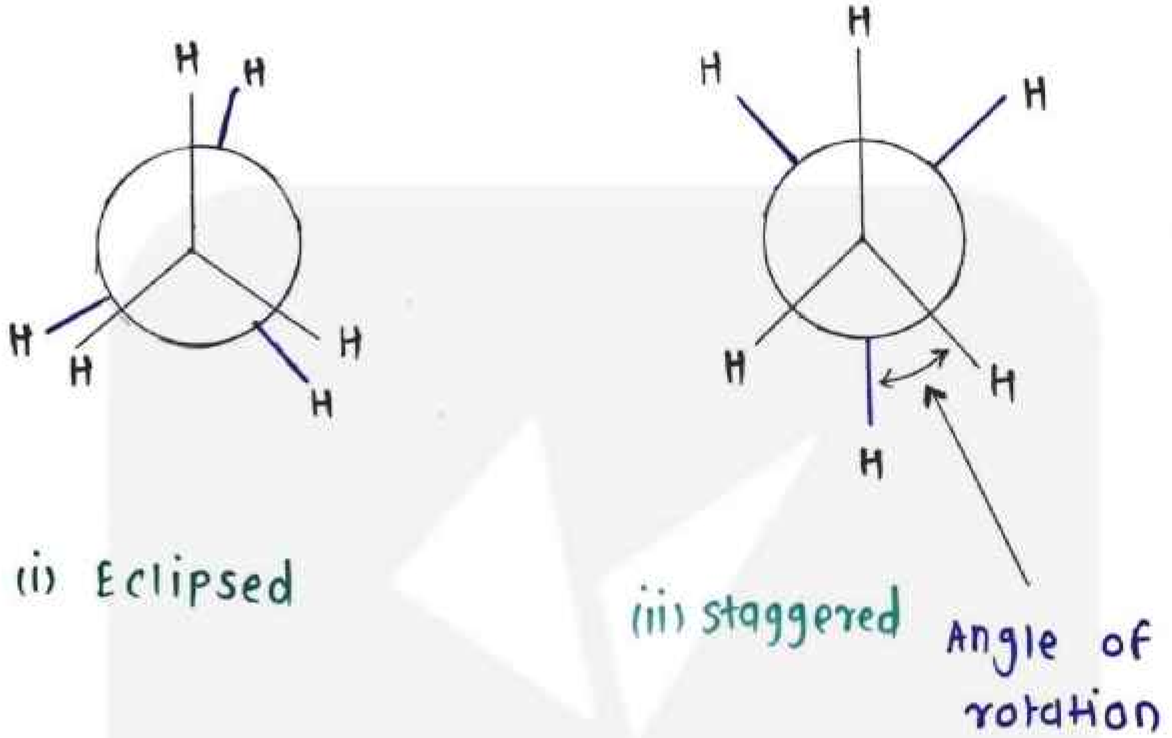


(i) Eclipsed

(ii) staggered

Fig: sawhorse projection of ethane.

Newman projections



(i) Eclipsed

(ii) staggered

Fig: Newman's Projection of ethane.

Relative stability of conformation :

- In the staggered form of ethane there are maximum repulsive forces, minimum energy and maximum stability of molecule.

- on the other hand, when the staggered form changes in the eclipsed form, the electron clouds of the carbon hydrogen bonds come closer to each other resulting in increase in electron cloud repulsions, molecules have to possess more energy and thus has lower stability.

Alkenes

Alkenes are hydrocarbons that contain a carbon - carbon double bond (C=C) in their molecules.

structure of Double bond

let us consider ($H_2C = CH_2$) for illustrating the orbital make up of alkenes.

In ethylene the carbon atoms are sp^2 hybridized - They are attached to each other by a π bond and a σ bond. The σ bond results from the overlapping of two sp^2 hybrid orbitals. and The π bond is formed from the overlap of the unhybridized p- orbitals. Ethylene is a planer molecule.

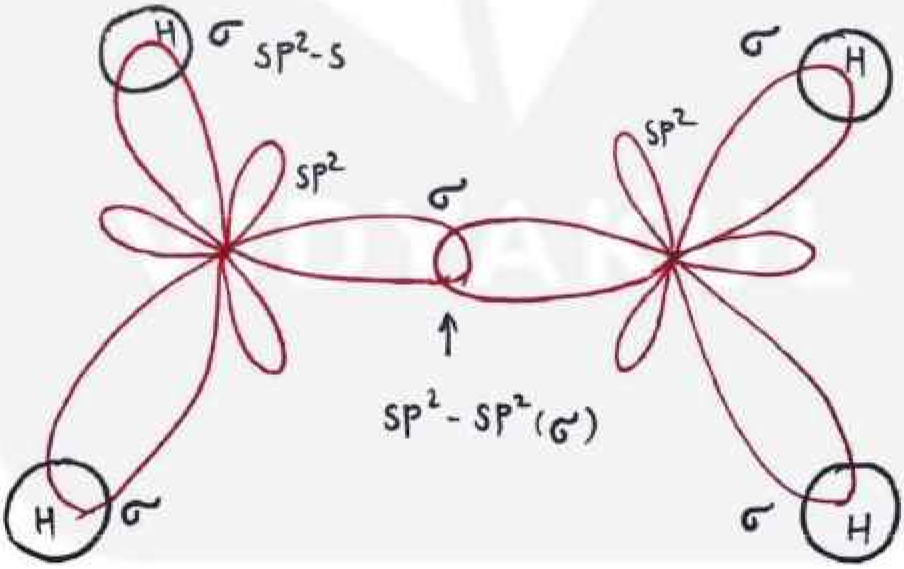


Fig: orbital picture of ethene depicting σ bonds only

- A carbon - carbon double bond in Alkenes is made up of one σ and one π - bond.

- Alkenes are more reactive than Alkanes. This is due to availability of n-electrons.

Nomenclature -

In IUPAC system

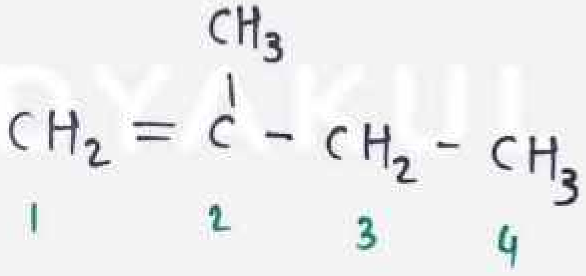
i) The name is based on the parent alkene having the longest carbon chain of which double bond is apart.

ii) This chain is numbered from the end, near the double bond and its position is indicated by the number of the carbon atom not which the double bond originates.

iii) The name of the parent alkene with the position number of the double bond is written first and then the names of other substituents prefixed to it.

examples: • $\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{CH}=\overset{1}{CH_2}$

1 - Butene.



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

2 - Methyl - 1 - butene

Isomerism

Alkenes show both structural and geometrical isomerism.

structural isomerism :

Ethene and propene have no structural isomers, but there are three structures of butenes.

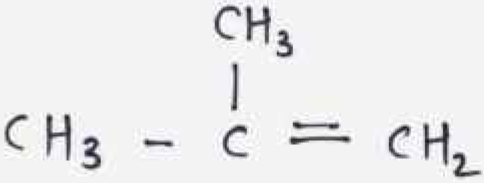
i) $CH_3 - CH_3 - CH = CH_2$

1- Butene

ii) $CH_3 - CH = CH - CH_3$

2- Butene

iii)



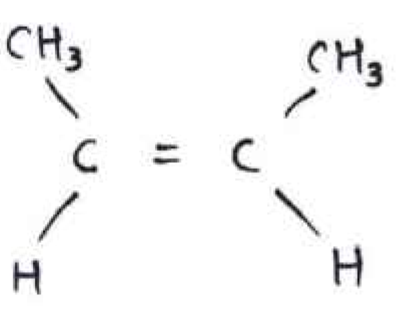
$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2$$

2- methyl propene.

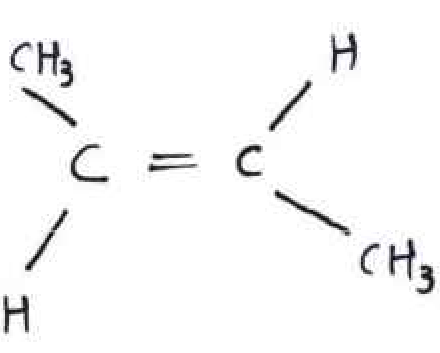
Of these, two are straight chain structures with the difference being in the position of double bond in the molecules.

Geometrical isomerism: An Alkene having a formula $RCH = CHR$ can have two stereoisomers, depending upon whether the two alkyl groups are on the same or opposite sides of the double bond. And if they are on the same side, then it is called cis-isomer. If they are on opposite side, then it is called trans-isomer.

- Due to the different arrangement of atoms or groups in space, these isomers differ in their properties like melting point, Boiling points, dipole moment, solubility etc.



cis-But-2-ene



trans-But-2-ene

preparation

1) **From alkynes :** Alkynes on partial reduction with partially deactivated palladised charcoal known as Lindlar's catalyst give alkynes

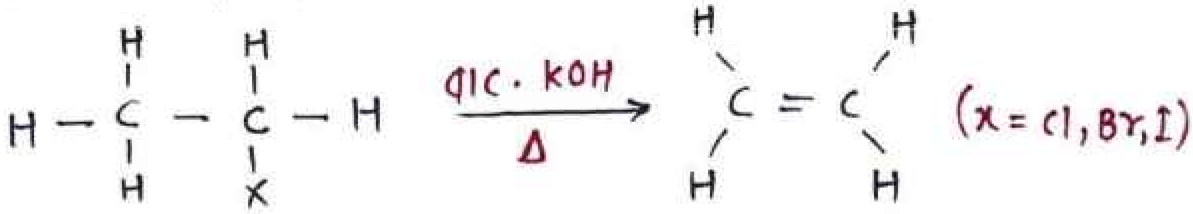
i) $CH \equiv CH + H_2 \xrightarrow{Pd/C} CH_2 = CH_2$

Ethyne Ethene

ii) $CH_3 - C \equiv CH + H_2 \xrightarrow{Pd/C} CH_3 - CH = CH_2$

Propyne Propene

2) **From alkyl halides :** Alkyl halides (R-X) on heating with alcoholic potash, takes out one hydrogen atom from the β-carbon atom.



$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{X}{C}}-H \xrightarrow[\Delta]{alc.\ KOH} \overset{H}{\underset{H}{>}}C=C\overset{H}{\underset{H}{<}}$$

(x = Cl, Br, I)

3) **From vicinal dihalides**: Dihalides in which two halogen atoms are attached to two adjacent carbon atoms are known as vicinal dihalides.

- vicinal dihalides on treatment with zinc metal lose a molecule of ZnX_2 to form an alkene. This reaction is known as dehalogenation.

$$CH_2Br - CH_2Br + Zn \longrightarrow CH_2 = CH_2 + ZnBr_2$$

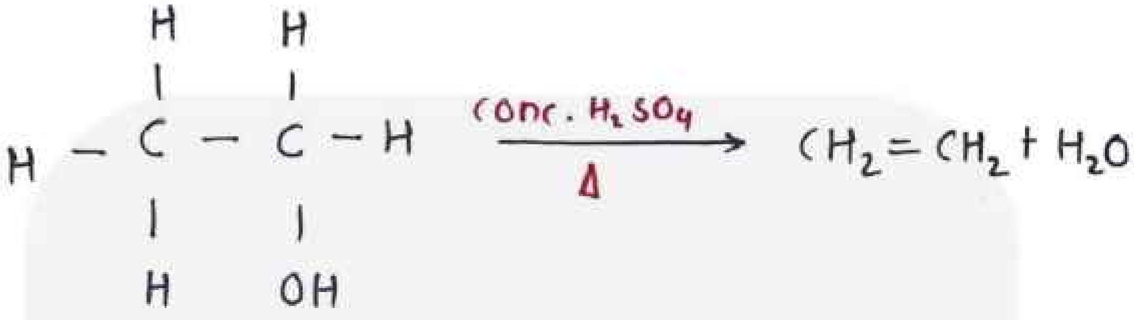
$$CH_2CHBr - CH_2Br + Zn \longrightarrow CH_3CH = CH_2 + ZnBr_2$$

4) **From alcohols**:

By acidic dehydration.

Alcohols on heating with concentrated sulphuric acid from alkenes with the elemination of one molecule of water.

- The reaction is known as acidic dehydration of alcohols.



$$H-\underset{H}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-H \xrightarrow[\Delta]{conc.\ H_2SO_4} CH_2=CH_2+H_2O$$

Ethanol Ethene

Properties

Physical properties :

- The first three members are gases, the next fourteen are liquids and the higher ones are solids.

- Ethene is a colourless gas with a faint sweet smell All othere alkenes are colourless and odourless, insoluble in water but fairly soluble in non polar solvents like benzene, petroleum ether.

- They show a regular increase in the Boiling point with increase in size.

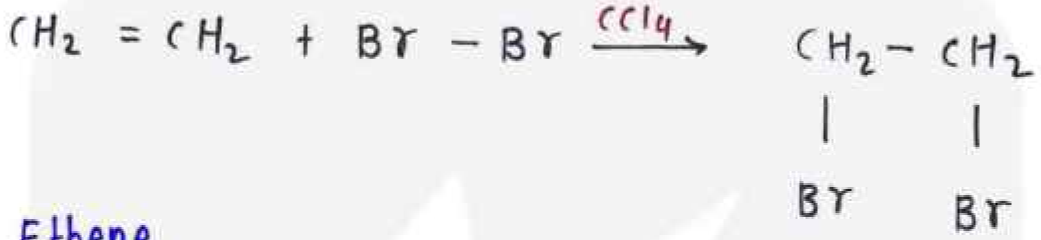
chemical properties

1) Addition Reaction : Alkene show electrophilic addition reaction.

i) **Addition of Hydrogen** : Alkenes add up one molecule of dihydrogen gas in the presence of finely divided nickel, palladium or platinum to form alkanes.

$$RCH=CH_2 \xrightarrow{H_2/Ni} RCH_2CH_3$$

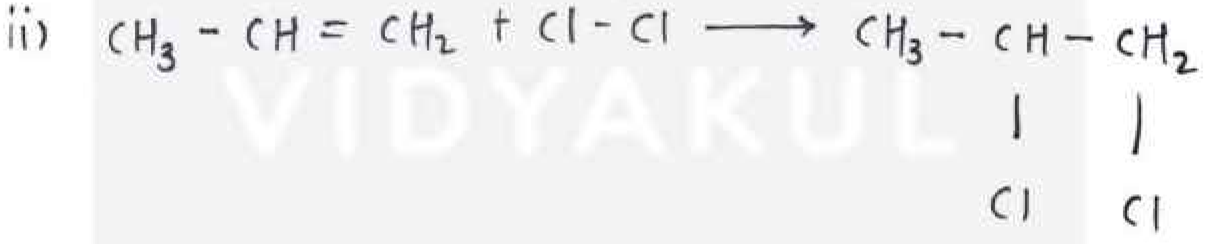
ii) **Addition of Halogens** : Halogens like bromine or chlorine add up to alkene to form vicinal dihalides.



i) $CH_2 = CH_2 + Br - Br \xrightarrow{CCl_4} \underset{\displaystyle Br}{\underset{|}{CH_2}} - \underset{\displaystyle Br}{\underset{|}{CH_2}}$

Ethene

1, 2 Dibrmoethene



ii) $CH_3 - CH = CH_2 + Cl - Cl \longrightarrow CH_3 - \underset{\displaystyle Cl}{\underset{|}{CH}} - \underset{\displaystyle Cl}{\underset{|}{CH_2}}$

Propene

1, 2-Dichloropropane

iii) **Addition of hydrogen halides** :

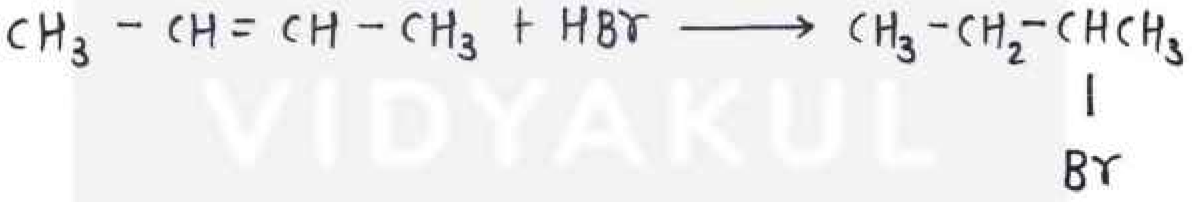
Hydrogen halides (HCl, HBr, HI) add up to alkenes to form alkyl halides. The order of reactivity of the hydrogen halides is

HI > HBr > HCl .

Let us illustrate this by taking addition of HBr to symmetrical and unsymmetrical alkenes.

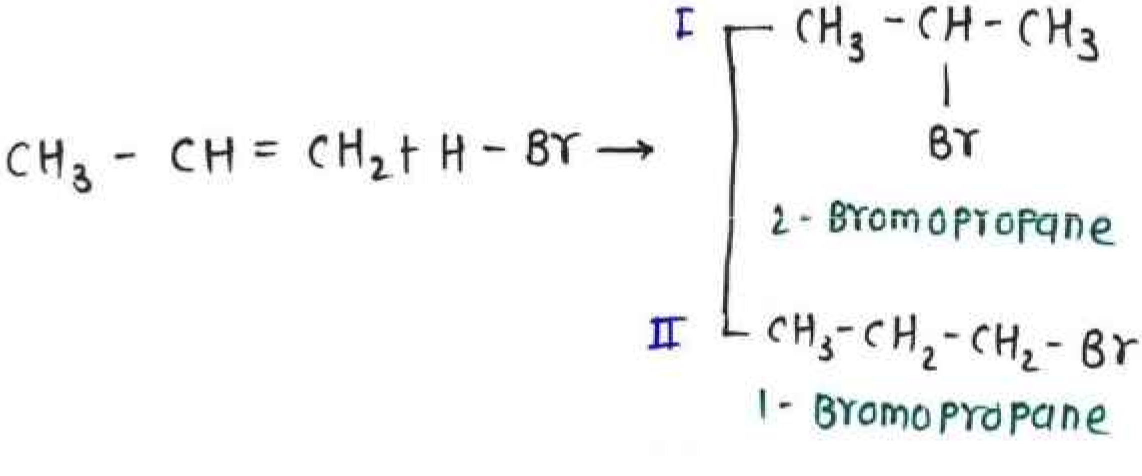
- Addition reaction of HBr to symmetrical alkenes.

$CH_2 = CH_2 + H - Br \longrightarrow CH_3 - CH_2 - Br$



$$CH_3 - CH = CH - CH_3 + HBr \longrightarrow CH_3 - CH_2 - \underset{\displaystyle Br}{\underset{|}{CH}}CH_3$$

- Addition reaction of HBr to unsymmetrical alkenes :



$$CH_3 - CH = CH_2 + H - Br \rightarrow \left[\begin{array}{ll} \text{I} & CH_3 - \underset{\displaystyle Br}{\underset{|}{CH}} - CH_3 \\ & \text{2-Bromopropane} \\ \text{II} & CH_3 - CH_2 - CH_2 - Br \\ & \text{1-Bromopropane} \end{array}\right.$$

- Addtion reaction of HBr to unsymmetrical alkenes takes place according to the Markovnikov Rule.

Markovnikov Rule : Negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms.

$$H_3\overset{3}{C} - \overset{2}{C}H = \overset{1}{C}H_2 + H-Br$$

$$\downarrow H^+$$

$$H_3C-CH_2-\overset{+}{C}H_2 + Br^- \qquad\qquad H_3C-\overset{+}{C}H-CH_3 + Br^-$$

(a) less stable

primary carbocation

(b) more stable

secondary carbocation

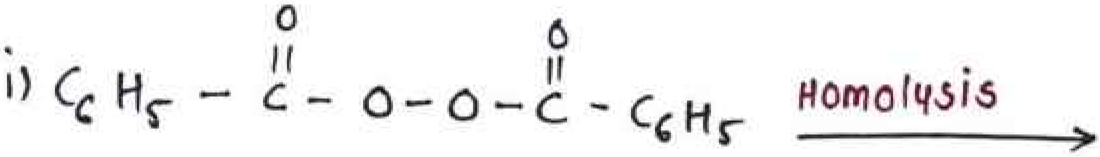
peroxide effect or kharasch (Anti markownikoff's addition) :

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 markownikov rule.

$$CH_3-CH=CH_2+HBr\xrightarrow{(C_2H_5CO)_2O_2}CH_3-CH_2-CH_2Br$$

1-Bromopropane

mechanism : peroxide effect proceeds via free radical chain machanism :

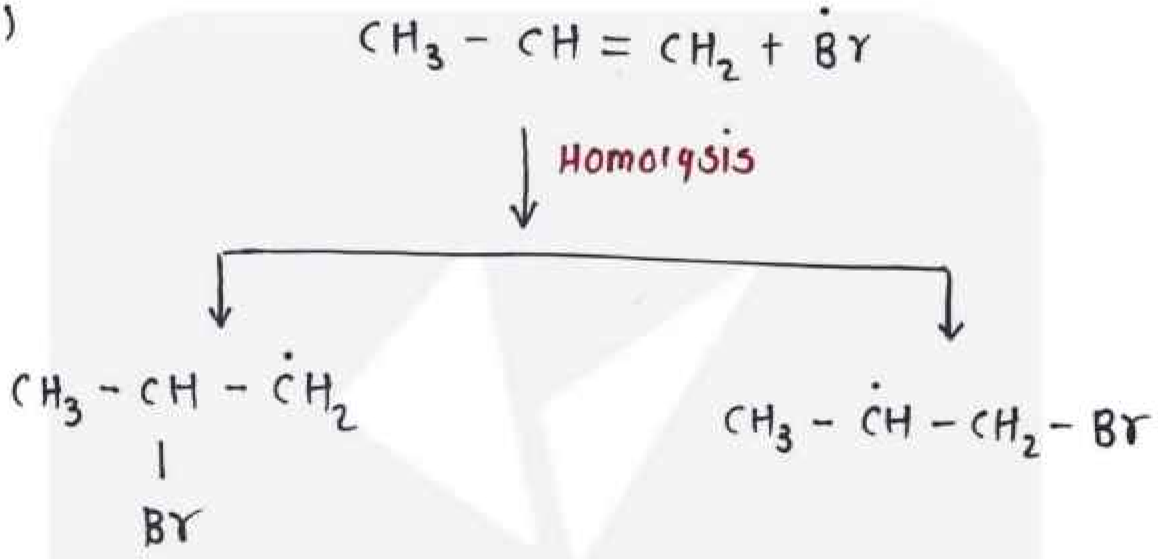

$$\text{i) } C_6H_5-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-C_6H_5\xrightarrow{\text{Homolysis}}$$

Benzoyl peroxide


$$2C_6H_5-\overset{\overset{O}{\|}}{C}-\ddot{\underset{..}{O}}:\longrightarrow 2\dot{C}_6H_5+2CO_2$$

ii) $\dot{C}_6H_5 + H-Br \xrightarrow{\text{Homolysis}} C_6H_6 + \dot{B}r$

iii)



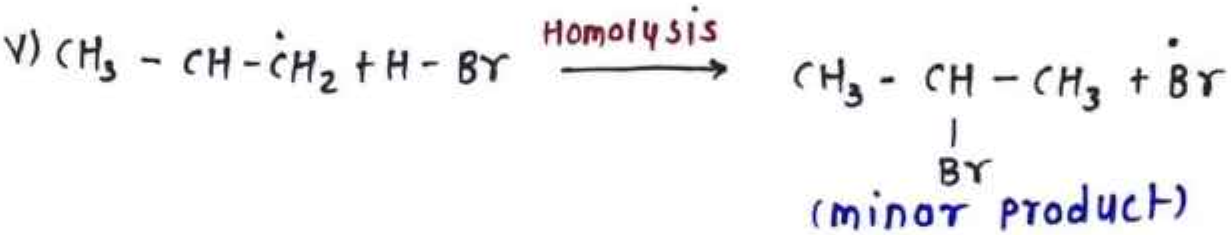
$$CH_3-CH=CH_2+\dot{B}r \xrightarrow{\text{Homolysis}} CH_3-\underset{\underset{Br}{|}}{CH}-\dot{C}H_2 \quad ; \quad CH_3-\dot{C}H-CH_2-Br$$

(a) less stable Primary free radical

(b) more stable Primary free radical

iv) $CH_3-\dot{C}H-CH_2Br + H-Br \xrightarrow{\text{Homolysis}} CH_3-CH_2-CH_2Br + \dot{B}r$

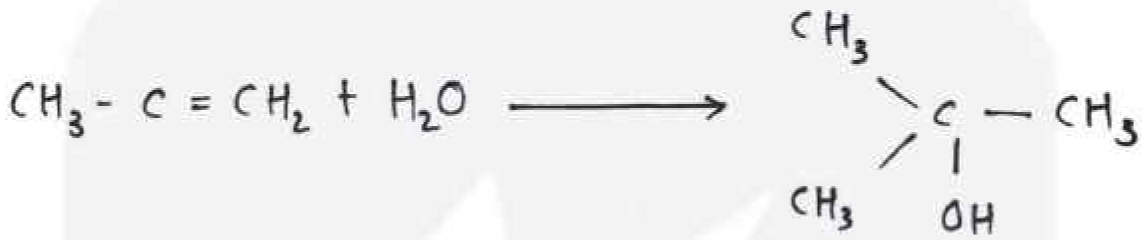
(major product)



$$\text{v) } CH_3-CH-\dot{C}H_2 + H-Br \xrightarrow{\text{Homolysis}} CH_3-\underset{\underset{Br}{|}}{CH}-CH_3 + \dot{B}r$$

(minor product)

iv) **Addition of Water** : In the presence of a few drops of concentrated sulphuric acid alkenes react with water to form alcohols.

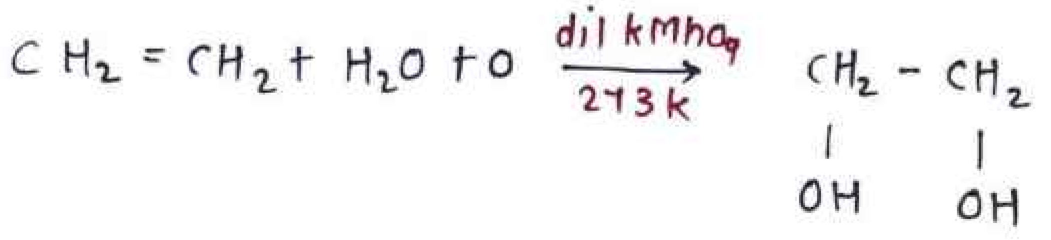


$$CH_3-C=CH_2 + H_2O \longrightarrow (CH_3)_2C(OH)-CH_3$$

2-Methyl Propene

2-MethylPropan-2-ol

v) **Oxidation** : Alkenes on reaction with cold, dilute, aqueous solution of potassium permaganate (Baeyer's reagent) produce vicinal glycols. Decolorisation of $KMnO_4$ solution is used as a test for unsaturation.



$$CH_2=CH_2 + H_2O + O \xrightarrow[273K]{dil\ kMnO_4} \underset{OH}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH_2}}$$

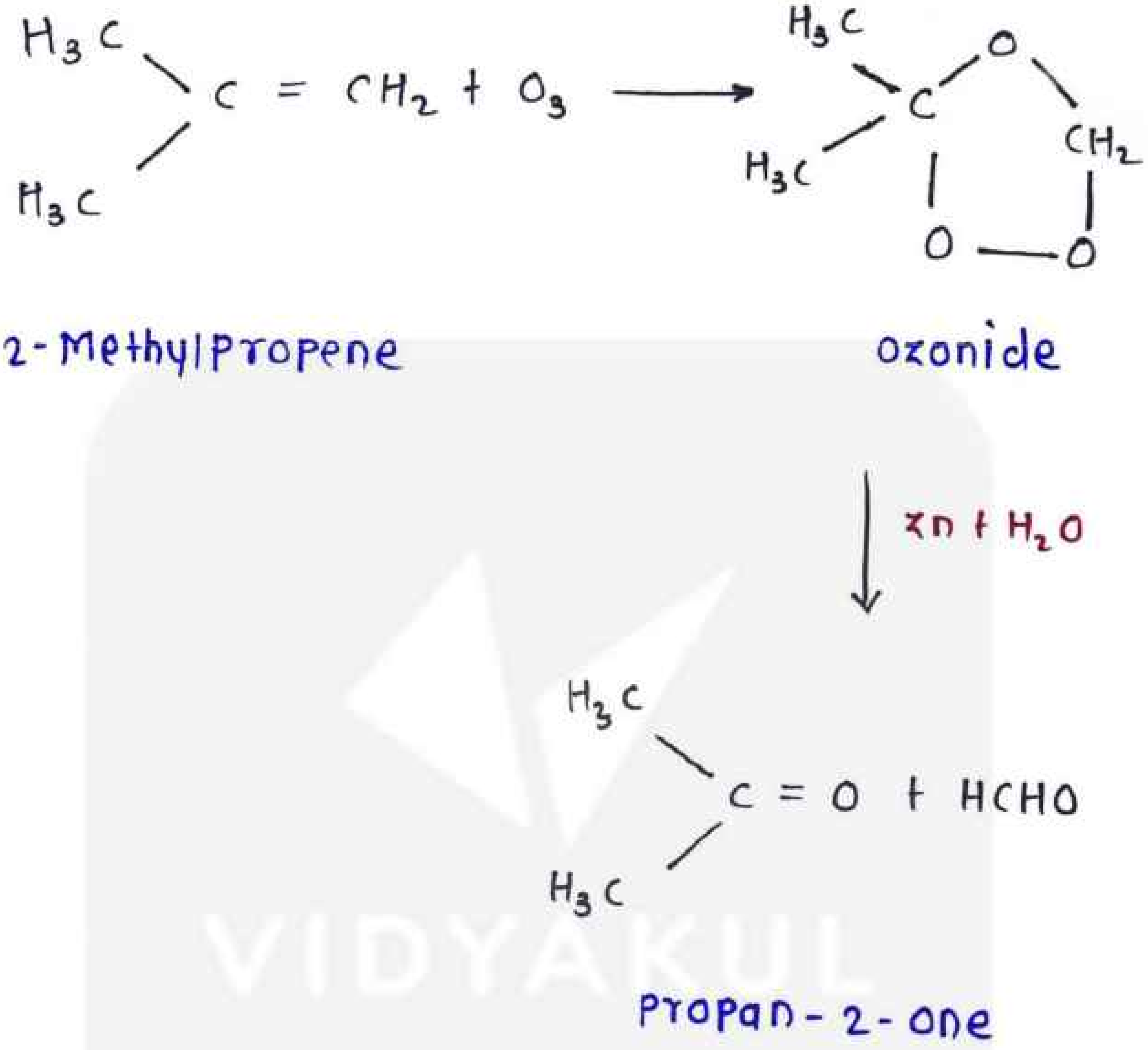
Ethane-1, 2-diol
(Glycol)

$$CH_3-CH=CH_2 + H_2O + O \xrightarrow[273K]{dil\ kMnO_4} CH_3CH(OH)CH_2OH$$

Propane-1, 2-diol

vi) **ozonolysis** : ozonolysis of alkenes involves the addition of ozone molecule to alkene to form ozonide and the cleavage of the ozonide by $Zn-H_2O$ to smaller molecules.

- ozonolysis is used to detect the position of double bond.



vii) **Polymerisation** : Polythene is obtained by the combination of large number of ethene molecules at high temperature, high pressure and in the presence of catalyst. This reaction is known as polymerisation.

- The large molecules thus obtained are called polymers. The simple compounds from which polymers are made are called monomers.

$$n(CH_2 = CH_2) \xrightarrow[\text{catalyst}]{\text{High temp./Pressure}} \left(CH_2 - CH_2 \right)_n$$

Polythene

Alkynes

- Alkynes are characterised by the presence of a triple bond in the molecule.

Their general formula is C_nH_{2n-2}.

- The first and the most important member of this series of hydrocarbons is acetylene, $HC \equiv CH$ and hence they are also called the Acetylenes.

Structure : let us consider ethyne $(HC \equiv CH)$ for illustrating the orbital make up of ethyne. In ethyne, the carbon atoms are sp hybridized. They are attached to each other by a σ - bond and two π - bonds.

- The σ - bond results from the overlap of two sp hybrid orbitals. The π bonds are formed from the separate overlap of the two p - orbitals from the two adjacent carbon atoms.

- The other sp hybrid orbitals of each carbon atom forms a σ bond with another carbon or hydrogen atom.

- Ethyne is a linear molecule.

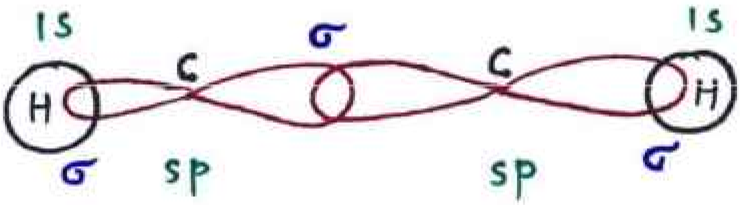


Fig: sigma overlap

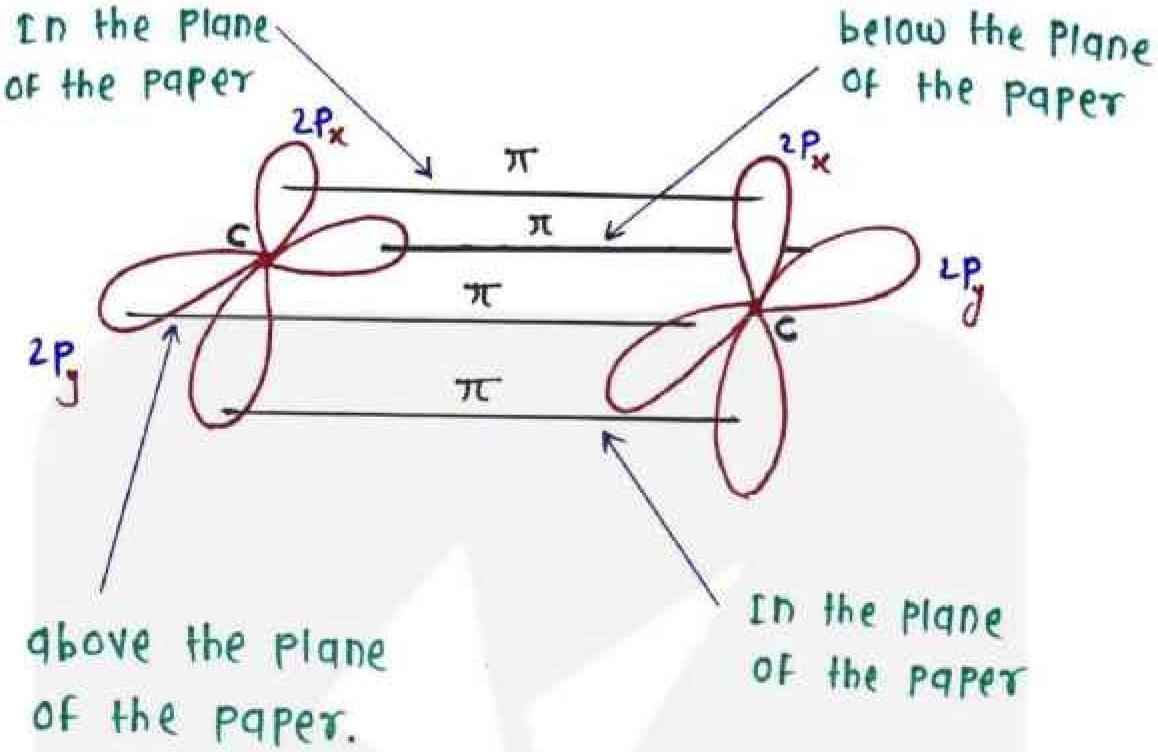


Fig: Pi overlaps

Nomenclature and Isomerism

- The IUPAC names of alkynes are obtained by dropping the ending -'ane' of the parent alkane and adding the suffix -'yne'.

- carbon chain including the triple bond is numbered from the end, nearest this bond.

- The position of the triple bond is indicated by prefixing the number of carbon preceding it to the name of the alkyne.

i) $H - C \equiv C - H$

Ethyne

ii) $CH_3 - C \equiv C - H$

Propyne

iii) $\overset{4}{CH_3} - \overset{3}{CH_2} - \overset{2}{C} \equiv \overset{1}{C} - H$

1 - Butyne

Preparation :

1) From calcium carbide :

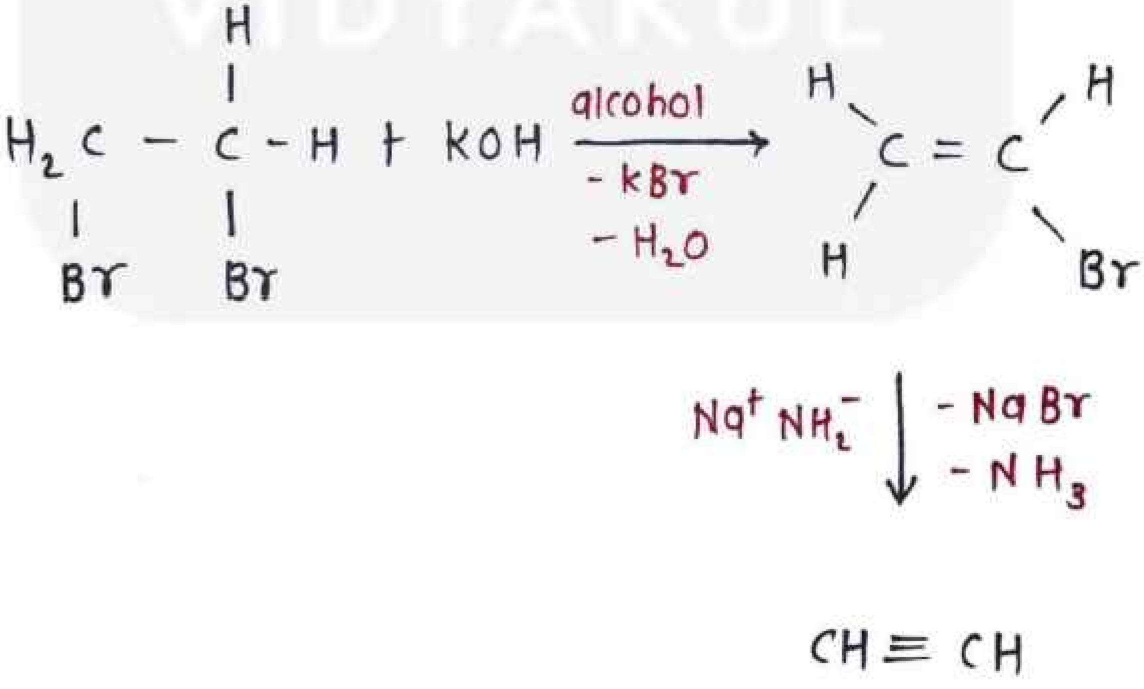
Ethyne is prepared by treating calcium carbide with water. calcium carbide is prepared by heating quick lime with coke.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

$$CaO + 3C \longrightarrow CaC_2 + CO$$

$$CaCO_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

2) From vicinal dihalides : vicinal dihalides on treatment with alcoholic Potassium hydroxide undergo dehydrohalogenation.



Properties

Physical Properties: Physical properties of alkynes follow the same trend of alkenes and alkanes. They are weakly polar in nature.

Chemical Properties:

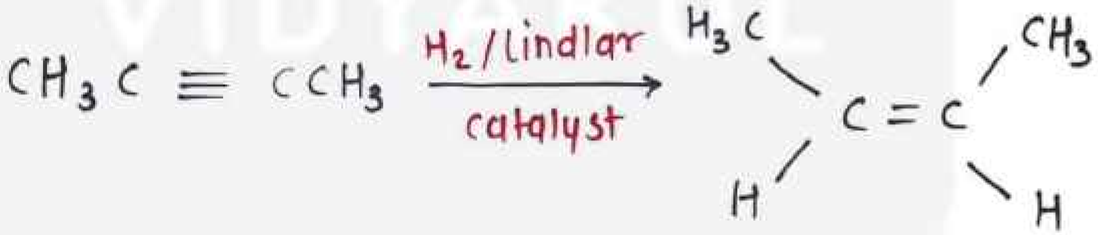
Addition Reaction: Alkyne show electrophilic addition reaction

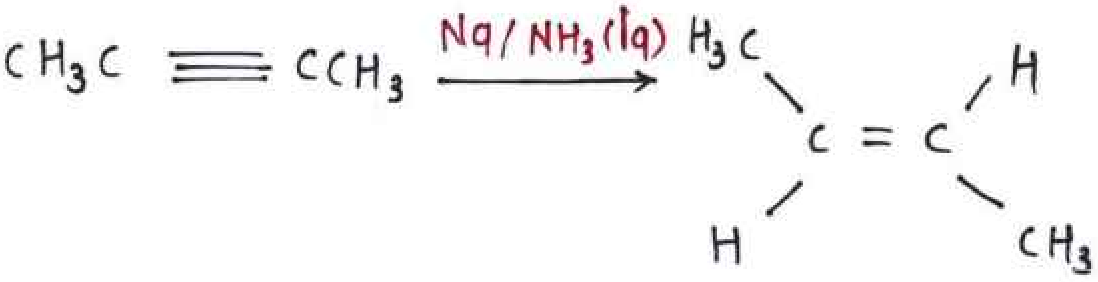
i) Addition of Hydrogen: Hydrogenation

$$\underset{\text{Propyne}}{CH_3C \equiv CH} + 2H_2 \xrightarrow{Pt/Ni/Pd} \underset{\text{Propane}}{CH_3CH_2CH_3}$$

- The hydrogenation can be controlled at the alkene stage only. This is possible by using by using a Lindlar's catalysts or sodium in liquid NH_3 at 200K temp.

- The catalytic reduction of alkynes in the presence of Lindlar's catalyst gives cis-alkenes while in the presence of sodium in liquid NH_3 (Birch reduction) gives trans-alkenes.



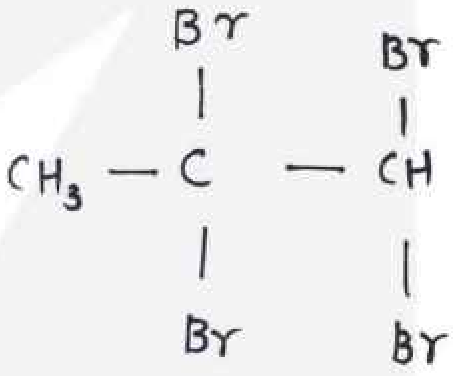


ii) Addition of halogens :

$CH_3-C\equiv CH + Br-Br \longrightarrow [CH_3CBr=CHBr]$

1,2-Dibromopropene

$\big\downarrow Br_2$



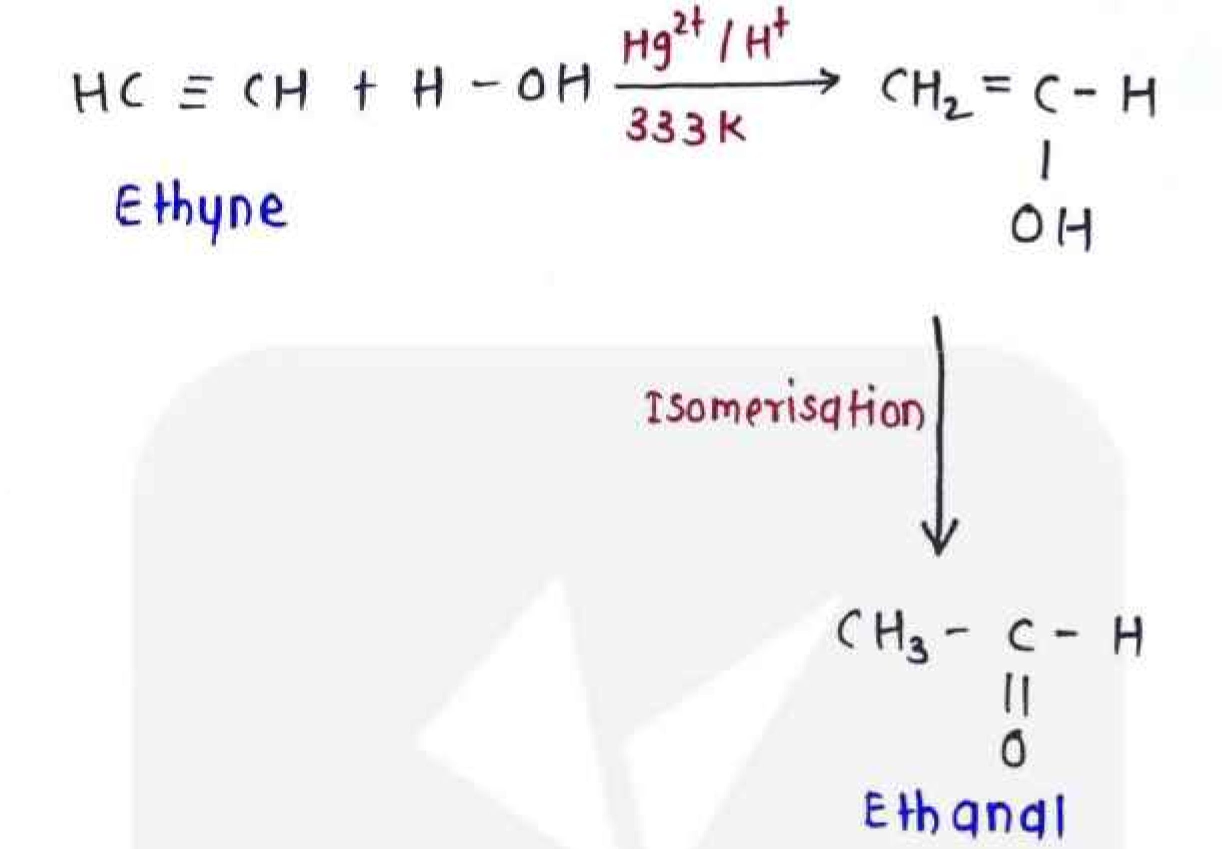
$CH_3-CBr_2-CHBr_2$

1,1,2,2-Tetrabromopropane

iii) Addition of hydrogen halides :

$HC\equiv CH + 2HBr \longrightarrow CH_3CHBr_2$

iv) Addition of Water (Hydration) : Acid catalyzed addition of water.

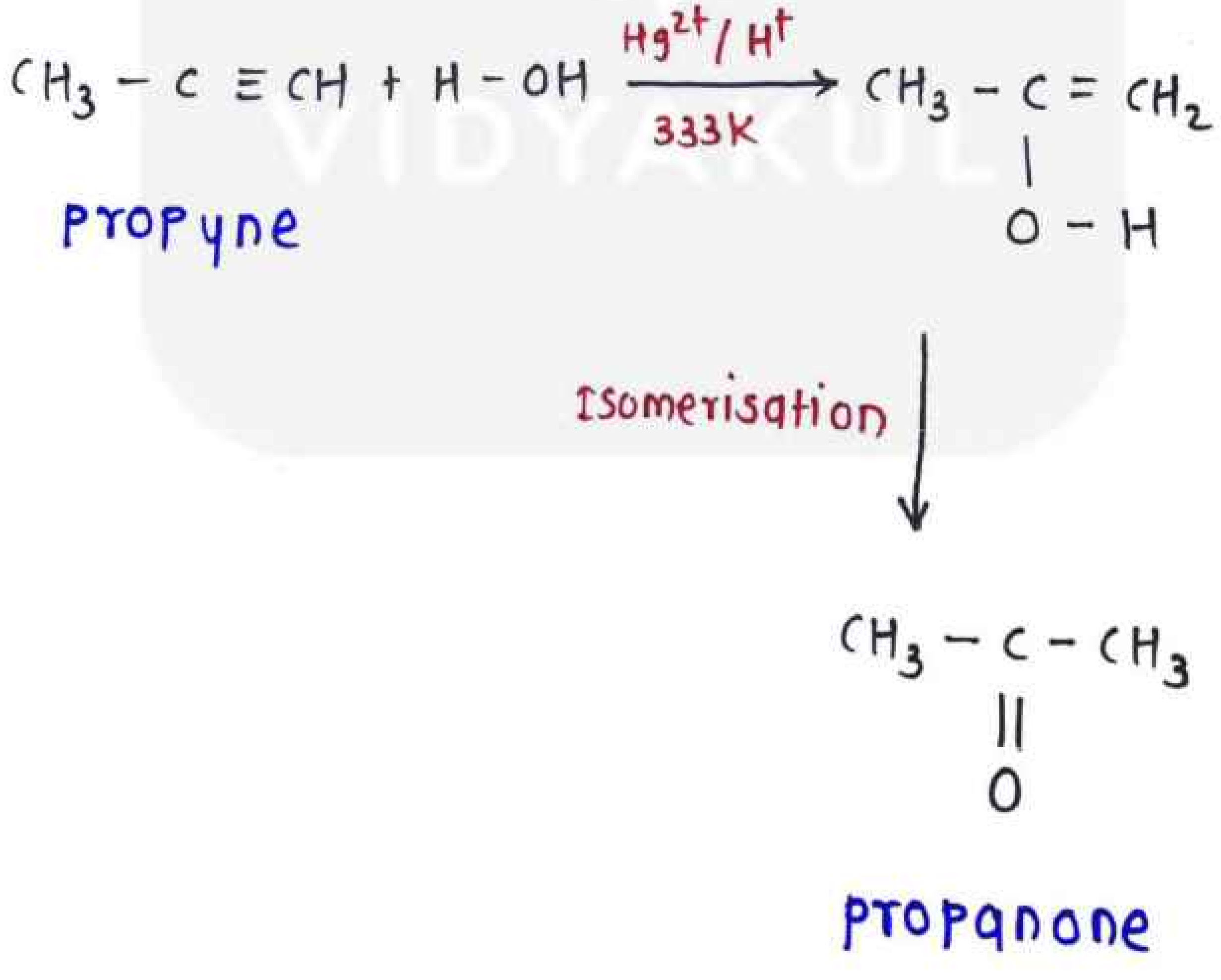


$$HC\equiv CH + H-OH \xrightarrow[333K]{Hg^{2+}/H^{+}} CH_2=\underset{\underset{OH}{|}}{C}-H$$

Ethyne

$$\xrightarrow{\text{Isomerisation}} CH_3-\underset{\underset{O}{\|}}{C}-H$$

Ethanal



$$CH_3-C\equiv CH + H-OH \xrightarrow[333K]{Hg^{2+}/H^{+}} CH_3-\underset{\underset{O-H}{|}}{C}=CH_2$$

Propyne

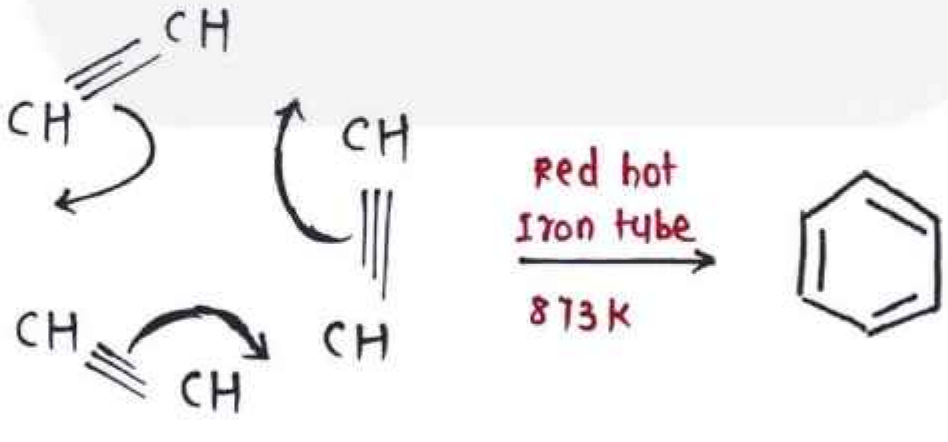
$$\xrightarrow{\text{Isomerisation}} CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

Propanone

v) <u>Polymerisation :</u>

(a) Linear polymerisation: of ethyne gives Polyacetylene or polyethyne which is a high molecular polyene containing repeating units of ($CH = CH - CH = CH$) and can be reprensented as $-(CH=CH-CH=CH)_n$

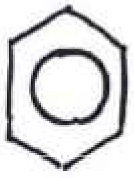
(b) Cyclic polymerisation: Results in the formation of aromatic compounds.

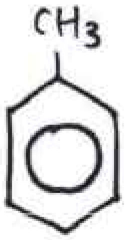


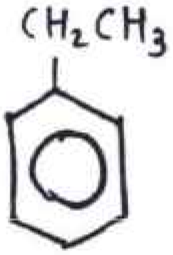
Aromatic Hydrocarbon

These hydrocarbons are known as 'arenes'. Aromatic compounds containing benzene ring are known as benzenoids and those not containing a benzene ring are known as non-benzenoids.

Nomenclature and isomerism : Benzene and its homologus are generally called by their common names which are accepted by IUPAC system. The homologus of benzene having a single alkyl group are named as Alkyl benzenes.

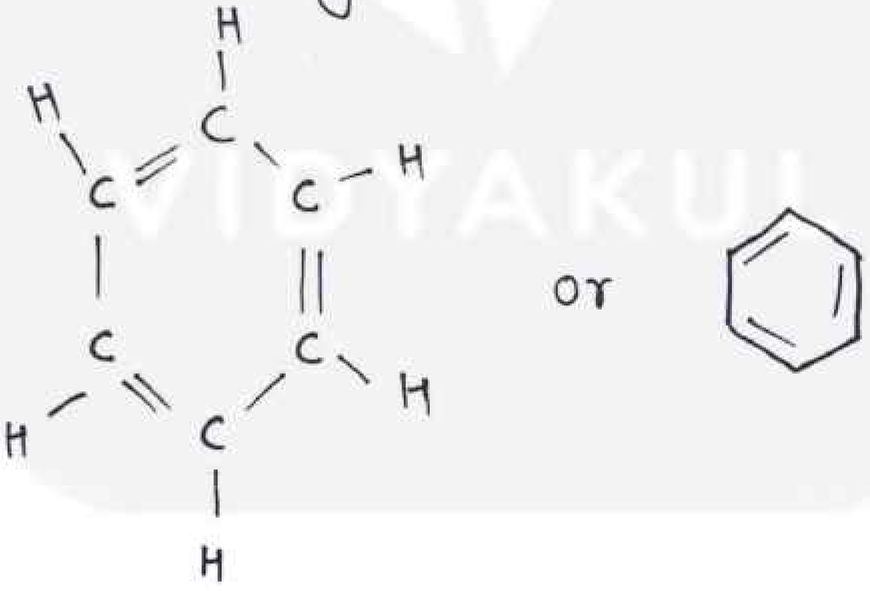

Benzene


Toluene (methyl benzene)

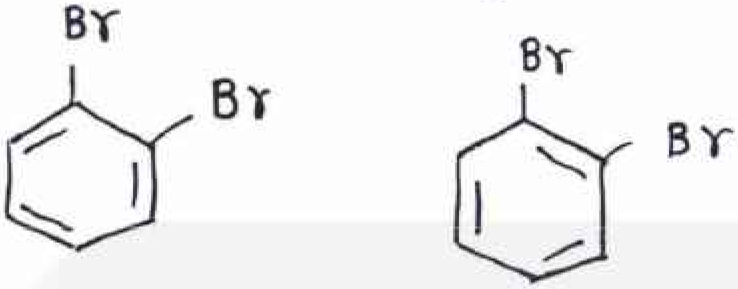

Ethyl Benzene

Structure of Benzene

By elemental analysis, it is found that molecular formula of benzene is C_6H_6. This indicates that benzene is highly unsaturated compound. In 1865, Kekule gave the cyclic planer structure of benzene with six carbon with alternate double and single bonds.



The Kekule structure indicates the possibility of two isomeric 1,2-dibromobenzenes. In one of the isomers, the bromine atoms are attached to the doubly bonded carbon atoms whereas in the other they are attached to the singly bonded carbon.



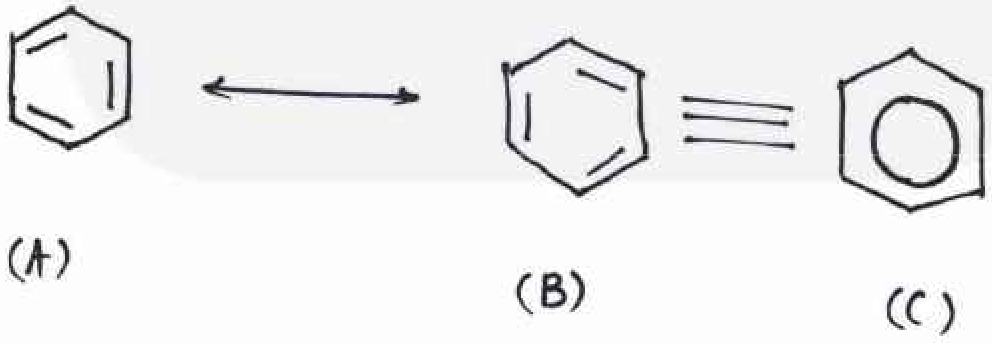
In fact, only one ortho - dibromobenzene could be prepared. To overcome this problem kekule suggested that benzene was a mixture of two forms.

Failure of kekyle's structure: kekule structure of benzene failed to explain the unique stability and its preference to substitution reaction that addition reactions

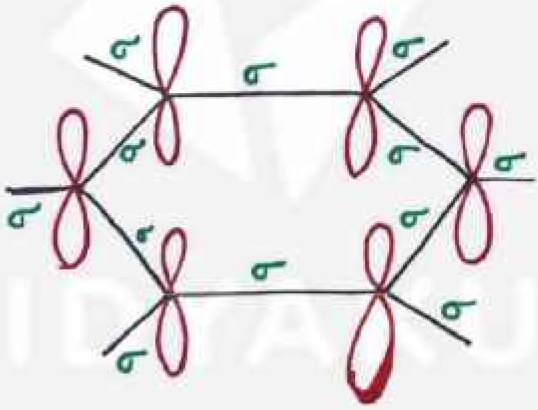
Resonance and stability of Benzene

The phenomenon in which two or more structures can be written for a substance which involves identical positions of atoms is called resonance.

- In benzene's kekule's structures (1) and (2) represent the resonance structure. Actual structure - of the molecule is represented by hybrid of these two structures.



orbital structure of benzene : All six carbon atoms in benzene are sp^3 hybridized. The sp^2 hybrid orbitals overlap with each other and with s-orbitals of the six hydrogen atoms forming C-C and C-H σ-bonds.



- X-Ray diffraction data indicates that benzene is a planar molecule. The data indicates that all the six C-C bond length are of the same order, which is intermediate between (C-C) single bond and C-C double bond.

Aromaticity :

It is the property of the sp^2 hybridized planar rings in which the p-orbitals allow cyclic delocalization of π electrons.

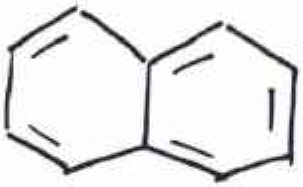
- Characteristics of Aromaticity :

i) planarity

ii) complete delocalisation of the π electrons in the ring

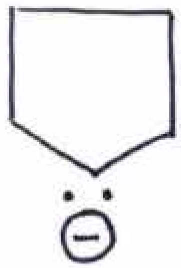
iii) presence of $(4n+2)$ π electrons in the ring where n is an integer

Examples :



Napthalene

($n=2$, 10 π electrons)



cyclopentadienyl anion

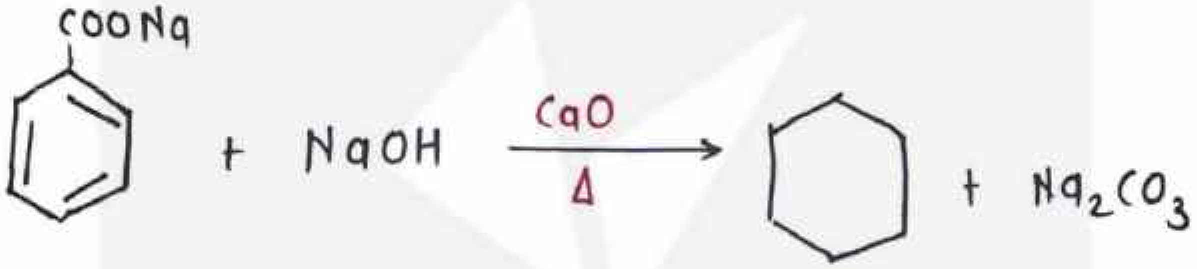
($n=1$, 6π electrons)

preparation of Benzene

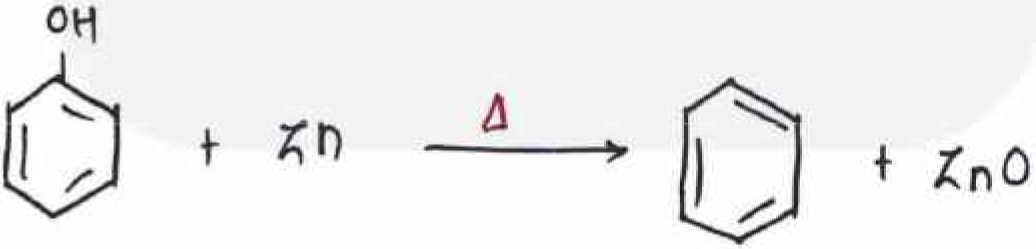
i) cyclic polymerisation of ethyne

ii) **Decarboxylation of aromatic acids:**

sodium salt of benzoic acid on heating with sodalime gives benzene.



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



properties

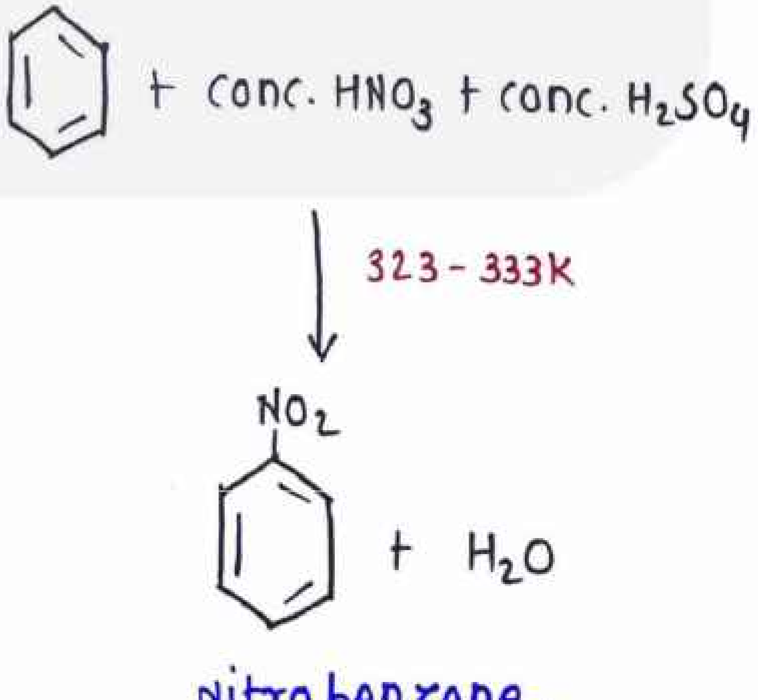
Physical properties: Benzene is a colourless liquid.

- It is insoluble in water but it is soluble in alcohol, ether, chloroform etc.
- Benzene itself is a good solvent for many organic substances.
- It Burns with a luminous, sooty flame in contrast to alkanes and alkenes which usually burn with a bluish flame.

chemical properties.

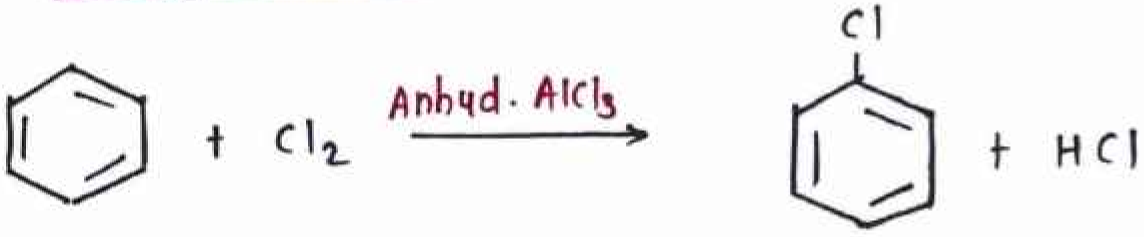
Electrophilic substitution reactions:

i) Nitration:



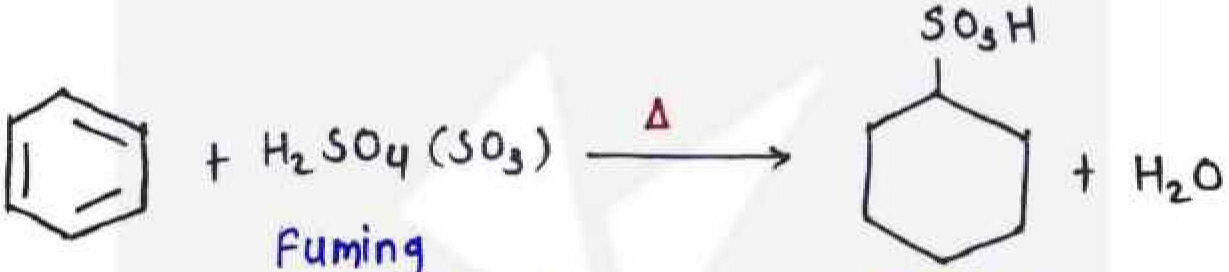
Nitrobenzene.

ii) Halogenation :



Chloro benzene

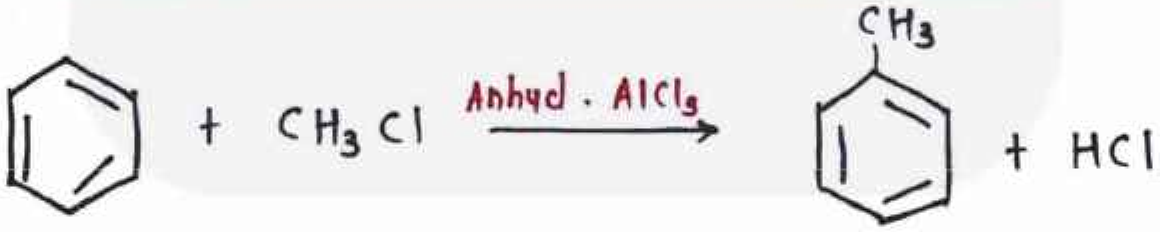
iii) Sulphonation :



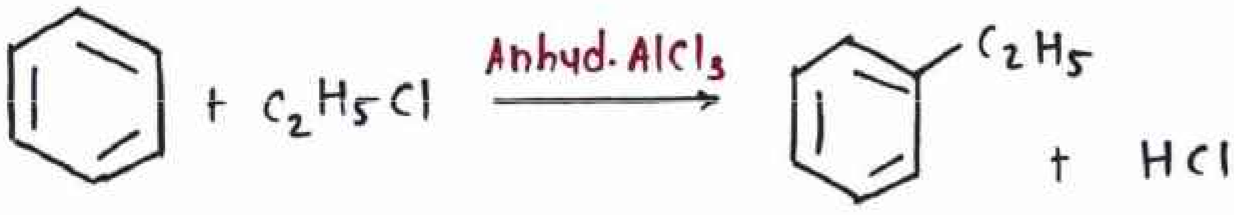
Fuming sulphuric acid

Benzene sulphonic acid

iv) Friedal - crafts alkylation reaction :

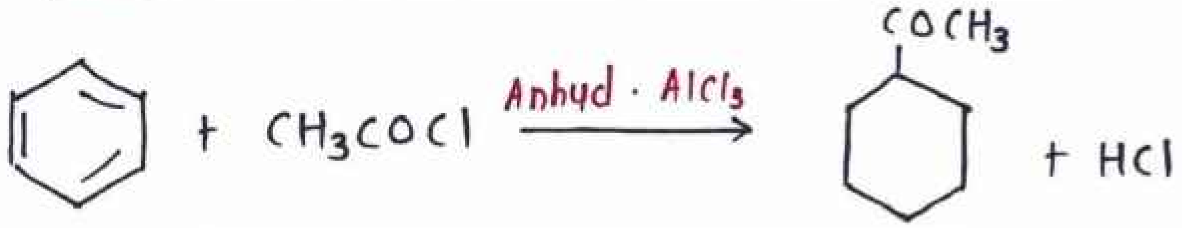


Toluene



Ethyl Benzene

v) Friedel - crafts acylation reaction:



Acetylchloride Acetophenone

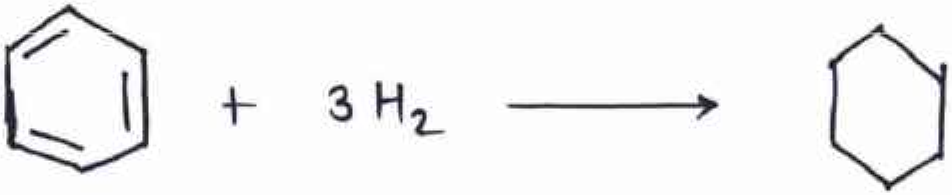
mechanism of electrophilic substitution reaction:

(a) Generation of the electrophile

(b) Formation of carbocation intermediate

(c) Removal of proton from the carbocation intermediate.

Addition reaction:



Cyclohexane

Directive influence of a functional group in monosubstituted benzene.

- **Activating groups:** These groups activates the benzene ring for the attack by an electro phile. Example: $-OH$, $-NH_2$, etc.

- **Deactivating groups:** Due to the deactivating group because of strong -I effect, overall electron density on benzene ring decreases. It makes further substitution difficult.

- **metadirecting group:** The group which direct the group incoming to meta position are called meta directing groups.

examples: $-NO_2$, $-CN$, $-CHO$ etc.

carcinogenicity and Toxicity

Benzene and polynuclear hydrocarbons containing more than two benzene rings fused together are toxic and said to possess cancer producing property.