Hydrocarbons

ALKANES   Section - 1

Hydrocarbons are the binary compounds of carbon and hydrogen only. Hydrocarbons occur in nature in the form of coal, natural gas and petroleum. All the organic compounds (other than hydrocarbons) are derived from hydrocarbons, by substituting hydrogen with a functional group or by adding a functional group. Hydrocarbons are classified into two categories: Aliphatic hydrocarbons (open chains) and Cyclic hydrocarbons (closed chains). Here, we will first study aliphatic type, which are further divided into Saturated hydrocarbons (Alkanes) and Unsaturated hydrocarbons (Alkenes, Alkynes), and then cyclic hydrocarbons, which are further divided into Cycloalkanes, Cycloalkenes and Aromatic Hydrocarbons.
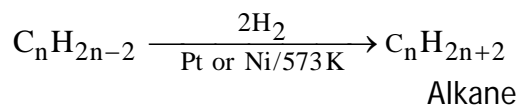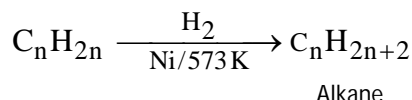
ALKANES : [C_nH_{2n+2}]

Alkanes form a homologous series, represented by a general formula : C_nH_{2n+2}. These have a tetrahedral structure around carbon atom or one can say that all the carbon atoms in alkanes show sp^3 type of hybridisation. The important members of alkanes are: Methane (CH_4), Ethane (CH_3CH_3), Propane ($CH_3CH_2CH_3$), n-Butane ($CH_3CH_2CH_2CH_3$) and its isomer, Iso-butane $\left(\begin{array}{c} CH_3 - CH - CH_3 \\ | \\ CH_3 \end{array} \right)$.

Generally, alkanes are also represented as : RH, RCH_3, R-R, R-R' (where R and R′ are alkyl radical)

Preparation of Alkanes :

1.   **Reduction of Alkenes and Alkynes :**

$$C_nH_{2n} \xrightarrow[\text{Ni/573 K}]{H_2} C_nH_{2n+2}$$
$$\text{Alkane}$$

$$C_nH_{2n-2} \xrightarrow[\text{Pt or Ni/573 K}]{2H_2} C_nH_{2n+2}$$
$$\text{Alkane}$$

This is known as Sabatatier-Sandern's reaction.

Note :   For the reduction of alkenes, and alkynes Pd – carbon/Ethanol at 25°C (50 atm) is generally used.

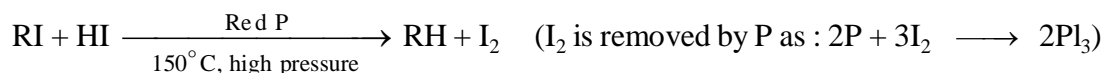$$\left(CH_3\right)_2 - C = CH_2 \xrightarrow[25°C, \text{ 50 atm}]{Pd-C/C_2H_5OH} \left(CH_3\right)_2 CHCH_3$$
$$\text{Isobutane}$$
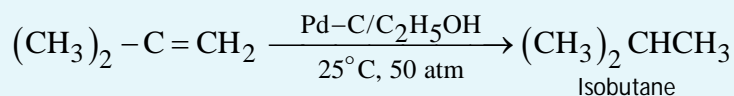
2. From Alkyl Halides :

(a)   By reducing Alkyl Halides :

Reducing agents : $Zn + CH_3COOH$; $Zn + HCl$; $Zn + NaOH$; $Zn–Cu$ Couple ; $Al – Hg$ amalgam.

$$RX + H_2 \longrightarrow RH + HX$$
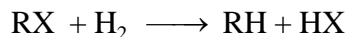
Alkyl iodides are reduced by HI in red P under high temperature and pressure.

$$RI + HI \xrightarrow[150°C,\ high\ pressure]{Red\ P} RH + I_2 \quad (I_2 \text{ is removed by P as : } 2P + 3I_2 \longrightarrow 2PI_3)$$

(b)   Wurtz Reaction :

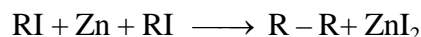It involves the condensation of two molecules of alkyl halide with Na and dry ether, to give symmetric alkanes

$$2RI + Na \xrightarrow[ether]{dry} R – R + NaI$$
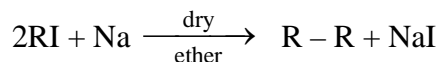
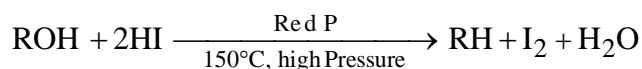If we start with R'I and RI, we get mixture of alkanes. Hence it is not good method for unsymmetric alkanes.

Note :   Methane cannot be formed by this method.

Order of reactivity of alkyl halides $RI > RBr > RCl > RF$.

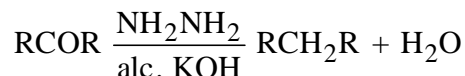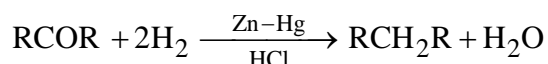### (c)   Frankland Reaction :

$$RI + Zn + RI \longrightarrow R – R + ZnI_2$$

3. Reduction of Alcohols :

$$ROH + 2HI \xrightarrow[150°C,\ high\ Pressure]{Red\ P} RH + I_2 + H_2O$$

4. Reduction of Aldehyde and Ketones :

$$RCHO + 2H_2 \xrightarrow[HCl]{Zn–Hg} RCH_3 + H_2O$$

$$RCH \frac{NH_2NH_2}{alc.\ KOH} RCH_3 + H_2O$$

$$RCOR + 2H_2 \xrightarrow[HCl]{Zn–Hg} RCH_2R + H_2O$$

$$RCOR \frac{NH_2NH_2}{alc.\ KOH} RCH_2R + H_2O$$
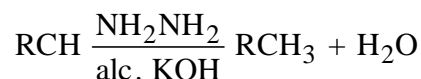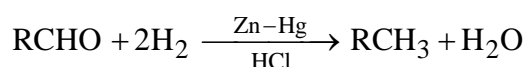
This is known as Clemmensen's Reduction.   This know as Woff-Kishner's Reduction.

5. From Carboxylic Acids :

(a)   Reduction :

$$RCOOH + 6HI \xrightarrow{Red\ P} RCH_3 + 2H_2O + 3I_2$$

(b)   **Decarboxylation :**

It is obtained by heating sodium salts of carboxylic acids with sodalime (NaOH - CaO).

$$RCOONa + NaOH \xrightarrow[\Delta]{CaO} RH + Na_2CO_3$$
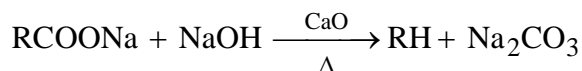
Note : In the product there is one carbon less than parent compound. So this reaction is an important method to reduce a carbon atom in organic synthesis (known as Step-down method).
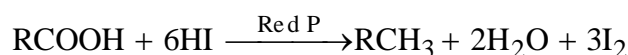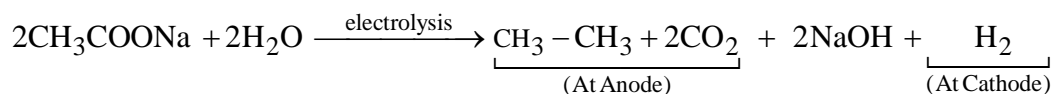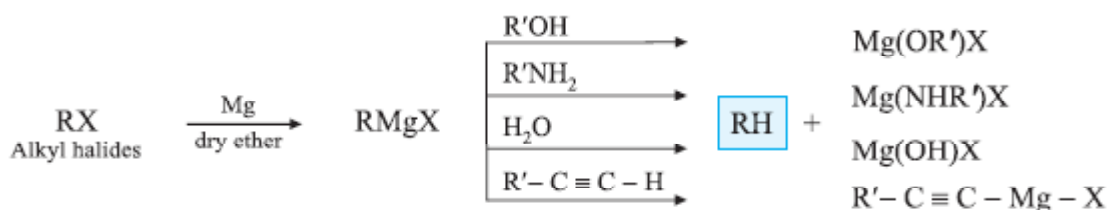
(c)   **Kolbe's Electrolysis :**

$$2CH_3COONa + 2H_2O \xrightarrow{electrolysis} \underbrace{CH_3 - CH_3 + 2CO_2}_{(At\,Anode)} + 2NaOH + \underbrace{H_2}_{(At\,Cathode)}$$

6.   **From Grignard Reagent** (Alkyl magnesium halides, RMgX) :

Note : Any copound having acidic H atom(s), decomposes Grignard reagent.

7.   **By action of water on Aluminium and Beryllium Carbide** :

$$Al_4C_3 + 12H_2O \longrightarrow 3CH_4 + 4Al(OH)_3$$

$$Be_2C + 4H_2O \longrightarrow CH_4 + 2Be(OH)_2$$
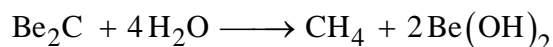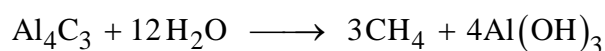
Note : Only Methane is formed by this reaction.

8.   **Through formation of Lithium Dialkycuprates :**

$$RX + 2Li \xrightarrow[ether]{diethyl} RLi + LiX$$

$$2RLi + CuI \longrightarrow \underset{\substack{Lithium\,diakyl\\cuprate\\[Gilman's\,Reagent]}}{R_2CuLi} + LiI$$

$$R_2CuLi + R'X \longrightarrow R—R' + RCu + LiX$$
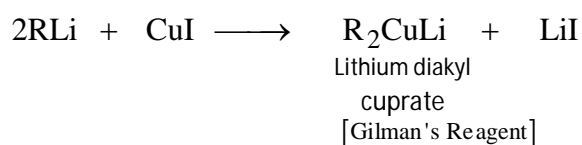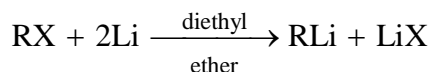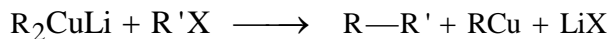
This is known as Corey House Synthesis

Note : **(i)** R can be 1°, 2°, 3° alkyl or aromatic group.

(ii) R′ should be 1° alkyl or 2° cycloalkyl group or even aromatic group.

Physical Properties of Alkanes :

The physical properties of alkanes such as boiling point, density and solubility depend upon the intermolecular forces of attraction. The magnitude of these forces of attraction depend upon the surface area of contact between adjacent molecules. Greater the surfae area, stronger are the forces of attraction.

1. **Physical State :** The normal alkanes C_1 to C_4 are colourless gases, C_5 to C_{17} are colourless liquids and from C_{18} onwards are colourless waxy solids.

2. **Boiling Point :** The boiling points of the unbranched alkanes show a regular increase with increasing molecular weight. The increase is by $20 – 30°C$ for each $–CH_2$ unit added to the chain. Branching of the alkane chain, however, lowers the boiling point.

|		
$CH_3CH_2CH_2CH_2 -CH_3$	$\underset{\overset{\vert}{CH_3}}{CH_3 – CH – CH_2CH_3}$	$CH_3 – \underset{\overset{\overset{\displaystyle CH_3}{\vert}}{\underset{\vert}{CH_3}}}{C} – CH_3$
n-Pentane	Isopentane	Neopentane
B.P. = 309 K	B.P. = 301 K	B.P. = 282.5 K

The explanation for these effects lies in the vander waals forces. With unbranched alkanes, as molecular weight increases, so does molecular surface areas. With increasing surface area, the van der Waals forces between molecules increase, therefore more energy is required to separate molecule from one another. Branching in the chain, on the other hand, makes a molecule more compact, reducing its surface area. As a result, the strength of the van der waals forces operating between the molecules decreases. This results in the lowering the boiling point.(Observe the boiling points of isomericpentanes above)

3. **Melting point :** The melting points of alkanes do not follow a very smooth gradation with the increase of molecular size. Alkanes with even number of carbon atoms have higher melting point than the next lower and next higher alkanes having odd number of carbon atoms.
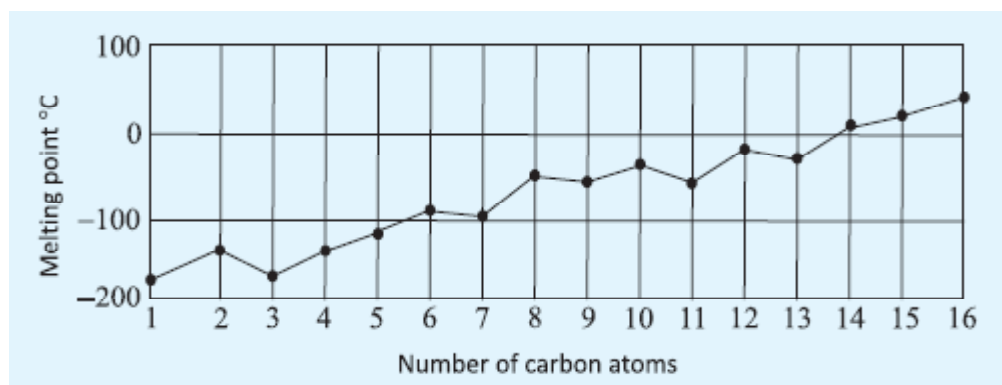
It is explained by the fact that alkanes with an odd number of carbon atoms have their end-carbon atoms on the same side of the molecule and the even numbered carbon atoms alkanes have their end-carbon atoms on the opposite sides of the molecules. Thus, alkanes with even number of carbon atoms pack closely in such a manner as to permit greater inter molecular attraction and therefore have slightly higher melting point.
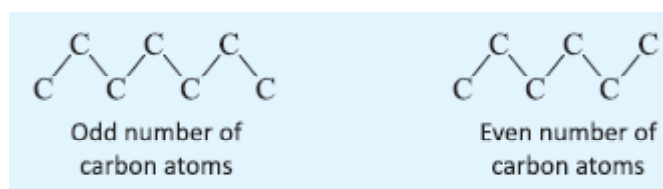
The more compact molecule, the more is the packing efficiency of a molecular solid. This results in higher melting point. For example, neopentane when packed (in solid form) has a higher melting point as compared to n-pentane (less effective packing due to open chain structure).

Name	Formula	B.P. (K)	M.P. (K)	Density (as liquids)
Methane	CH_4	111.0	90.5	0.4240
Ethane	CH_3CH_4	184.4	101.0	0.5462
Propane	$CH_3CH_2CH_3$	230.9	85.3	0.5824
n-Butane	$CH_3(CH_3)_2CH_3$	272.4	134.6	0.5788
Isobutane	$\left(CH_3\right)_2 CH-CH_3$	261.0	114.7	-
n-Pentane	$CH_3(CH_2)_3CH_3$	309.1	143.3	0.6264
Isopentane	$\left(CH_3\right)_2 CH-CH_2-CH_3$	300.9	113.1	-
Neopentane	$\left(CH_3\right)_3 C-CH_3$	282.5	256.4	-

3. **Solubility :** 'Like dissolves like' is the general rule of solubility. In the light of this rule, alkanes which are predominantly non-polar are insoluble in polar solvents such as water, alcohol, etc. but are highly soluble in non-polar solvents such as Petroleum either, Benzene, Carbon tetrachloride, etc.

4. **Density :** The density of alkanes increases with the increase in the molecular masses till the limiting value of about 0.8 g cm^{-3} is reached. This means that all alkanes are lighter than water.

Reaction of Alkanes :

Alkanes being saturated compounds undergo only substitution reactions, at $C-H$ bond. The hydrogen atom is replaced by other atom(s) such as : X-(halogens), NO_2 (nitro), etc.

1. **Halogenation :**

    Replacement of H-atom by X-atom (X = Cl, Br, I) in presence of UV light. The substitution reaction is explained by free radical mechanism.

$$CH_4 \xrightarrow{Cl_2/h\nu} CH_3Cl \xrightarrow{Cl_2/h\nu} CH_2Cl_2 \xrightarrow{Cl_2/h\nu} CHCl_3 \xrightarrow{Cl_2/h\nu} CCl_4$$

The bromination is same as chlorination but it is relatively slow and high temperature favours it.

The iodination is reversible reaction : $CH_4 + I_2 \rightleftharpoons CH_3I + HI$

Note :   HI is a reducing agent, so oxidising agents, such as HIO_3, HNO_3, HgO are used to oxidise HI.

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

Fluorination of alkanes is too vigorous to be controlled under ordinary conditions. Further-more, fluorination brings about extensive rupture of $C-C$ and $C-H$ bonds leading to a mixture of product. Alkyl fluorides are more conveniently prepared indirectly by heating suitable chloroalkanes with inorganic fluorides such as AsF_3, SbF_3, AgF, HgF_2 etc. For example,

$$2 CH_3CH_2 - Cl + Hg_2F_2 \longrightarrow 2 CH_3CH_2 - F + HgCl_2$$
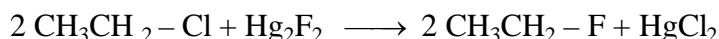
The above reaction is known as *Swarts reaction.*

Ease of halogenation : $3° H > 2°H > 1°H > CH_4$
Reactivity of X_2 : $F_2 > Cl_2 > Br_2 > I_2$

The reactivity decreases with the electronegativity of the halogens.

Consider halogenation in Isobutane.

$$CH_3 - CH - CH_3 \xrightarrow[25°C]{Cl_2, h\nu} CH_3 - CH - CH_2Cl + CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{Cl}{|}}{C}} - CH_3$$
$$\underset{CH_3}{|} \qquad\qquad \underset{\underset{(63\%)}{CH_3}}{|} \qquad \underset{(37\%)}{}$$

$$CH_3 - CH - CH_3 \xrightarrow[127°C]{Br_2} CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}} - CH_3$$
$$\underset{CH_3}{|} \qquad\qquad \underset{(99\%)}{}$$
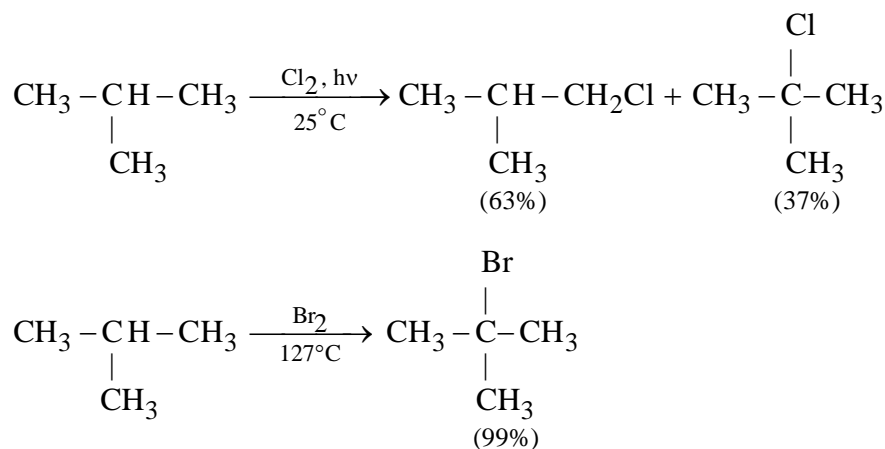
The above reactions show that Bromine is *less reactive* toward alkanes (in general) than chlorine. But bromine shows greater ability to identify among different types of hydrogen atom (i.e., primary, secondary and tertiary). It gives exclusive replacement of tertiary hydrogen atom. Chlorine, on the other hand is less selective than Bromine. Fluorine is even *less selective* than Chlorine and gives equal percentage of substituted products. (*We will discuss mechanism of this reaction later*)

Note: ➤ Laboratory chlorination of alkanes is often done with SO_2Cl_2 (sulphuryl chloride), instead of Cl_2 and an organic perioxide, ROOR is used as an indicator.

➤ During monchlorination, number of monochlorinated products formed are equal to number of different types of hydrogen atoms in the alkane.

2. Nitration:

Lower members do not react with conc. HNO_3 at ordinary temperatures but long chain members on heating with HNO_3 yield nitro-alkanes.

$$\underset{\text{(vapour)}}{C_6H_{13} - H} + HONO_2 \xrightarrow{400°C} C_6H_{13}NO_2 + H_2O$$
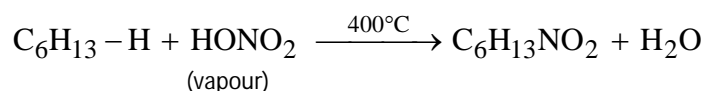
However, when a mixture of vapour of an alkane and nitric acid is heated at 400 - 450°C, nitroalkane is formed readily. By this process lower as well as higher alkanes can be converted into nitroalkanes.

$$\underbrace{CH_3 - H + HONO_2}_{\text{(vapour)}} \xrightarrow{450°C} CH_3NO_2 + H_2O$$
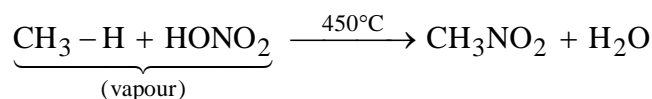
In alkanes having two or more carbon atoms, there is always a possibility that the C - C bonds may break at high temperature and a mixture of nitro alkanes is formed.

$$CH_3CH_2CH_3 \xrightarrow[400°C]{HNO_3} CH_3CH_2CH_2NO_2 + CH_3 - \underset{\underset{NO_2}{|}}{CH} - CH_3 + CH_3CH_2NO_2 + CH_3NO_2$$
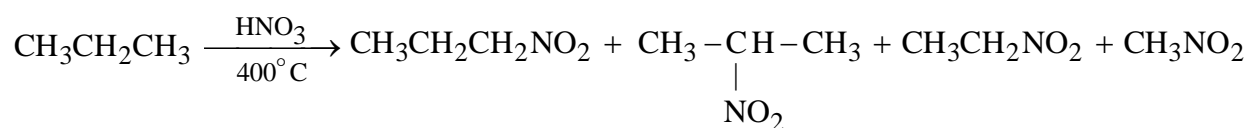
3.   Sulphonation :

Lower alkanes do not undergo sulphonation but higher member (from hexane onwards) are sulphonated slowly when treated with fuming sulphuric acid at about 400°C.
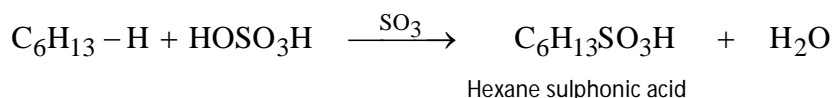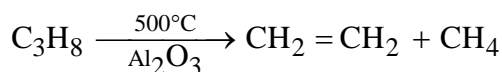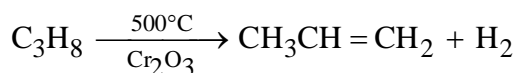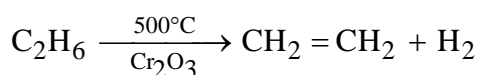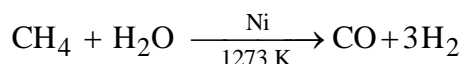
$$C_6H_{13} - H + HOSO_3H \xrightarrow{SO_3} C_6H_{13}SO_3H + H_2O$$

Hexane sulphonic acid

However lower members such as Propane, Butane, Pentane, etc., react with SO_3 in vapour phase to form Sulphonic acids.

4.   Cracking : (Pyrolysis)

The decomposition of a compound by heat is called pyrolysis. The alkanes, on heating under high temperature in absence of air, are broken down into lower alkanes, alkenes and hydrogen during cracking of alkanes, either rupture of carbon-hydrogen bonds or rupture of carbon-carbon bonds take place resulting in the formation of mixture of lower alkanes, alkenes and hydrogen. The rupture of $C - H$ bonds is catalysed by oxide of Chromium, Vandium, Molybednum, etc., and the rupture of $C - C$ bonds is catalysed by Silica, Alumina, Zinc oxide, etc.

$$C_2H_6 \xrightarrow[Cr_2O_3]{500°C} CH_2 = CH_2 + H_2$$

$$C_3H_8 \xrightarrow[Cr_2O_3]{500°C} CH_3CH = CH_2 + H_2$$

$$C_3H_8 \xrightarrow[Al_2O_3]{500°C} CH_2 = CH_2 + CH_4$$

5.   Reaction with Steam :

$$CH_4 + H_2O \xrightarrow[1273\ K]{Ni} CO + 3H_2$$

6.   Combustion :

(a)   Complete Combustion :

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

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)\ H_2O + heat$$
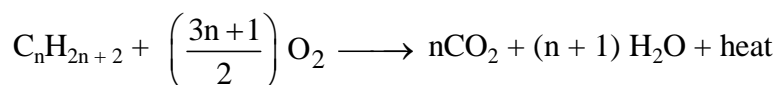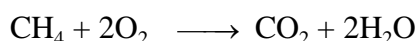
Note :   Enthalpy of combustion increases with increase in number of carbon atoms in alkane. For isomeric alkane, enthalpy of combustion decreases with increase in branching

(b)   **Incomplete Combustion :** If the combustion of alkanes is carried out in limited supply of air or oxygen, CO is produced along with unburnt carbon in the form of carbon black or soot.

$$2CH_4 \ + \ 3O_2 \ \longrightarrow \ 2CO + 4H_2O$$
$$\text{(limited)}$$

$$CH_4 \ + \ O_2 \ \longrightarrow \ \underset{\text{Carbonblack}}{C} \ + \ H_2O$$
$$\text{(limited)}$$

Carbon black is used in the preparation of black inks, paints, polishes etc.

(c)   **Catalyst Oxidation :** Different prodcuts are formed under different conditions.

(i)   When a mixture of methane and oxygen (9 : 1 by volume) at a pressure of 100 atm. is passed through a copper tube at 573 K, methanol is formed.

$$\underset{\text{Methane}}{2CH_4} \ + \ O_2 \ \xrightarrow[\text{Cu tube}]{\text{100 atm. 573 K}} \ \underset{\text{Methanol}}{2CH_3OH}$$

(ii)   When a mixture of methane and oxygen under pressure is passed over heated molybdenum oxide, it is oxidised to methanal.

$$\underset{\text{Methane}}{CH_4} \ + \ O_2 \ \xrightarrow[\Delta,\ \text{pressure}]{Mo_2O_3} \underset{\text{Methanal}}{HCHO} \ + \ H_2O$$

(iii)   Higher alkanes on oxidation in presence of silver oxide give carboxylic acids.

$$\underset{\text{Alkane}}{2\,R-CH_3} + 3O_2 \ \xrightarrow[\Delta]{Ag_2O} \ \underset{\text{Carboxylic acid}}{2\,RCOOH} \ + \ 2\,H_2O$$

(iv)   In presence of oxidising agents such as $KMnO_4$, $K_2Cr_2O_7$ etc.

$$\underset{\text{Isobutane}}{\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{CH_3-\overset{|}{\underset{|}{C}}-H}}} + (O) \ \xrightarrow[KMnO_4]{\text{alk.}} \ \underset{\text{tert-Butyl alcohol}}{\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{CH_3-\overset{|}{\underset{|}{C}}-OH}}}$$

7.   Aromatisation :

$$CH_3-\left(CH_2\right)_4-CH_3 \ \xrightarrow[600^{\circ}C/15\,atm]{Cr_2O_3-Al_2O_3} \ C_6H_6 \text{ (Benzene)} + 4H_2$$

8. Isomerization :

When n-alkanes are heated with anhydrous aluminium chloride and hydrogen chloride at 573 K under a pressure of about 35 atm, they are converted into branched chain alkanes. For example,
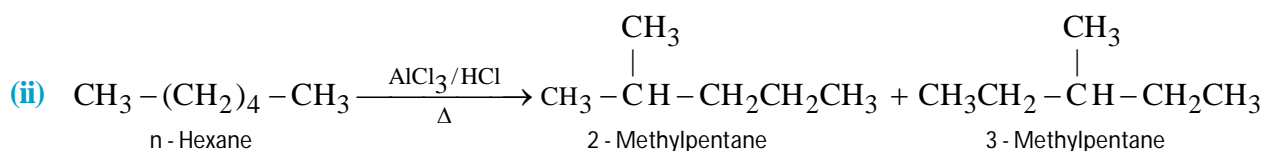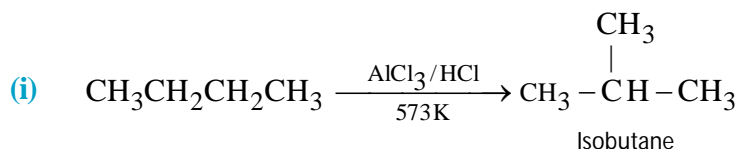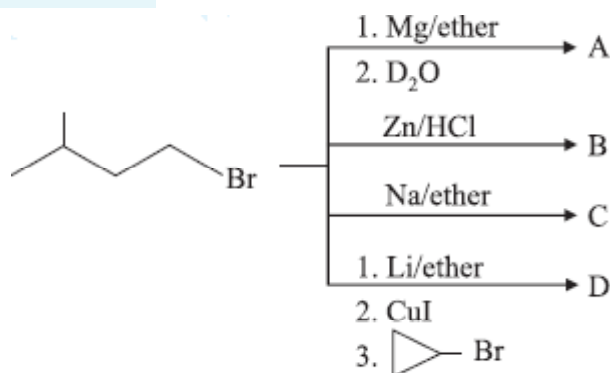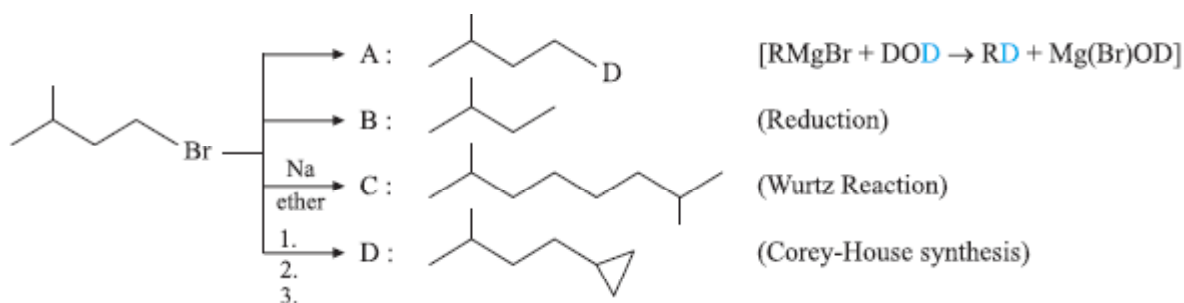
(i) $CH_3CH_2CH_2CH_3 \xrightarrow[573K]{AlCl_3/HCl} CH_3-\underset{\underset{CH_3}{|}}{C}H-CH_3$

Isobutane

(ii) $CH_3-(CH_2)_4-CH_3 \xrightarrow[\Delta]{AlCl_3/HCl} CH_3-\underset{\underset{CH_3}{|}}{C}H-CH_2CH_2CH_3 + CH_3CH_2-\underset{\underset{CH_3}{|}}{C}H-CH_2CH_3$

n - Hexane   2 - Methylpentane   3 - Methylpentane

Illustration - 1   *Identify A, B, C, D.*

1. Mg/ether
2. D$_2$O → A

Zn/HCl → B

Na/ether → C

1. Li/ether
2. CuI
3. ▷— Br → D

SOLUTION :

A : [RMgBr + DOD → RD + Mg(Br)OD]

B : (Reduction)

C : (Wurtz Reaction)

D : (Corey-House synthesis)

NOW ATTEMPT IN-CHAPTER EXERCISE-A BEFORE PROCEEDING AHEAD IN THIS EBOOK

ALKENES : $[C_nH_{2n}]$ Section - 2

Alkenes form a homologous series, represented by a general formula : C_nH_{2n}. These have one C=C bond or one can say that two carbon atoms (adjacent) in alkenes show sp^2 type of hybridisation. The important members of alkenes are: Ethene ($CH_2 = CH_2$), Propene ($CH_3 CH = CH_2$), 1-Butene ($CH_3CH_2CH = CH_3$)

and its isomers, 2-Butene ($CH_3CH = CHCH_3$) and Iso-butene $\begin{pmatrix} CH_3 - C = CH_2 \\ | \\ CH_3 \end{pmatrix}$.

Generally, alkenes are also represented as :

1.   Terminal alkenes $RCH = CH_2, R_2C = CH_2$

2.   Non-terminal alkenes $RCH = CHR, R_2C = CHR, R_2C = CR_2$ (where R : alkyl radical)

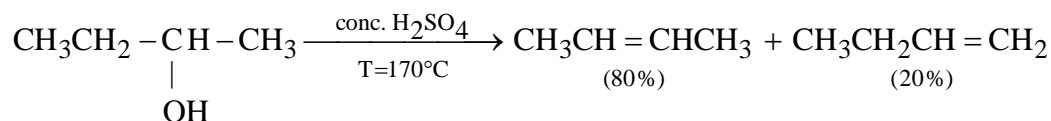### Preparation of Alkenes :

1.   Dehydration of Alcohols :

The dehydration of alcohols is generally carried out in either of two ways :

(a)   Heating the alcohol with conc. H_2SO_4 or H_3PO_3 to temperature as high as 170°C.

(b)   Passing the vapours of alcohol over alumina (Al_2O_3) at 350 – 400°C.

$$RCH_2CH_2OH \longrightarrow RCH = CH_2 \text{ (alkene)} + H_2O$$

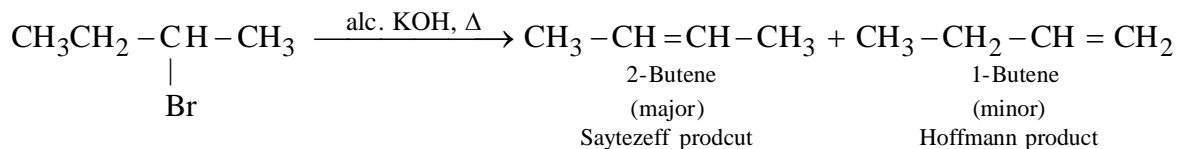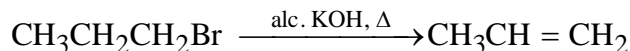Ease of dehydration is 3° alcohol > 2° alcohol > 1° alcohol.

Dehydration is governed by Saytzeff or Zaitsev rule i.e., the greater is number of alkyl groups attached to doubly bonded 'C' atoms, the more stable is the alkene.

$$CH_3CH_2 - \underset{\underset{OH}{|}}{C}H - CH_3 \xrightarrow[T=170°C]{conc. H_2SO_4} \underset{(80\%)}{CH_3CH = CHCH_3} + \underset{(20\%)}{CH_3CH_2CH = CH_2}$$

Order of Stability : $R_2C = CR_2 > R_2C = CHR > R_2C = CH_2 > RCH = CHR > RCH = CH_2 > CH_2 = CH_2$

Note :   If there are two geometric isomers, i.e., *cis* and *trans* isomers, then it is the trans isomer which is more stable than the *cis* one.
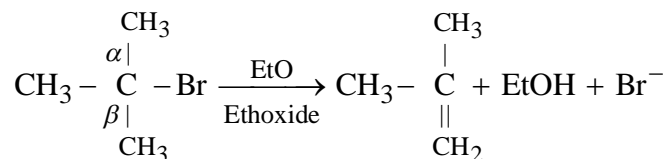
2. **Dehydrohalogenation of Alkyl Halides :**

$$CH_3CH_2CH_2Br \xrightarrow{\text{alc. KOH, } \Delta} CH_3CH = CH_2$$

$$CH_3CH_2 - \underset{\underset{Br}{|}}{CH} - CH_3 \xrightarrow{\text{alc. KOH, } \Delta} CH_3 - CH = CH - CH_3 + CH_3 - CH_2 - CH = CH_2$$

$$\begin{array}{cc} \text{2-Butene} & \text{1-Butene} \\ \text{(major)} & \text{(minor)} \\ \text{Saytezeff prodcut} & \text{Hoffmann product} \end{array}$$

The formation of less substituted alkene in an elimination reaction is called as a Hoffmann Elimination and that of more substituted alkene as a Zaitsev Elimination or Saytzeff's elimination.

Ease of dehydrohalogenation is in the order : $3°$ alkyl halide $> 2°$ alkyl halide $> 1°$ alkyl halide.

Ease of dehydrohalogenation for different halogens is in the order : Iodine $>$ Bromine $>$ Chlorine.

We can also used alkoxide ion, RO^-, which acts as a strong base. The alkoxide ion abstracts a proton from $\beta - carbon$. Then dehydrohalogenation is known as $\beta - elimination \ or \ 1, 2 - elimination$.
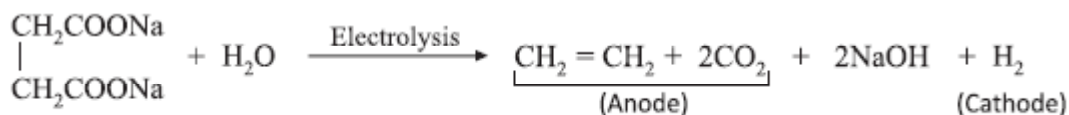
$$CH_3 - \underset{\underset{CH_3}{\overset{\alpha|}{\underset{\beta|}{C}}}}{C} - Br \xrightarrow[\text{Ethoxide}]{EtO} CH_3 - \underset{\underset{CH_2}{||}}{\overset{CH_3}{\overset{|}{C}}} + EtOH + Br^-$$

Note : **(i)** In case of $1°$ RX, alkoxide ($R'O^-$) does nucleophilic substitution of form ethers $[R'-O-R]$.

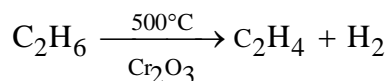**(ii)** By using alc. KOH $[KOH / ROH]$, $1°, 2°, 3°$ alkyl halides give elimination products.

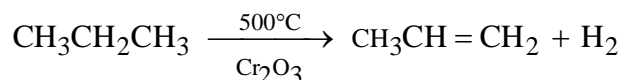**3.** **By dehalogenation of Viccinal Halides :**

$$CH_2BrCH_2Br + Zn \longrightarrow CH_2 = CH_2 + ZnBr_2$$
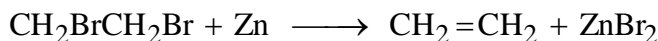
4. **Electrolysis of aqueous solution of sodium salts of dicarboxylic acids :** (only for Ethene)

$$\underset{\underset{CH_2COONa}{|}}{CH_2COONa} + H_2O \xrightarrow{\text{Electrolysis}} \underset{\text{(Anode)}}{\underline{CH_2 = CH_2 + 2CO_2}} + \underset{\text{(Cathode)}}{2NaOH + H_2}$$

5. **Cracking of Alkanes :**

$$C_2H_6 \xrightarrow[Cr_2O_3]{500°C} C_2H_4 + H_2$$

$$CH_3CH_2CH_3 \xrightarrow[Cr_2O_3]{500°C} CH_3CH = CH_2 + H_2$$

6. Partial Hydrogenation of Alkynes :

The hydrogenation of alkynes to an alkene is brought about by the use of special catalysts. This is an example of "Stereospecific reaction".

Note : Reaction that produce a particular stereoismers of the product is called as steroselective reaction.

(a) Using Lindlar catalyst ($Pd/CaCO_3$ or $Pd/BaSO_4$) in quinoline to give a *cis* alkene.

$$R-C \equiv C - R \xrightarrow[quinoline]{H_2,\ Lindlar\ Catalyst} \underset{H}{\overset{R}{>}}C = C\underset{H}{\overset{R}{<}} \quad cis\text{ - alkene}$$
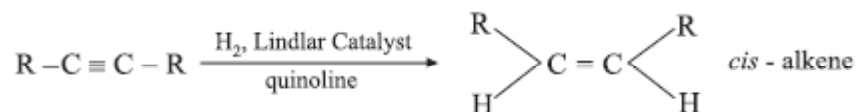
This is also called as *syn* addition, as two H-atoms are added to the same side.

This reaction can also be achieved by using Ni_2B (called as P - 2 catalyst)

$$R - C \equiv C - R \xrightarrow{H_2,\ Ni_2B} \underset{H}{\overset{R}{>}}C = C\underset{H}{\overset{R}{<}} \quad cis\text{- alkene}$$
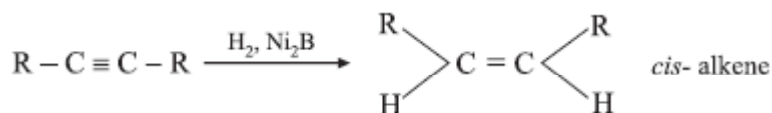
(b) Using Lithium (or Sodium) in NH_3 (or in ethyl amine) at low temperature, gives *trans* alkene.

$$R - C \equiv C - R \xrightarrow[NH_3]{liq.\ Li} \underset{H}{\overset{R}{>}}C = C\underset{R}{\overset{H}{<}} \quad trans\text{ - alkene}$$
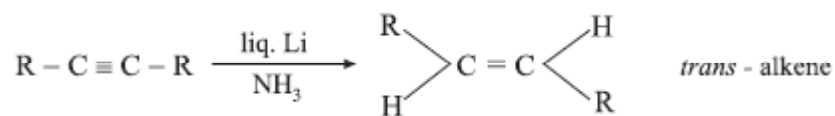
This is also called as *anti* addition, as two H-atoms are added to the opposite side of the bond.

Stability of Alkenes :

The reactivity of different types of alkenes in decreasing order is as follows : (As per heat of hydorgenation)

$$CH_2 = CH_2 > R - CH = CH_2 > R - CH = CH - R > R_2C = CH_2 > R_2C = CHR > R_2C = CR_2$$
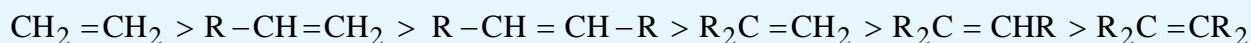
The heat of hydrogenation is always exothermic and experimentally it has been found that :

Stability of alkene $\propto \dfrac{1}{\text{Heat of hydrogenation}}$ (i.e., higher is the heat of hydrogenation, higher is reactivity and lower is the stability of an alkene)

Thus stability of alkenes in decreasing order is as follows:

$$R_2C = CR_2 > R_2C = CHR > R_2C = CH_2 > RCH = CHR > RCH = CH_2 > CH_2 = CH_2$$
$$\text{trans} > \text{cis}$$
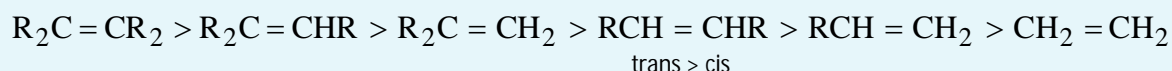
Physical Properties of Alkenes :

1. **Physical state and smell :** The first three members of the family, i.e., Ethene, Propene and Butene are colourless gases. The next eleven members $(C_5 - C_{15})$ are liquids while the higher ones are solids. Except Ethene which has a pleasant smell, all other alkenes are odourless.

2. **Melting points :** The melting points of alkenes do not show regular gradation. However, the melting points of alkenes are higher than those of the corresponding alkenes.

    Amongst isomer of alkenes, trans-alkenes have higher melting points than their corresponding cis-isomers.

3. **Boiling points :** The boiling points of alkenes, like alkanes, show a regular gradation with the increase in the number of carbon atoms. Amongst the alkenes which show geometrical isomerism, *cis*-alkenes have higher boiling points than the corresponding *trans*-isomers. This is due to the reason that *cis*-alkenes being polar have stronger dipole-dipole interactions while *trans*-alkenes being non-polar (or weakly polar) have weak induced dipole interactions.

4. **Solubility :** Alkenes like alkanes being either non-polar or weakly polar molecules are practically insoluble in water and other polar solvents but are quite soluble in non-polar solvents such as benzene, CCl_4, petroleum ether, etc. and weakly polar solvents such as ether.

5. **Density :** The densities of alkenes, like those of alkanes, increase with the increase in molecular mass till they have a limiting value of 0.89 g cm^{-3}. Thus, all alkenes are lighter than water.
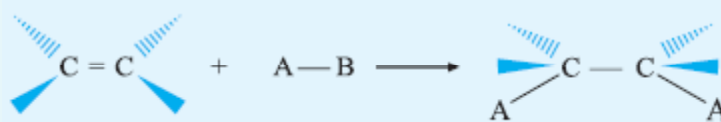
Compound	M.P. (°C)	B.P. (°C)	Density (g/mL)
Ethene	−169	−104	0.384
Propene	−185	−47	0.514
1-Butene	-	−6.3	0.595
cis-2-Butene	−139	3.7	0.621
trans-2-Butene	−106	0.9	0.604
1-Pentene	−165	30	0.641
2-Methyl-1-butene	−138	31	0.650

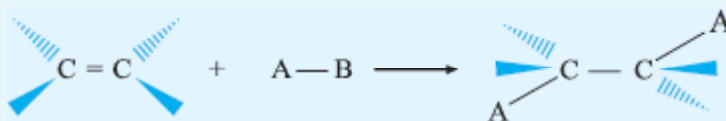## Reaction of Alkenes :

Alkenes undergo mainly addition reactions.
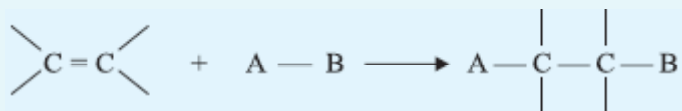
An addition that puts the part of AB on the same face of the reactant is called as *syn addition*.
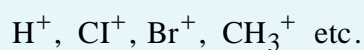

The opposite of *syn-addition* is an *anti-addition*. An anti-addition puts the parts of AB on opposite faces of reactants.


The addition reaction of alkenes are usually electrophilic addition.

Electrophile (E⁺) : An electron loving species looking for electron rich regions such as localised $pi(\pi)$ electron in alkenes and lakynees. Important Electrophiles :
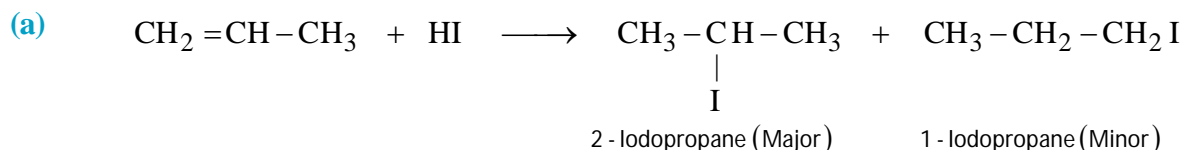
H^+, CI^+, Br^+, CH_3^+ etc.

Nucleophile (Nu) : A nucleus loving (electron rich) species looking to attack the electrophilic sites.

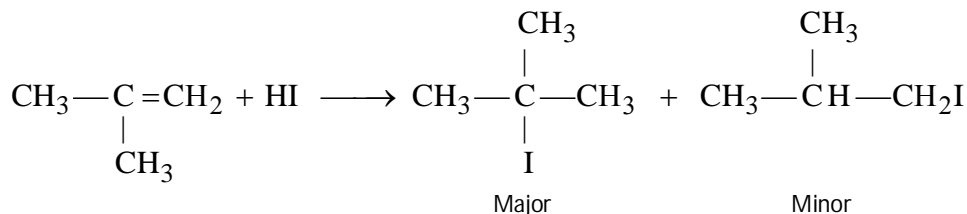Important Nucleophiles : X^-, OH^-, OR^-, CH_3^- etc.
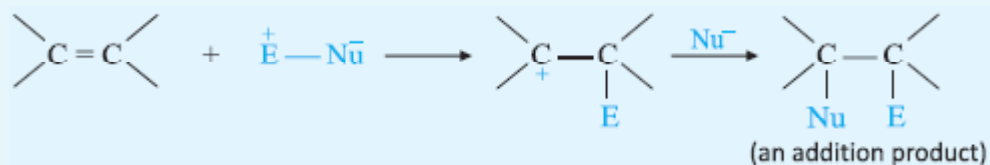
1.   Addition of hydrogen halides (HX) :

The addition of HX to alkene is an electrophilic addition reaction. The reactivity order follows : $HI > HBr > HCl$. The addition follows Markonikov's rule. It states that in the addition of HX to an alkene, the hydrogen atom adds to the carbon atom of the double bond that has the greater number of hydrogen atoms, or the negative part of reagent adds to carbon having less number of hydrogen. The following examples illustrate Markonikov's addition.

(a)

$$CH_2 = CH - CH_3 \ + \ HI \ \longrightarrow \ CH_3 - \underset{\underset{I}{|}}{CH} - CH_3 \ + \ CH_3 - CH_2 - CH_2 I$$

2 - Iodopropane (Major)   1 - Iodopropane (Minor)

(b)   When 2-Methylpropene reacts with HI, the major product is tert.– butyl iodide.

$$CH_3 - \underset{\underset{CH_3}{|}}{C} = CH_2 + HI \ \longrightarrow \ CH_3 - \underset{\underset{I}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3 \ + \ CH_3 - \underset{\overset{CH_3}{|}}{CH} - CH_2 I$$

Major   Minor

Anti Markonikov's addition : When addition of HBr takes place in presence of perioxides (R–O–O–R or benzoyl peroxide), addition occurs in an anti-markonikov's manner, i.e., Br is added to the carbon having large number of H-atom.

$$CH_3 CH = CH_2 + HBr \ \xrightarrow{\ ROOR\ } \ CH_3 CH_2 CH_2 Br$$
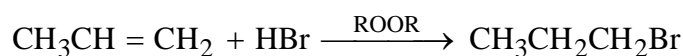
In presence of peroxides, free radical addition occurs in an anti-Markonikov's fashion unlike the electrophillic addition in above case (i.e., Markonikov's addition).
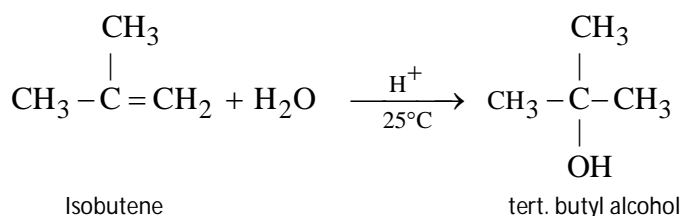

***Note* : (i)**   Addition of HX in cycloalkenes also follows Markonikov's addition.

1-Methylcyclohexene
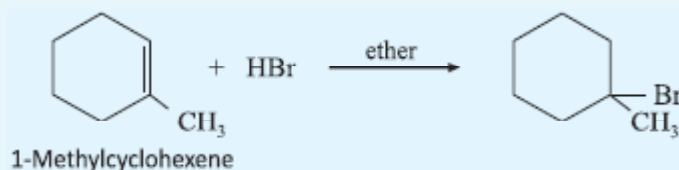
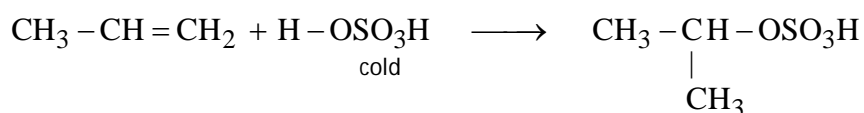**(ii)**   Addition of HCl and HI in presence of perioxide follows Markonikov's rule.

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2. Addition of H_2O :

The acid catalysed addition of H_2O produces alcohols and follows Markonikov's addition. The acids used to catalyse the reaction are H_2SO_4 or H_3PO_4 (phosphoric acid).
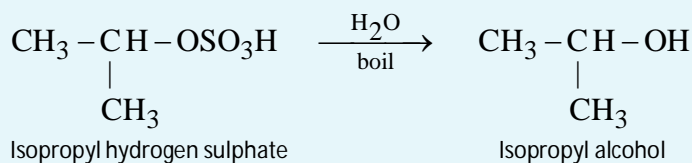
$$\underset{\text{Isobutene}}{CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2} + H_2O \quad \xrightarrow[25°C]{H^+} \quad \underset{\text{tert. butyl alcohol}}{CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}} - CH_3}$$

3. Addition of H_2SO_4 (cold and concentrated) :

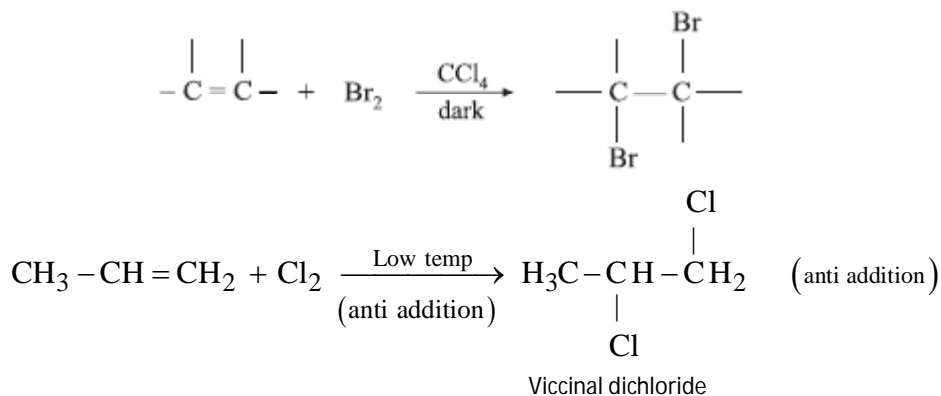Alkene react with cold concentrated H_2SO_4 to give alkyl hydrogen sulphates following Markonikov's addition.

$$CH_3 - CH = CH_2 + \underset{\text{cold}}{H - OSO_3H} \quad \longrightarrow \quad CH_3 - \overset{\overset{\displaystyle }{|}}{\underset{\underset{\displaystyle CH_3}{|}}{CH}} - OSO_3H$$

> **Note :** Alkyl hydrogen sulphates when boiled with water give alcohols. It is an irreversible reaction.
>
> $$\underset{\text{Isopropyl hydrogen sulphate}}{CH_3 - \overset{\overset{\displaystyle }{|}}{\underset{\underset{\displaystyle CH_3}{|}}{CH}} - OSO_3H} \quad \xrightarrow[\text{boil}]{H_2O} \quad \underset{\text{Isopropyl alcohol}}{CH_3 - \overset{\overset{\displaystyle }{|}}{\underset{\underset{\displaystyle CH_3}{|}}{CH}} - OH}$$

4. Addition of Halogens (Cl_2, Br_2, I_2) :

Alkenes decolourises Bromine water (Br_2 in CCl_4) following addition of Br_2 across double bond. This serves as a test of unsaturation. It follows *anti-addition*.
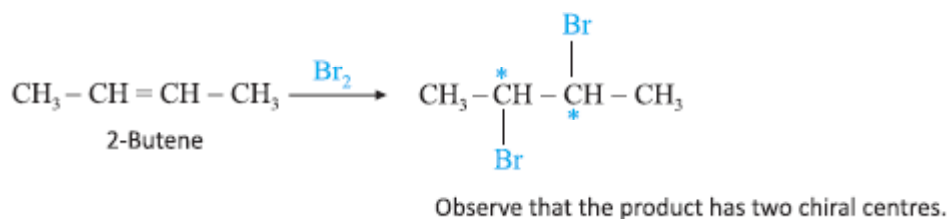
$$-\overset{\overset{\displaystyle |}{}}{C} = \overset{\overset{\displaystyle |}{}}{C} - \ + \ Br_2 \quad \xrightarrow[\text{dark}]{CCl_4} \quad -\overset{\overset{\displaystyle |}{}}{\underset{\underset{\displaystyle Br}{|}}{C}} - \overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle |}{}}{C}} -$$

$$CH_3 - CH = CH_2 + Cl_2 \quad \xrightarrow[\left(\text{anti addition}\right)]{\text{Low temp}} \quad \underset{\text{Viccinal dichloride}}{H_3C - \overset{\overset{\displaystyle }{|}}{\underset{\underset{\displaystyle Cl}{|}}{CH}} - \overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle }{}}{C}H_2}} \quad \left(\text{anti addition}\right)$$

Note : **(i)** The addition of Br_2 to cycloalkenes also follows anti-addition.

Cyclo Hexene   trans-1, 2-dibromocyclohexane
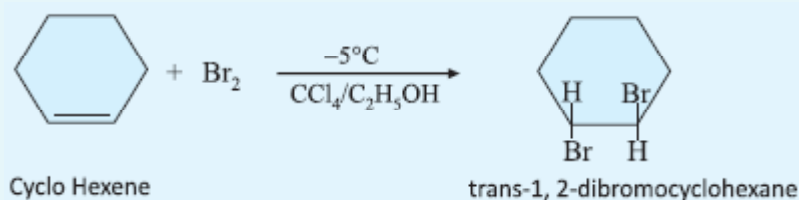
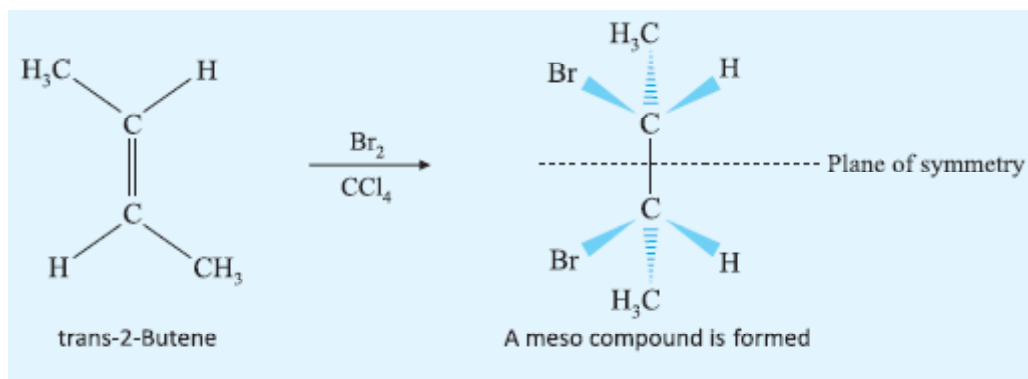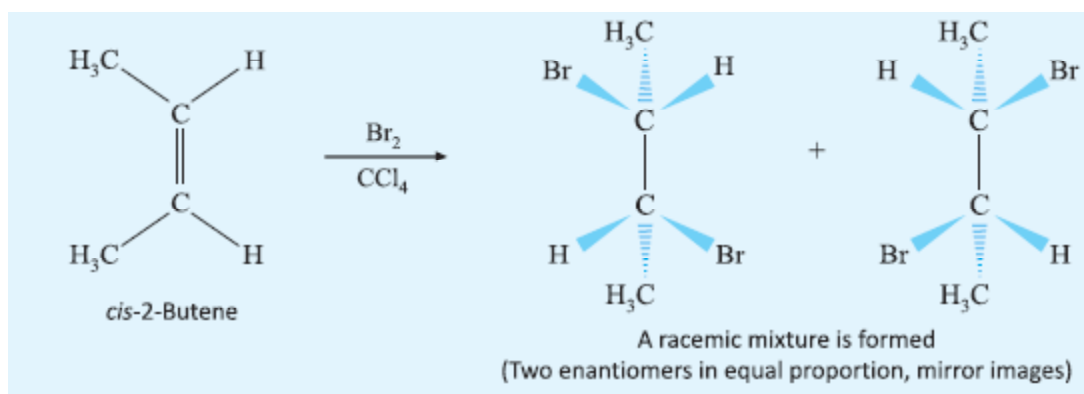**(ii)** The addition of halogens to alkene is an anti-addition and provides an illustration for a stereoselective and stereospecific reaction. For example, cyclohexene gives *trans*-1, 2-Dibromocyclohexane (geometric isomer) is an example of stereoselective reaction. Consider addition of Br_2 to *cis* and *trans*-2- Butenes, which is an example of stereospecific reaction as the reactant (2-Butene) also shows stereochemistry).

Note : The details of reaction mechanisms of all the addition reactions will be discuss later in the Chapter "Organic Concepts".

2-Butene

Observe that the product has two chiral centres.

The above reaction, it is visulised as follows and remember the nature of product(s) : (Refer to the next page)

trans-2-Butene   A meso compound is formed

cis-2-Butene

A racemic mixture is formed
(Two enantiomers in equal proportion, mirror images)

5. **Addition of halogen in aqueous solution :**

When halogens are added in presence of H_2O / THF (tetrahydrofuran) or NBS (N-bromo succinimide), halohydrins are formed.
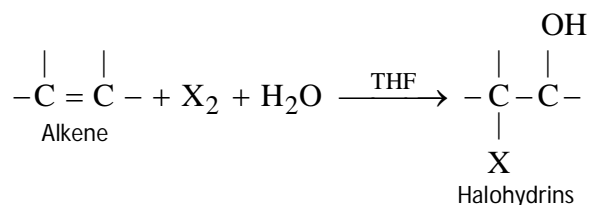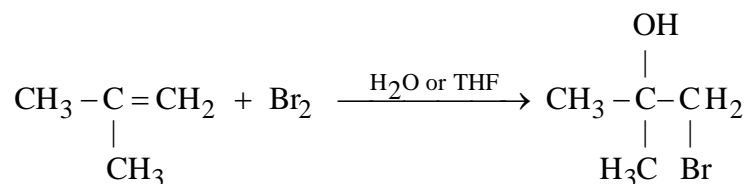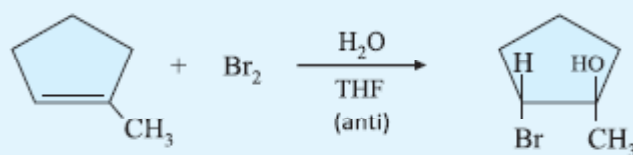

The above reaction follows Markovnikov's rule. It is an *anti-addition* reaction.

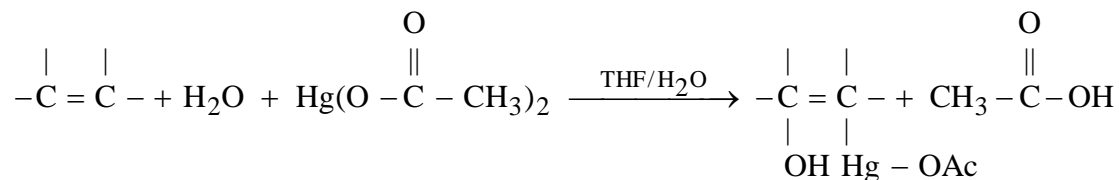*Note* : **(i)**   The cycloalkenes also reacts with aqueous Br_2 to give anti-addition products.
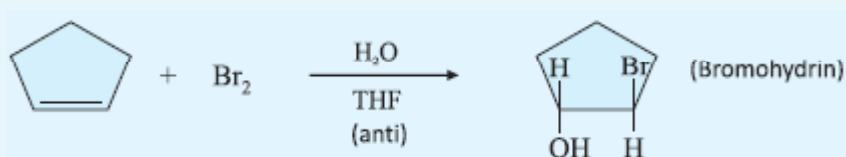
(ii)   In case of unsymmetrical alkene, halogen is added to the carbon atom with greater number of H-atom, (i.e., Markonikov's addition).
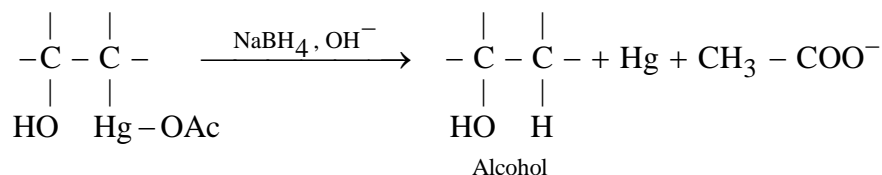
6. Oxymercuration - Demercuration :

An important method of formation of alcohols from alkenes. It occurs in two steps.

(i) Alkenes react with mercuric acetate Hg $(CH_3COO)_2$ or represented as, Hg $(OAc)_2$ in a mixture of THF and water to give a mercury compound.

$$-\overset{|}{C}=\overset{|}{C}- + H_2O + Hg(O-\overset{O}{\overset{||}{C}}-CH_3)_2 \xrightarrow{THF/H_2O} -\overset{|}{\underset{OH}{C}}=\overset{|}{\underset{Hg-OAc}{C}}- + CH_3-\overset{O}{\overset{||}{C}}-OH$$

This step is known as Oxymercuration.

(ii) The mercury compound is reduced to alcohol with sodium borohydride.

$$-\overset{|}{\underset{HO}{C}}-\overset{|}{\underset{Hg-OAc}{C}}- \xrightarrow{NaBH_4, OH^-} -\overset{|}{\underset{HO}{C}}-\overset{|}{\underset{H}{C}}- + Hg + CH_3-COO^-$$
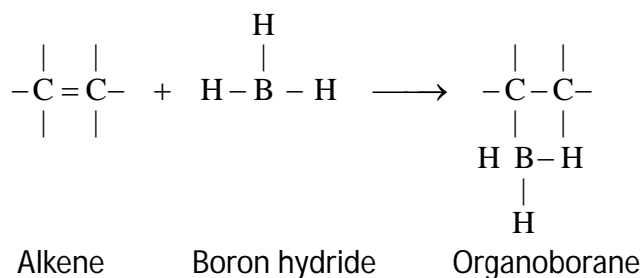
Alcohol

The above reaction occurs in accordance with Markonikov's addition. The 'H' becomes attached to the carbon atom of the double bond with greater number of hydrogen atom.

$$R-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-H \xrightarrow[\text{2. } NaBH_4, OH^-]{\text{1. } Hg(OAc)_2/THF, H_2O} R-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H$$

2° alcohol

$$\xrightarrow[\text{2. } NaBH_4, OH]{\text{1. } Hg(OAc)_2/THF-H_2O}$$

(Markonikov's addition)   1 - Methyl cyclopentanol
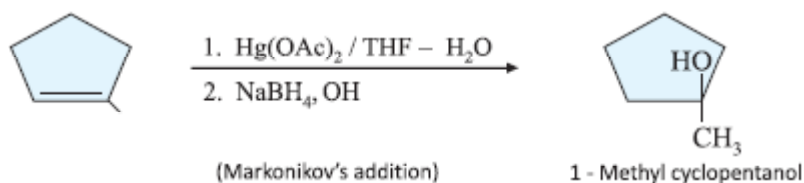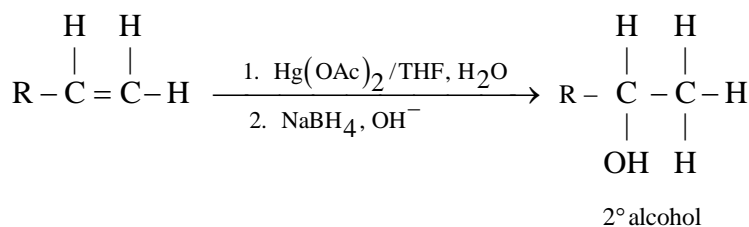
Note : Observe that in the final product, OH comes from H_2O and H comes from $NaBH_4/OH^-$.
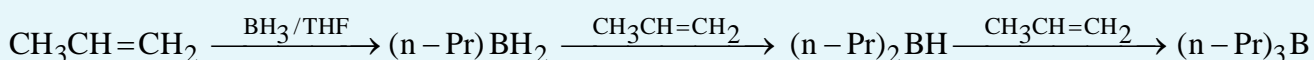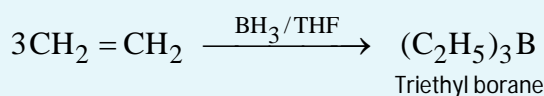
7. Hydroboration - Oxidation :

Hydrocration-oxidation serves as an important method for synthesis of alcohol $(1° \& 2°)$. It can be represented as :
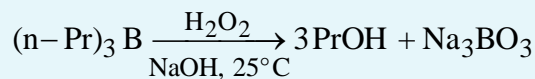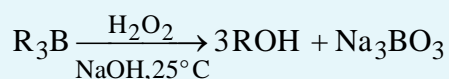
$$-C = C- \quad + \quad H - \overset{\overset{\displaystyle H}{\displaystyle |}}{B} - H \quad \longrightarrow \quad -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$$

Alkene   Boron hydride   Organoborane

Note : **(i)** The addition of boron hydride is syn-addition.

It is generally carried out by BH_3 (boron hydride) B_2H_6 (diborane) in THF.

$$3 CH_2 = CH_2 \xrightarrow{BH_3/THF} \underset{\text{Triethyl borane}}{(C_2H_5)_3 B}$$

$$CH_3 CH = CH_2 \xrightarrow{BH_3/THF} (n-Pr) BH_2 \xrightarrow{CH_3CH=CH_2} (n-Pr)_2 BH \xrightarrow{CH_3CH=CH_2} (n-Pr)_3 B$$

(ii) In each addition, the boron atom becomes attached to the less substituted carbon atom of double bond and H is transferred from boron atom to the other carbon atom of double bond. Thus it follows Anti-Markonikoff's addition.

The organoboranes formed are oxidised and hydrolysed to alcohols by the addition of hydrogen peroxides in an aqueous base.

$$R_3 B \xrightarrow[\text{NaOH,25°C}]{H_2O_2} 3 ROH + Na_3 BO_3 \qquad\qquad (n-Pr)_3 B \xrightarrow[\text{NaOH, 25°C}]{H_2O_2} 3 PrOH + Na_3 BO_3$$

Note that alcohol formed is a primary alcohol (unlike that in Markonikov's addition)

Consisder hydrobration and oxidation in 1-Methyl cyclopentene. It show syn-addition and anti-Markonikov's addition of H₂O to alkene.
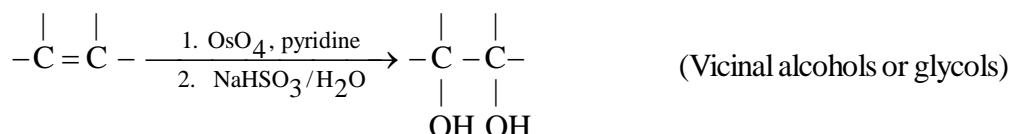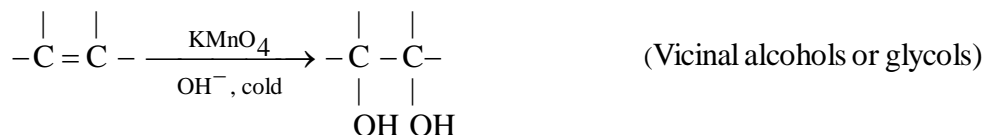
Note : Observe that in the final product, OH comes from H_2O_2/OH^- and H comes from BH_3.

trans - 2 - Methyl cyclopentanol

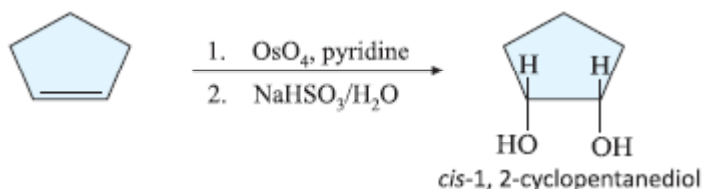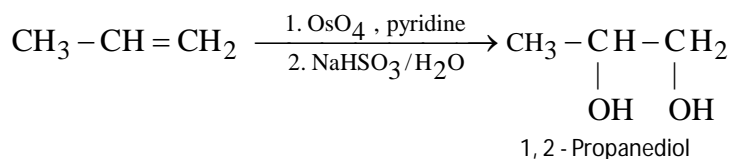2-Methyl-2-butene   Anti-Markonikov's addition of H₂O
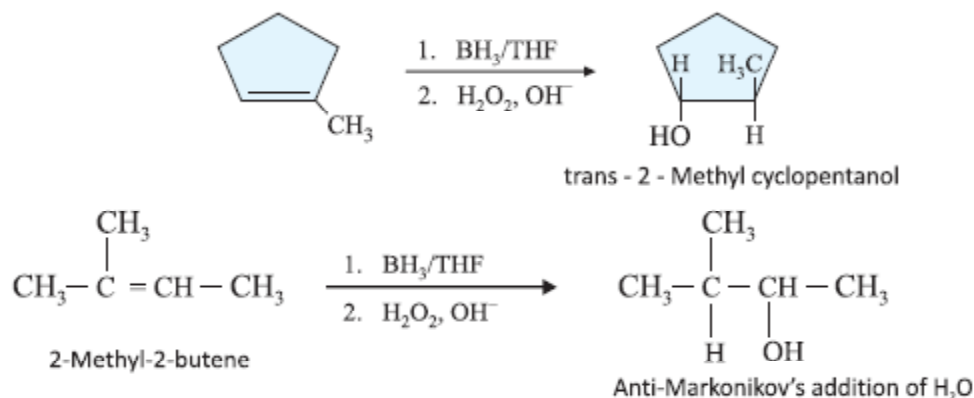
Note : Compare the alcohols formed above with those formed by Oxymercuration-Demercuration.

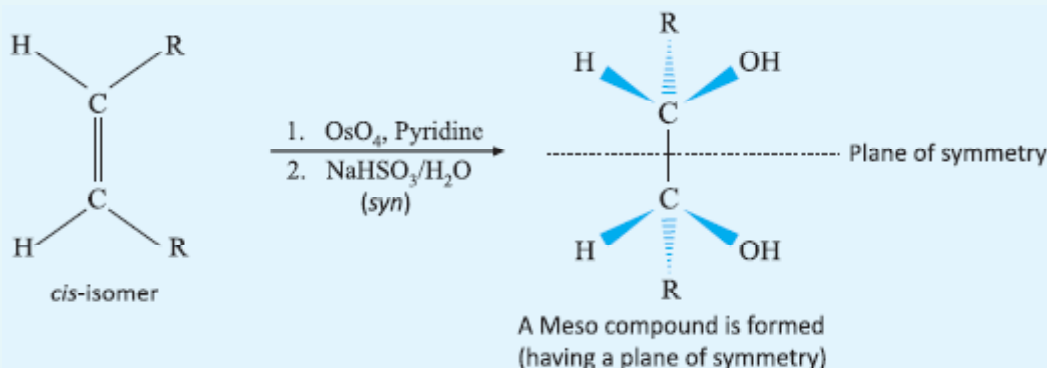## 8. Hydroxylation of alkenes (Oxidation by cold alkaline KMnO$_4$) :

The hydroxylation of alkene is brought about by alkaline KMnO$_4$ or osmium tetraoxide (OsO$_4$) to give 1, 2-diols (or glycols).
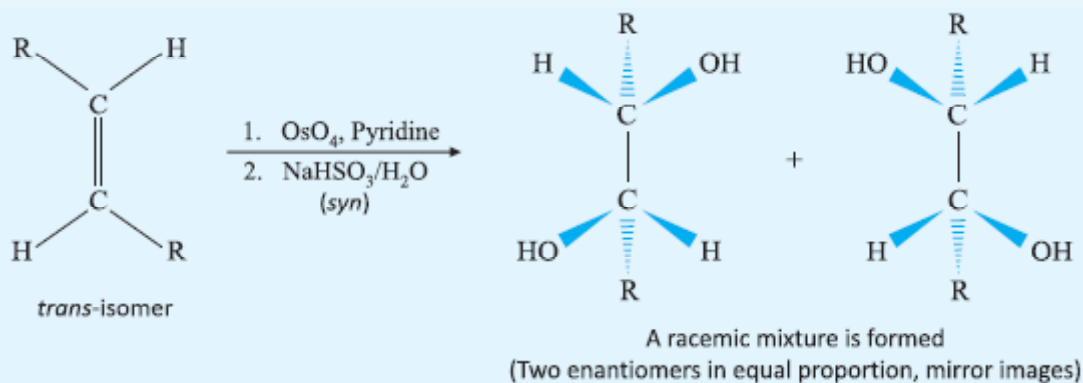
$$-\overset{|}{C}=\overset{|}{C}- \xrightarrow[\text{OH}^-,\ \text{cold}]{\text{KMnO}_4} -\overset{|}{\underset{\underset{\text{OH}}{|}}{C}}-\overset{|}{\underset{\underset{\text{OH}}{|}}{C}}- \qquad \text{(Vicinal alcohols or glycols)}$$

$$-\overset{|}{C}=\overset{|}{C}- \xrightarrow[\text{2. NaHSO}_3/\text{H}_2\text{O}]{\text{1. OsO}_4,\ \text{pyridine}} -\overset{|}{\underset{\underset{\text{OH}}{|}}{C}}-\overset{|}{\underset{\underset{\text{OH}}{|}}{C}}- \qquad \text{(Vicinal alcohols or glycols)}$$

It represents *syn-addition*.

$$\text{CH}_3-\text{CH}=\text{CH}_2 \xrightarrow[\text{2. NaHSO}_3/\text{H}_2\text{O}]{\text{1. OsO}_4,\ \text{pyridine}} \text{CH}_3-\underset{\underset{\text{OH}}{|}}{\text{CH}}-\underset{\underset{\text{OH}}{|}}{\text{CH}_2}$$

1, 2 - Propanediol

cis-1, 2-cyclopentanediol

Note : Osmium tetra oxide, OsO$_4$ gives a better yield than KMnO$_4$. The hydroxylation like addition of Br$_2$ is also stereospecific. Consider hydroxylation in *cis* and *trans* isomeric alkenes.
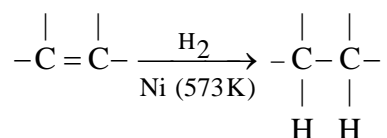

A Meso compound is formed
(having a plane of symmetry)

A racemic mixture is formed
(Two enantiomers in equal proportion, mirror images)

9. Hydrogenation :
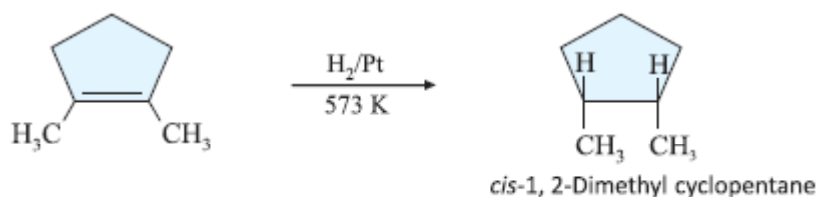
The hydrogenation of alkenes is a *syn-addition,* carried out by many reagents such as :

Na in liquid NH_3 and alcohol ; H_2, PtO_2/CH_3COOH ; H_2/Ni at 573 K ; H_2/Pd-Carbon in ethanol.

$$-\overset{|}{C}=\overset{|}{C}- \xrightarrow[\text{Ni (573K)}]{H_2} -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{H}{C}}-$$

This reaction also follows *syn*-addition rule.sheel

Consider hydrogenation in 1, 2-Dimethyl cyclohexene.
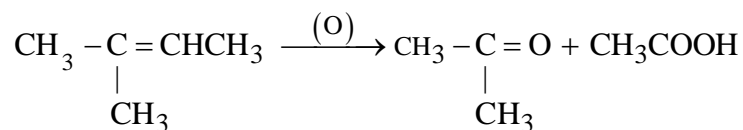

cis-1, 2-Dimethyl cyclopentane

10. Oxidation of Alkenes :

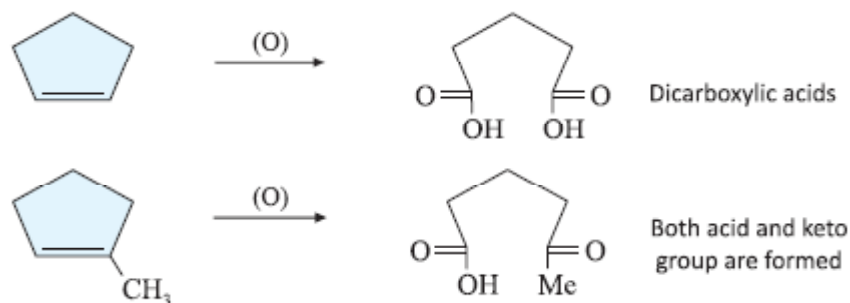### (a) Oxidation by hot. conc. $KMnO_4$:

It gives acids or ketones depending upon structure of alkenes. The terminal alkenes gives acids (ketones) and CO_2, whereas non-terminal alkenes gives mixture of acids and ketones.

$$CH_2 = CH_2 \xrightarrow{(O)} 2CO_2 + 2H_2O \qquad (\text{HCOOH formed is oxidised further})$$

$$CH_3CH = CH_2 \xrightarrow{(O)} CH_3COOH + CO_2 + H_2O$$

$$R - CH = CH - R' \xrightarrow{(O)} RCOOH + R'COOH$$

$$CH_3 - \underset{\underset{CH_3}{|}}{C} = CHCH_3 \xrightarrow{(O)} CH_3 - \underset{\underset{CH_3}{|}}{C} = O + CH_3COOH$$
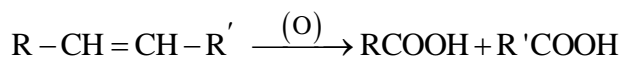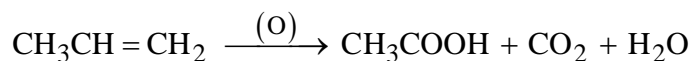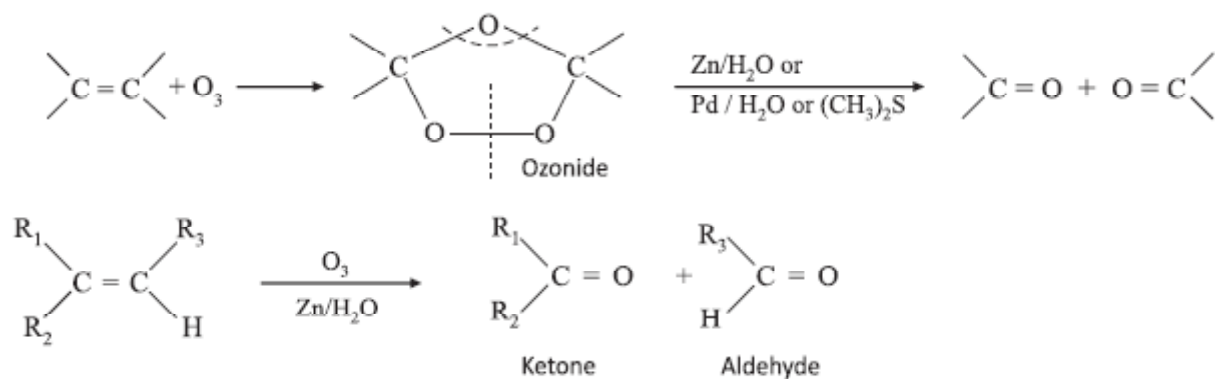
Note : Observe that the dialkylated side of double bond gives corresponding ketone.

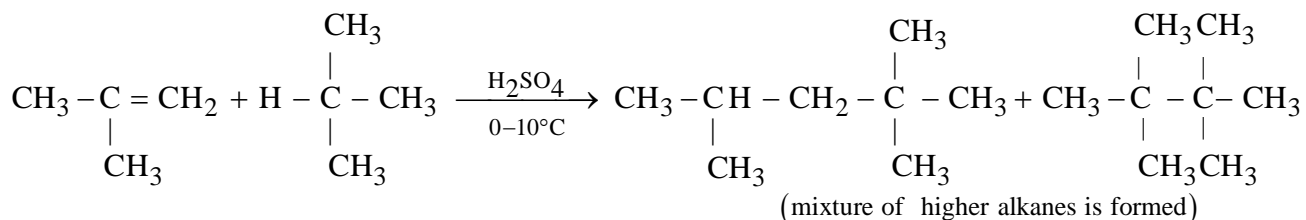Oxidation of cycloalkenes leads to the ring opening and gives dicarboxylic acids or keto acids.

Dicarboxylic acids

Both acid and keto group are formed

(b)   By Ozone (ozonolysis) :

Ozonide

Ketone   Aldehyde

Consider the ozonolysis of cycloalkenes :
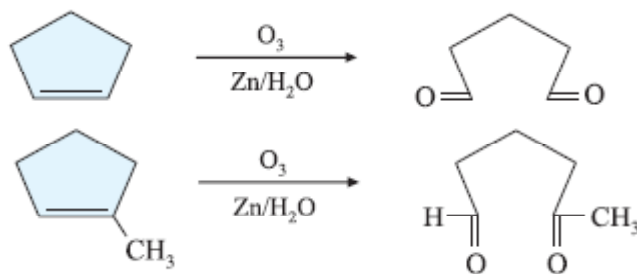
Note :   In ozonolysis, observe that we are using Zn/H_2O or Pb/H_2O or $(CH_3)_2S$ which reduces the nascent oxygen (O) given by ozonide. This is referred to as Reductive Ozonolysis. If Zn/H_2O is not used, the product aldehyde is oxidised to acid.
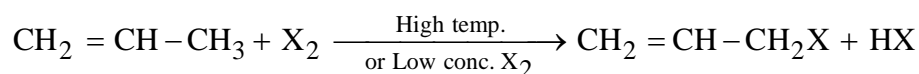
11. Alkylation :

$$CH_3-C(CH_3)=CH_2 + H-C(CH_3)_2-CH_3 \xrightarrow[0-10°C]{H_2SO_4} CH_3-CH(CH_3)-CH_2-C(CH_3)_2-CH_3 + CH_3-C(CH_3)(CH_3)-C(CH_3)(CH_3)-CH_3$$

$$\left(\text{mixture of higher alkanes is formed}\right)$$

12. Addition of oxygen :

$$CH_2=CH_2 + \tfrac{1}{2}O_2 \begin{cases} \xrightarrow[\text{Catalyst}]{Ag} H_2C\!\!\underset{O}{-}\!\!CH_2 \quad \text{Ethylene oxide (epoxide) or Oxirane} \\ \xrightarrow[\text{Peroxy acid}]{RCO_3H} H_2C\!\!\underset{O}{-}\!\!CH_2 + RCOOH \end{cases}$$
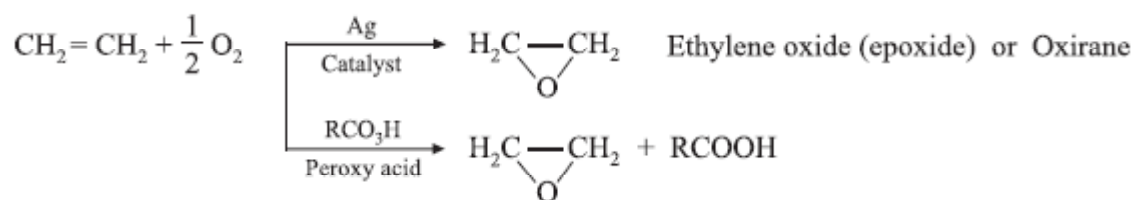
13. Substitution in alkenes : (Partial Oxidation)

$$CH_2=CH-CH_3 + X_2 \xrightarrow[\text{or Low conc. } X_2]{\text{High temp.}} CH_2=CH-CH_2X + HX$$

Here, halogen replaces one of the hydrogen atoms of the methyl group. These hydrogen are allylic hydrogen atom and hence the substitution is called as *allylic substitution.*
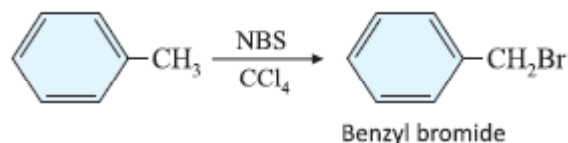
$$CH_2=CH-CH_3 + Cl_2 \xrightarrow[\text{gas phase}]{400°C-500°C} CH_2=CH-CH_2Cl + HCl$$
$$\text{Allyl Chloride}$$
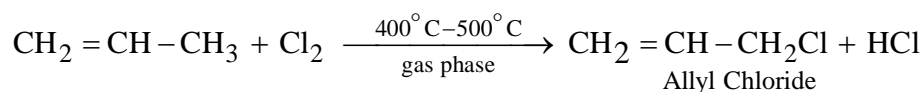
Propene undergoes allylic bromination when it is treated with N-bromo succinimide (NBS) in CCl_4 in presence of perioxides or light.

$$CH_2=CH-CH_3 \xrightarrow[\text{in ROOR or light}]{NBS/CCl_4} CH_2=CH-CH_2Br$$
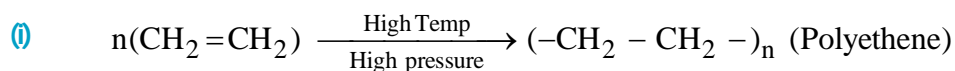$$\text{Allyl bromide}$$
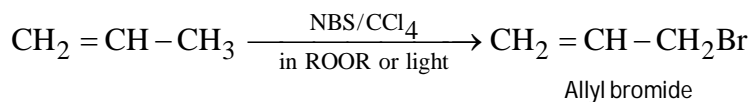
The mechanism is free radical substitution initiated by $Br^°$ (bromide free radical) to give intermediate allyl radical which is stable. Consider allylic substitution in cyclohexene using NBS in CCl_4.
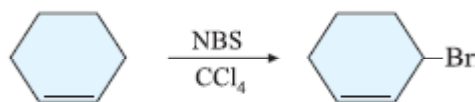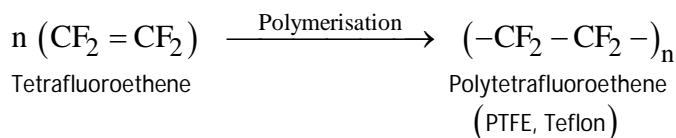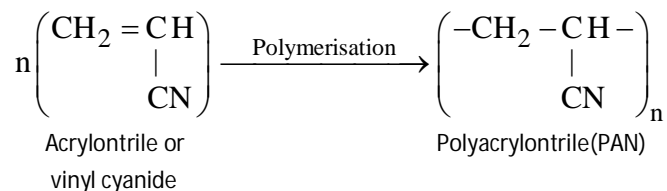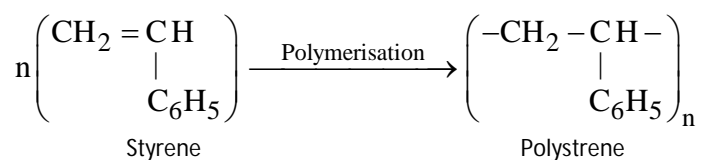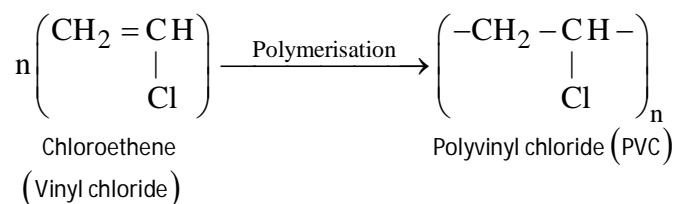
Another intersting aspect of this reaction is that it also occurs in alkyl benzens.

Benzyl bromide

14. Polymerisation :

(i) $n(CH_2=CH_2) \xrightarrow[\text{High pressure}]{\text{High Temp}} (-CH_2-CH_2-)_n$ (Polyethene)

(ii)   **Polymerization of substituted ethenes :** A number of polymers can be obtained by using substituted ethenes as monomers in place of ethene. For example,

$$n\begin{pmatrix} CH_2=CH \\ | \\ Cl \end{pmatrix} \xrightarrow{\text{Polymerisation}} \begin{pmatrix} -CH_2-CH- \\ | \\ Cl \end{pmatrix}_n$$

Chloroethene   Polyvinyl chloride $\left(PVC\right)$

$\left(\text{Vinyl chloride}\right)$

$$n\begin{pmatrix} CH_2=CH \\ | \\ C_6H_5 \end{pmatrix} \xrightarrow{\text{Polymerisation}} \begin{pmatrix} -CH_2-CH- \\ | \\ C_6H_5 \end{pmatrix}_n$$

Styrene   Polystrene

$$n\begin{pmatrix} CH_2=CH \\ | \\ CN \end{pmatrix} \xrightarrow{\text{Polymerisation}} \begin{pmatrix} -CH_2-CH- \\ | \\ CN \end{pmatrix}_n$$

Acrylontrile or   Polyacrylontrile(PAN)
vinyl cyanide

$$n\left(CF_2=CF_2\right) \xrightarrow{\text{Polymerisation}} \left(-CF_2-CF_2-\right)_n$$

Tetrafluoroethene   Polytetrafluoroethene
                                $\left(PTFE,\ Teflon\right)$

Polyvinyl chloride (PVC) is used for making plastic bottles, syringes, etc. Polyacrylontrile is used for making Orlon and Acrilan fibres used for making clothes, carpets and blankets.
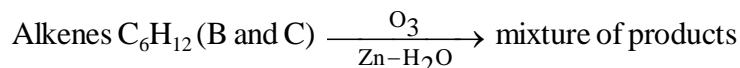
Illustration - 2 *Compound A ($C_6H_{13}Cl$) on treatment with hot alcoholic potassium hydroxide gave a mixture of two isomeric alkense B and C, having formula C_6H_{12}. The mixture of (B) and (C), on ozonolysis, furnished four compounds :*
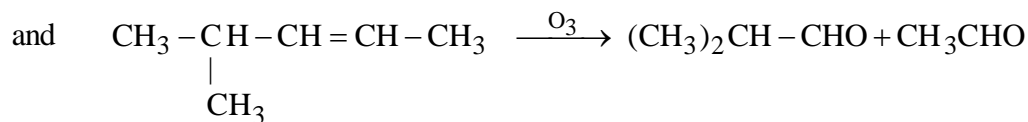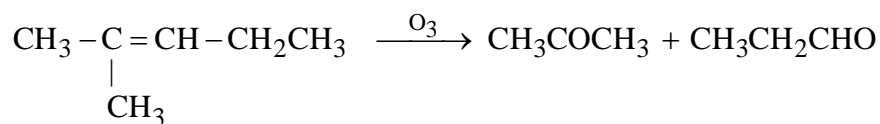
(i) CH_3CHO **(ii)** C_2H_5CHO **(iii)** CH_3COCH_3 **(iv)** $(CH_3)_2CHCHO$

What are the structures of A, B and C ?

SOLUTION :

$$\text{Alkenes } C_6H_{12} \text{ (B and C)} \xrightarrow[Zn-H_2O]{O_3} \text{mixture of products}$$

Try to draw the structures of alkenes (working backwards in ozonolysis reaction). Note that while joining the products, keep in mind that on combining two products the sum of carbon atom must be six.

On carefully examining the products, alkenes B and C are :

$$\underset{\underset{CH_3}{|}}{CH_3-C}=CH-CH_2CH_3 \xrightarrow{O_3} CH_3COCH_3 + CH_3CH_2CHO$$

and

$$\underset{\underset{CH_3}{|}}{CH_3-CH}-CH=CH-CH_3 \xrightarrow{O_3} (CH_3)_2CH-CHO + CH_3CHO$$

The structure of A must be :

$$\underset{\underset{CH_3}{|}\ \underset{Cl}{|}}{CH_3-CH-CH}-CH_2-CH_3 \xrightarrow[KOH, \Delta]{alc.} \underset{\underset{CH_3}{|}}{CH_3-C}=CH-CH_2-CH_3 + \underset{\underset{CH_3}{|}}{CH_3-CH}-CH=CH-CH_3$$

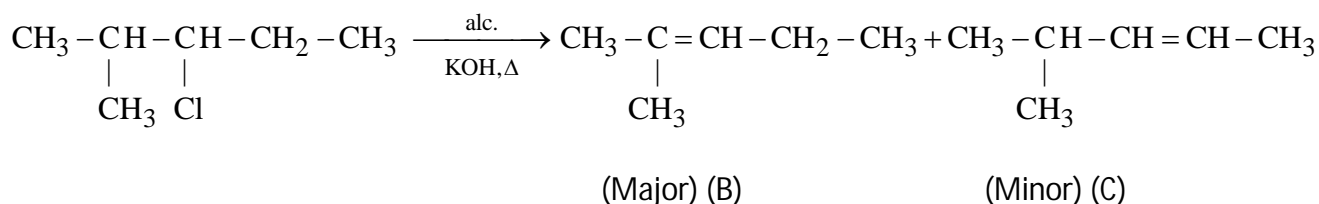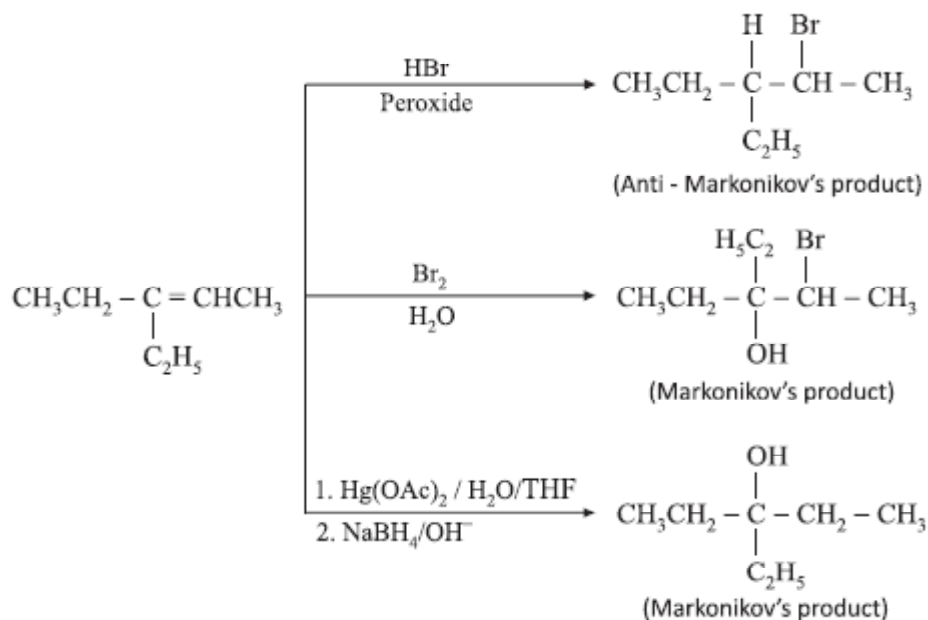$$\text{(Major) (B)} \qquad\qquad \text{(Minor) (C)}$$

Illustration - 3 *Give the stucture of the major organic products form 3-Ethy-l-2-pentene form under each of the following reaction conditions :*
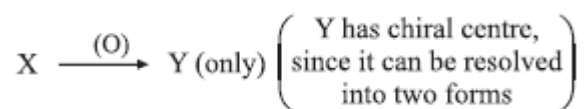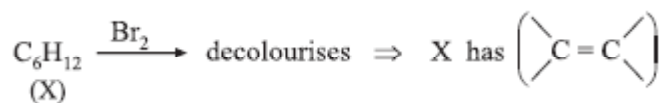
(A) *HBr in the presence of peroxide*   **(B)** *Br_2/H_2O*   **(C)** *$Hg(OAc)_2/THF/H_2O, NaBH_4/OH^-$*

SOLUTION :

$$CH_3CH_2 - C = CHCH_3$$
$$\quad\quad\quad |$$
$$\quad\quad\quad C_2H_5$$

$\xrightarrow[\text{Peroxide}]{\text{HBr}}$

$$\begin{array}{cc} H & Br \\ | & | \end{array}$$
$$CH_3CH_2 - C - CH - CH_3$$
$$\quad\quad\quad\quad |$$
$$\quad\quad\quad\quad C_2H_5$$
(Anti - Markonikov's product)

$\xrightarrow[\text{H}_2\text{O}]{\text{Br}_2}$

$$\begin{array}{cc} H_5C_2 & Br \\ | & | \end{array}$$
$$CH_3CH_2 - C - CH - CH_3$$
$$\quad\quad\quad\quad |$$
$$\quad\quad\quad\quad OH$$
(Markonikov's product)

$\xrightarrow[\text{2. NaBH}_4/\text{OH}^-]{\text{1. Hg(OAc)}_2 / \text{H}_2\text{O/THF}}$

$$\quad\quad\quad\quad OH$$
$$\quad\quad\quad\quad |$$
$$CH_3CH_2 - C - CH_2 - CH_3$$
$$\quad\quad\quad\quad |$$
$$\quad\quad\quad\quad C_2H_5$$
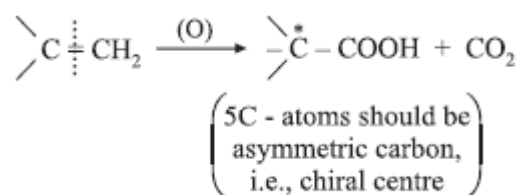(Markonikov's product)

Illustration - 4 *A hydrocarbon X, C_6H_{12} decolorizes bromine water and is oxidized to an acid Y by hot acidic potassium permanganate solution. The acid Y can be resolved into two forms. Identify X and Y.*
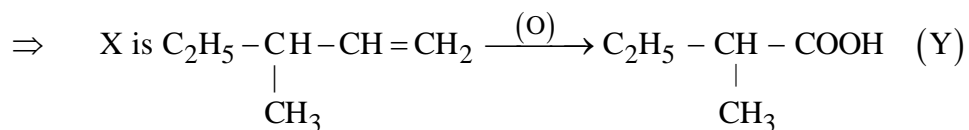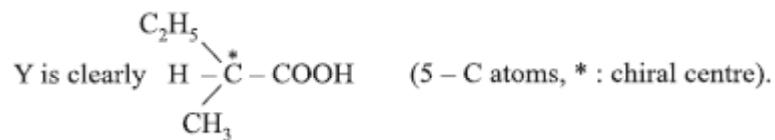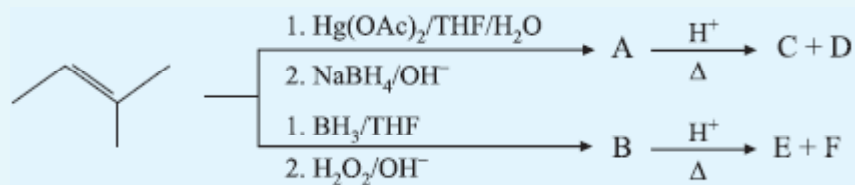
SOLUTION :

$$C_6H_{12} \xrightarrow{\text{Br}_2} \text{decolourises} \Rightarrow \text{X has } \left(\searrow C = C \nearrow \right)$$
$$(X)$$

$$X \xrightarrow{(O)} Y \text{ (only)} \left(\begin{array}{c} \text{Y has chiral centre,} \\ \text{since it can be resolved} \\ \text{into two forms} \end{array} \right)$$

X is terminal alkene as it gives only Y.

$$\searrow C \doteq CH_2 \xrightarrow{(O)} \searrow \overset{*}{C} - COOH + CO_2$$

$$\left(\begin{array}{c} \text{5C - atoms should be} \\ \text{asymmetric carbon,} \\ \text{i.e., chiral centre} \end{array} \right)$$

Visualise the structure of Y (having a chiral centre) :

Y is clearly $H - \overset{\overset{\displaystyle C_2H_5}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{\overset{*}{C}}} - COOH$ (5 – C atoms, * : chiral centre).

$\Rightarrow$ X is $C_2H_5 - \underset{\underset{\displaystyle CH_3}{|}}{CH} - CH = CH_2 \xrightarrow{(O)} C_2H_5 - \underset{\underset{\displaystyle CH_3}{|}}{CH} - COOH$ (Y)

Illustration - 5   *Identify A, B, C, D. . . . .*

1. $Hg(OAc)_2/THF/H_2O$
2. $NaBH_4/OH^-$ → A $\xrightarrow[\Delta]{H^+}$ C + D

1. BH_3/THF
2. H_2O_2/OH^- → B $\xrightarrow[\Delta]{H^+}$ E + F

SOLUTION :

(Markonikov's addition) $\xrightarrow[\Delta]{H^+}$ (Dehydration)   (Major) (Saytzeff's Product)   +   (Minor)

(Anti-Markonikov's addition) $\xrightarrow[\Delta]{H^+}$ (Dehydration)   (Major) (Saytzeff's Product)   +   (Minor)
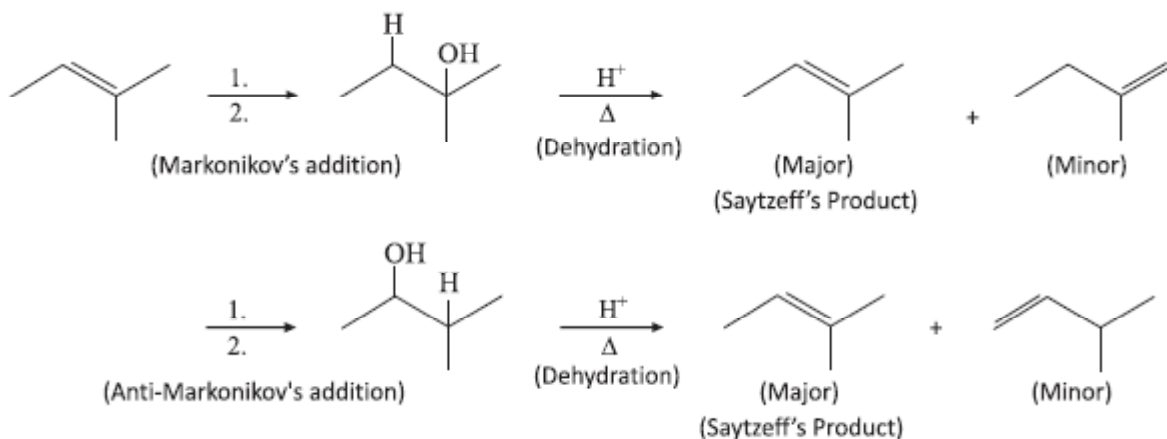
Illustration - 6   *Identify the products*

$\xrightarrow{O_3}$
$Zn - H_2O$ → Products

$\xrightarrow{(O)}$ → Products

SOLUTION :

$\xrightarrow[Zn/H_2O]{O_3}$ → + OHC

$\xrightarrow{(O)}$ → + HOOC
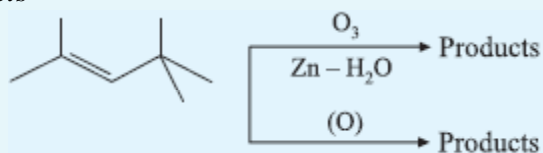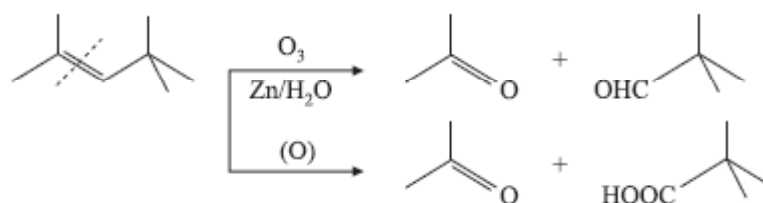
Note that the dialkylated site in alkene give the same producer (Ketone) on oxidation and ozonolysis.

NOW ATTEMPT IN-CHAPTER EXERCISE-B BEFORE PROCEEDING AHEAD IN THIS EBOOK

ALKYNES : [C_nH_{2n-2}]   Section - 3
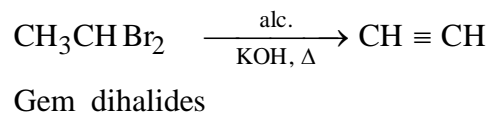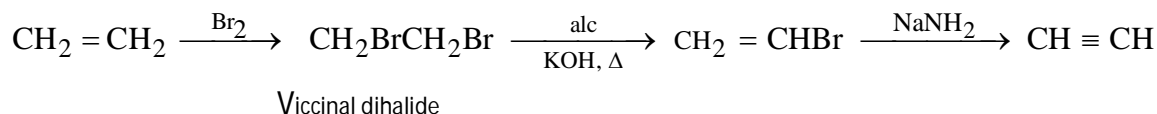
Alkynes form a homologous series, represented by a general formula : C_nH_{2n-2}. These have one $C \equiv C$ bond or one can say that two carbon atoms (adjacent) in alkynes show sp type of hybridisation. The important members of alkynes are: Ethyne ($CH \equiv CH$), Propyne ($CH_3C \equiv CH$), 1-Butyne ($CH_3CH_2C \equiv CH$) and its isomer, 2-Butyne ($CH_3C \equiv CCH_3$).

Generally, alkynes are also represented as :

1.   Terminal alkynes $RC \equiv CH$
2.   Non-terminal alkynes $RC \equiv CR$, $RC \equiv CR'$ (where R : alkyl radical)

Preparation of Alkynes :

1.   Dehydrohalogenation of Dihalides : (Gem and Vicinal)

$$CH_2 = CH_2 \xrightarrow{Br_2} \underset{\text{Viccinal dihalide}}{CH_2BrCH_2Br} \xrightarrow[\text{KOH, } \Delta]{\text{alc}} CH_2 = CHBr \xrightarrow{NaNH_2} CH \equiv CH$$

$$CH_3CHBr_2 \xrightarrow[\text{KOH, } \Delta]{\text{alc.}} CH \equiv CH$$
$$\text{Gem dihalides}$$

If alcoholic KOH to be used, vinylic halides are formed, as it is unable to remove vinylic hydrogen. So $NaNH_2$ Sodamide) is used to produce alkynes.
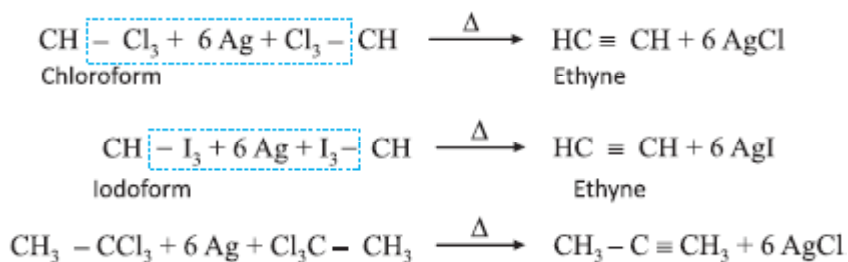
2.   Dehalogenation of Tetrahalides :

$$\underset{\overset{|}{Br} \quad \overset{|}{Br}}{\overset{\overset{Br \quad Br}{|} \quad \overset{}{|}}{H - C - C - H}} + Zn \longrightarrow \underset{}{\overset{\overset{Br \quad Br}{|} \quad \overset{}{|}}{H - C = C - H}} \xrightarrow{Zn} CH \equiv CH$$
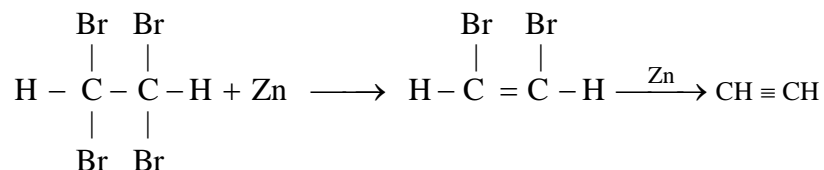
3.   By dehalogenation of haloform :

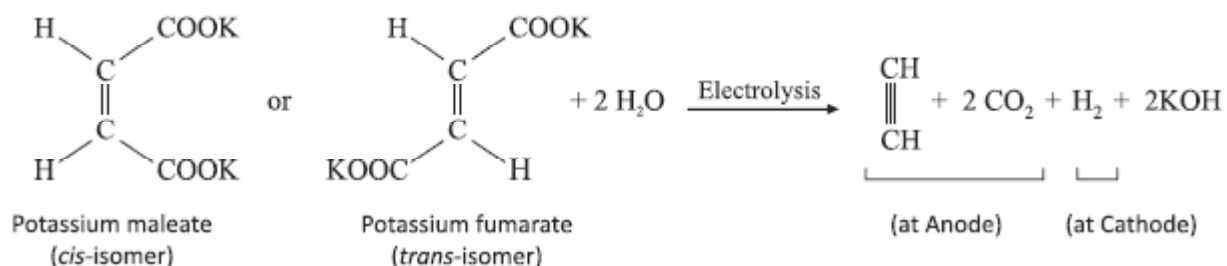Trihaloderivative of methane is knwon as haloform (CHX_3).

Chloroform and Iodoform on heating with silver powder undergo dehalogenation to form ethyne.

Trihaloalkane $(R - CX_3)$ on heating with silver powder also undergo dehalogentation to form symmetrical internal alkyne.

$$CH - Cl_3 + 6\,Ag + Cl_3 - CH \xrightarrow{\Delta} HC \equiv CH + 6\,AgCl$$
Chloroform $\qquad\qquad$ Ethyne

$$CH - I_3 + 6\,Ag + I_3 - CH \xrightarrow{\Delta} HC \equiv CH + 6\,AgI$$
Iodoform $\qquad\qquad$ Ethyne

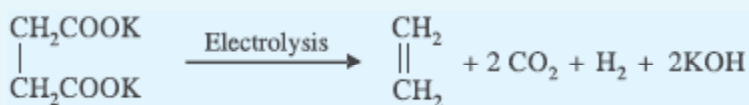$$CH_3 - CCl_3 + 6\,Ag + Cl_3C - CH_3 \xrightarrow{\Delta} CH_3 - C \equiv CH_3 + 6\,AgCl$$

4. Kolbe's electrolytic reaction :

Acetylene can be prepared by electrolysis of a concentrated solution of sodium or potassium salt of Maleic acid or Fumaric acid. Thus,

Potassium maleate (*cis*-isomer) $\qquad$ Potassium fumarate (*trans*-isomer) $\qquad$ (at Anode) $\quad$ (at Cathode)

This reaction is called Kolbe's electrolytic reaction.

Note : On electrolysis of aqueous solution of Potassium succinate, we get Ethylene (C_2H_4) as a product at anode.

$$\begin{array}{l} CH_2COOK \\ | \\ CH_2COOK \end{array} \xrightarrow{Electrolysis} \begin{array}{l} CH_2 \\ || \\ CH_2 \end{array} + 2\,CO_2 + H_2 + 2KOH$$

5. From Graphite :

$$2C(s) + H_2(g) \xrightarrow[1000^\circ C]{Electric\ arc} CH \equiv CH \qquad (\textit{Only acetylene can be formed})$$

6. From calcium carbide :

$$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2 \qquad (\textit{Only acetylene can be formed})$$

Note : **(i)**   Calcium carbide is formed as follows :

$$CaCO_3 \xrightarrow[\Delta]{2000°C} CaO + CO_2$$

$$CaO + C \xrightarrow{2500°C} CaC_2 + CO\uparrow$$
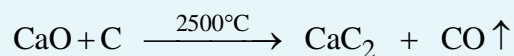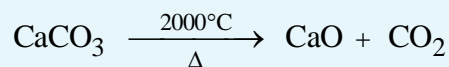
   (ii)   Carbides of Na, K, Ca, Mg, Ba are considered to be ionic and give acetylene with H_2O.

   (iii)   However, carbides of Cu and Ag are covalent and hence do not give acetylene with H_2O.

7.   Higher alkynes from Lower alkynes :

$$\underset{\text{excess}}{CH \equiv CH} \xrightarrow[\text{1.0 eq.}]{NaNH_2,\ liq.\ NH_3} CH \equiv CNa \xrightarrow{R'X} CH \equiv C - R' \qquad \text{(Terminal alkynes)}$$

$$CH \equiv CH \xrightarrow[\text{2.0 eq.}]{NaNH_2,\ liq.\ NH_3} Na - C \equiv C - Na \xrightarrow[\text{excess}]{R'X} R' - C \equiv C - R' \quad \text{(Non-terminal Alkynes)}$$

$$R - C \equiv CH \xrightarrow[\text{1.0 eq}]{NaNH_2,\ liq.\ NH_3} R - C \equiv C - Na \xrightarrow{R'X} R - C \equiv C - R' \quad \text{(Non-terminal alkynes)}$$
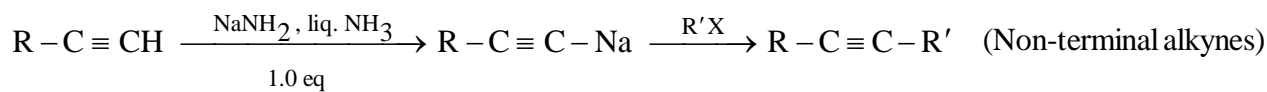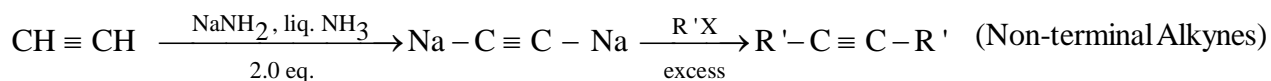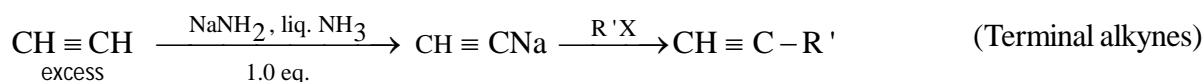
Note : R' can only be 1° and 2° alkyl or cycloalkyl groups only.

Physical Properties of Alkynes:

1.   Physical state : The first three members of this family (Ethyne, Propyne and Butyne) are colourless gases, the next eight are liquids while the higher ones are solids.

2.   Smell : All the alkynes are odourless. However acetylene has garlic smell due to the presence of phosphine as impurity.

3.   Melting and boiling points : The boiling points and melting points of alkynes are slightly higher than those of the corresponding alkenes and alkanes. This is probably due to the reason that because of the presence of a triple bond, alkynes have linear structures and hence their molecules can be more closely packed in the crystal lattice as compared to those of corresponding alkenes and alkanes.

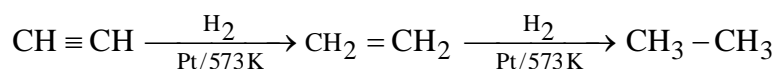| Hydrocarbon	Ethane	Ethene	Ethyne
M.P. (K)	101	104	191
B.P. (K)	184.5	171	198

4. **Solubility :** Alkynes like alkanes and alkenes being non-polar are insoluble in water but readily dissolve in organic solvents such as petroleum ether, benzene, carbon tetrachloride etc.

5. **Density :** Densities of alkynes increase as the molecular size increases. However, they are all lighter than water since their densities lie in the range $0.69 - 0.77 \text{ g/cm}^3$.

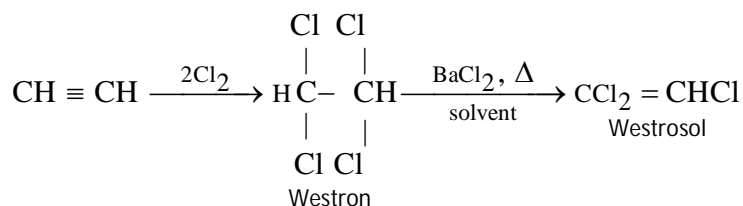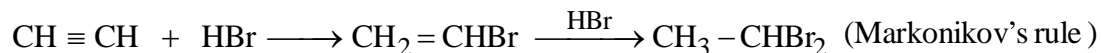## Reactions of Alkynes :

1. **Electrophillic Addition Reactions :**

$$-C \equiv C- \xrightarrow{\text{XY}} -\overset{\overset{\displaystyle X}{\mid}}{C} = \overset{\overset{\displaystyle Y}{\mid}}{C}- \xrightarrow{\text{XY}} -\underset{\underset{\displaystyle X}{\mid}}{\overset{\overset{\displaystyle X}{\mid}}{C}} - \underset{\underset{\displaystyle Y}{\mid}}{\overset{\overset{\displaystyle Y}{\mid}}{C}}-$$

(a) **Addition of Hydrogen :**

$$CH \equiv CH \xrightarrow[\text{Pt/573K}]{H_2} CH_2 = CH_2 \xrightarrow[\text{Pt/573K}]{H_2} CH_3 - CH_3$$
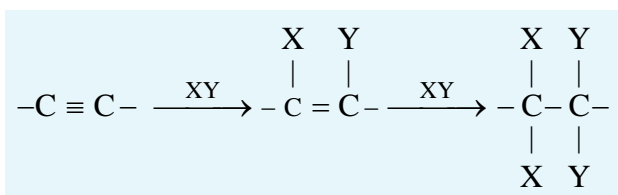
Read hydrogenation of alkynes in the preparation of alkenes.

(b) **Addition of Halogens : (X = Cl, Br, I)**

$$CH \equiv CH \xrightarrow{2Cl_2} H\underset{\underset{\displaystyle Cl}{\mid}}{\overset{\overset{\displaystyle Cl}{\mid}}{C}} - \underset{\underset{\displaystyle Cl}{\mid}}{\overset{\overset{\displaystyle Cl}{\mid}}{CH}} \xrightarrow[\text{solvent}]{BaCl_2,\ \Delta} CCl_2 = CHCl$$

Westron   Westrosol

(c) **Addition of Halogen acids : (HX)**

$$CH \equiv CH \ + \ HBr \longrightarrow CH_2 = CHBr \xrightarrow{HBr} CH_3 - CHBr_2 \ (\text{Markonikov's rule})$$

(d) **Addition of Hypohalous acids(HOX) :**

$$HC \equiv CH + HOCl \longrightarrow [Cl - CH = CH - OH] \underset{}{\overset{\text{Tautomerises}}{\rightleftharpoons}} Cl - CH_2 - \overset{\overset{\displaystyle}{}}{\underset{\underset{\displaystyle O}{\parallel}}{C}} - H$$

Ethyne   (2-Chloroethen-1-ol)

Similarly,

$$CH_3-C \equiv CH \xrightarrow[\text{Mark. addn.}]{\overset{\delta+ \quad \delta-}{Cl-OH}} \left[CH_3 - \underset{\underset{OH \quad Cl}{|\quad\quad|}}{C=CH}\right] \underset{\text{Tautomerises}}{\rightleftharpoons} Cl-CH_2-\underset{\underset{O}{||}}{C}-CH_3$$

Propyne

(e)   Addition of water (H₂O) is presence of acid :

$$CH \equiv CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} \underset{\text{enol}}{CH_2=CHOH} \underset{\rightleftharpoons}{\xrightarrow{\text{Tautomerises}}} CH_3-CHO \text{ (Acetaldehyde)}$$

$$CH_3-C \equiv CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} CH_3-\underset{\underset{\text{enol}}{}}{\overset{OH}{\underset{|}{C}}}=CH_2 \underset{\rightleftharpoons}{\xrightarrow{\text{Tautomerises}}} CH_3-\underset{\underset{O}{||}}{C}-CH_3 \text{ (Acetone)}$$
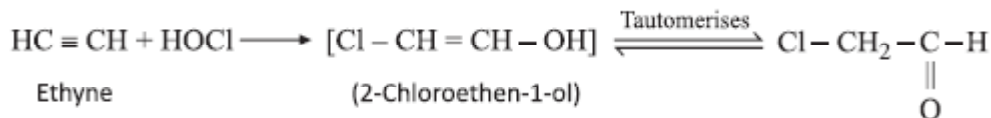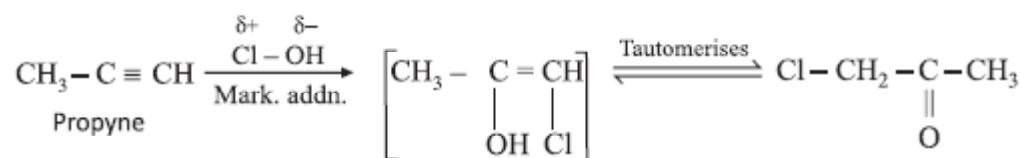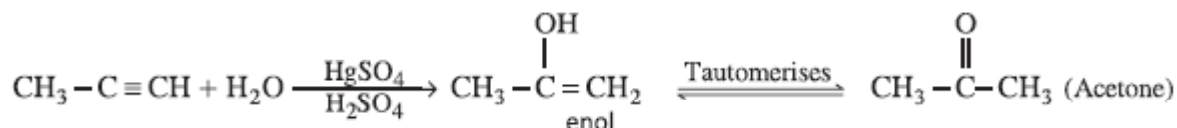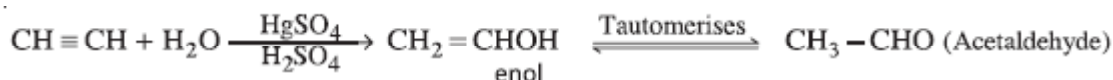
Note :   The addition of water to alkynes also follows Markonikow's rule. The hydrogen atom become attached to the carbon atom with the greater number of hydrogen atoms. Therefore, when higher terminal alkynes are hydrated, ketones, rather than aldehydes are formed.

However, if the unsymmetrical alkyne is nonterminal, a mixture of two isomeric ketones is obtained in which the methyl ketone predominates. In case of benzene ring, phenyl ketones is major product .

➤ $$CH_3CH_2-C \equiv C-CH_3 \xrightarrow[333 \text{ K}]{HgSO_4/H_2SO_4} CH_3CH_2CH_2-\underset{\underset{O}{||}}{C}-CH_3 + CH_3CH_2-\underset{\underset{O}{||}}{C}-CH_3CH_3$$

                                              2 - Pentanone (Major)   2 - Pentanone (Minor)

➤ $$\bigcirc\!\!\!\!\bigcirc -C \equiv C-CH_3 \xrightarrow[333 \text{ K}]{HgSO_4/H_2SO_4} \bigcirc\!\!\!\!\bigcirc -\underset{\underset{O}{||}}{C}-CH_2CH_3 + \bigcirc\!\!\!\!\bigcirc -CH_2-\underset{\underset{O}{||}}{C}-CH_3$$

                                                                    (Major)   (Minor)

(f)   Addition of HCN :

$$CH \equiv CH + HCN \longrightarrow CH_2=CHCN \qquad \text{(Vinyl cyanide also known as acrylonitrile)}$$
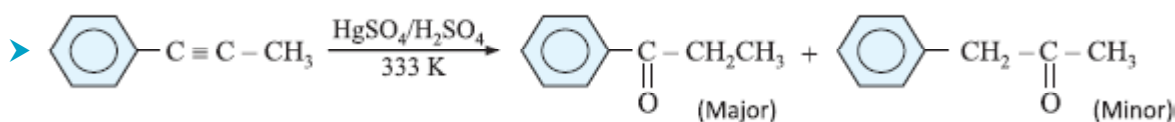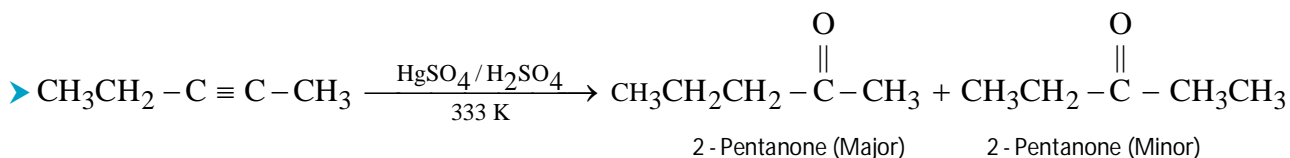
Note :   Acrylonitrile is used in manufacture of BuNa-S rubber and Orlon fibre.

(g)   Addition of Acetic acid (CH₃COOH) :

$$CH \equiv CH + CH_3COOH \xrightarrow{Hg^{2+}} H_2C=HC-OAc \xrightarrow{CH_3COOH} CH_3-CH(OAc)_2$$

                                       Vinyl acetate   Ethylidine acetate
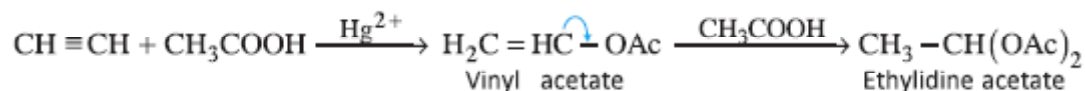
(h)   Addition of Arsenic trichoride (AsCl$_3$) :

$$CH \equiv CH + ClAsCl_2 \longrightarrow ClHC = CHAsCl_2$$
$$\text{(Lewisite, a poisonous gas)}$$

2.   Nucleophillic Addition reactions :

$$CH \equiv CH + Nu^- \longrightarrow \underset{\underset{Nu}{|}}{H-C} = C-H$$
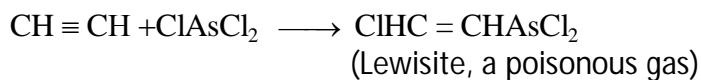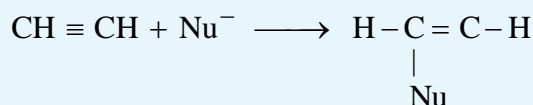
(Vinylic carbanion)

Vinylic Carbanion is formed which is more stable than vinylic carbonium ion.
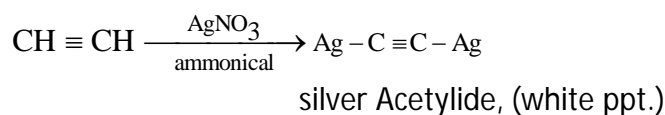
Addition of Methanol :

$$\underset{\text{Acetylene}}{HC \equiv CH} + CH_3OH \xrightarrow[\text{433–473 K}]{CH_3O^-K^+} \underset{\text{Methyl vinyl ether}}{CH_2 = CH - OCH_3}$$
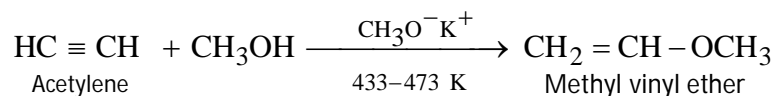
Methyl vinyl ether is used for making polyvinyl ether plastics.

3.   Oxidative - Hydroboration

$$CH_3 - C \equiv CH \xrightarrow{BH_3, THF} \left(CH_3 - CH = CH - \right)_3 B \xrightarrow{H_2O_2, OH^-}$$

$$\underset{\text{enol}}{CH_3 - CH = CH - OH} \underset{\text{Tautomerise}}{\rightleftharpoons} \underset{\text{Aldehyde}}{CH_3CH_2CHO}$$

$$CH_3 - C \equiv C - CH_3 \xrightarrow{BH_3, THF} \left(\underset{}{CH_3 - CH = \overset{\overset{CH_3}{|}}{C} -} \right)_3 B \xrightarrow{H_2O_2, OH^-}$$

$$\underset{\text{enol}}{CH_3 - CH = \overset{\overset{CH_3}{|}}{C} - OH} \underset{\text{Tautomerise}}{\rightleftharpoons} \underset{\text{Ketone}}{CH_3CH_2 \overset{\overset{O}{\|}}{C} CH_3}$$

4.   Acetylide Formation :

$$CH \equiv CH \xrightarrow[\text{ammonical}]{AgNO_3} Ag - C \equiv C - Ag$$

silver Acetylide, (white ppt.)
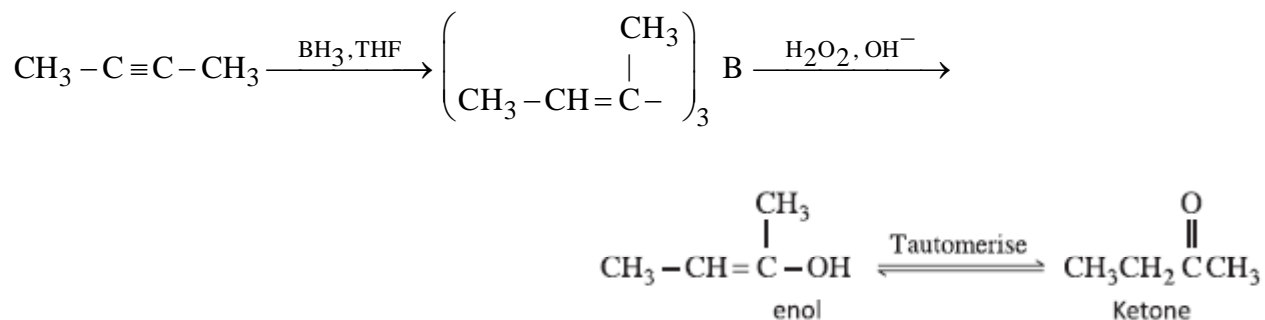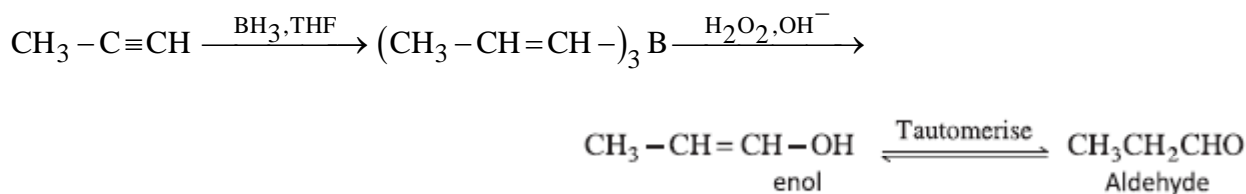
Note : This reaction shows the acidity of terminal alkynes and serves as a test for terminal alkynes.

$$CH \equiv CH \xrightarrow[\text{amm.}]{\text{CuCl}_2} Cu - C \equiv C - Cu$$

Copper Acetylide (Red ppt.)
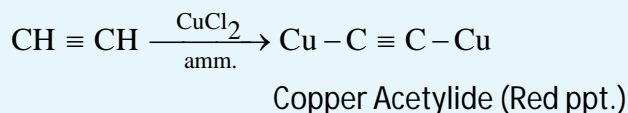
5.   Oxidation of Alkynes :

(a)   Oxidation in Neutral KMnO$_4$:

$$CH_3 - C \equiv C - CH_3 + 2(O) \xrightarrow[\text{298-303 K}]{\text{KMnO}_4, \text{H}_2\text{O}} CH_3 - \underset{\underset{O}{\|}}{C} - \underset{\underset{O}{\|}}{C} - CH_3$$

But-2-yne

$$\left(\text{Butan-2, 3-dione}\right)$$
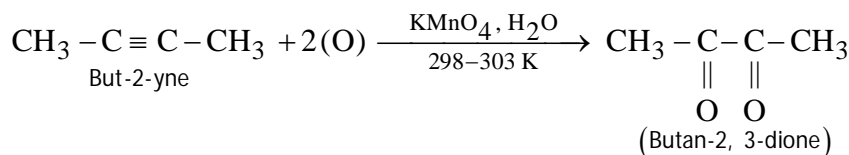
(b)   Oxidation with cold dilute alkaline KMnO$_4$:

Alkynes are readily oxidised by cold dilute alkaline KMnO$_4$ solution to give dicarbonyl compounds. In case of terminal alkynes, $\equiv$ CH part is oxidised to – COOH group while in case of non-terminal alkynes, $\equiv$ CR part is oxidised to $R - \overset{|}{C} = O$ group, For example :

$$CH_3 - C \equiv CH + 3(O) \xrightarrow[\substack{298 - 303 \text{ K} \\ 2. \ \text{H}^+}]{1. \ \text{NaOH, KMnO}_4} CH_3 - \underset{\underset{O}{\|}}{C} - COOH$$

Propyne

2-Oxopropanoic acid

$$CH_3 - C \equiv C - CH_3 \xrightarrow[\text{298-303 K}]{\text{NaOH, KMnO}_4} CH_3 - \underset{\underset{O}{\|}}{C} - \underset{\underset{O}{\|}}{C} - CH_3$$
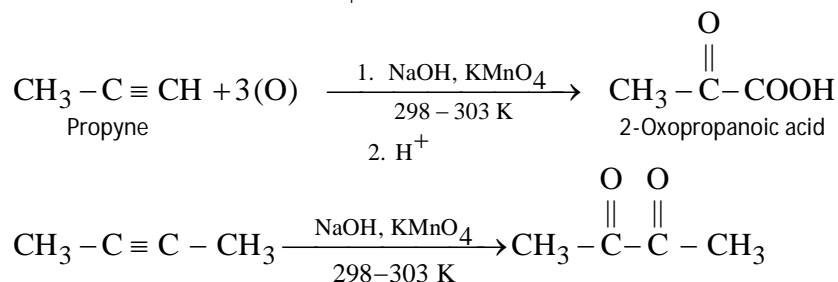
Acetylene, however, under these conditions gives oxalic acid probably due to further oxidation of the initially formed glyoxal.

$$HC \equiv CH + 2(O) \xrightarrow[\text{298-303 K}]{\text{KMnO}_4, \text{NaOH}} \left[OHC - CHO\right] \xrightarrow[\text{H}^+]{+2(O)} HOOC - COOH$$

Acetylene   Glyoxal   Oxalic acid

During this reaction, the pink colour of the KMnO$_4$ solution is discharged and a brown precipitate of manganese dioxide is obtained. This reaction is, therefore, used as a test for unsaturation under the name Baeyer's test.

(c)   Oxidation by acidic KMnO$_4$ (hot) :

$$R - C \equiv C - R' \xrightarrow[\text{H}^+, \text{heat}]{\text{KMnO}_4} R - COOH + R'COOH$$
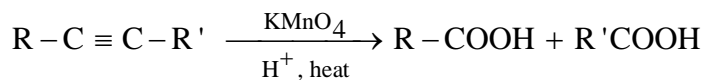
Not that it is similar to the oxidation of alkenes.

6. Ozonolysis :

(a) For non-terminal alkynes :

$$R - C \equiv C - R' \xrightarrow[\text{2. Zn, H}_2\text{O}]{\text{1. O}_3} R - \overset{\overset{O}{\|}}{C} - \overset{\overset{O}{\|}}{C} - R'$$
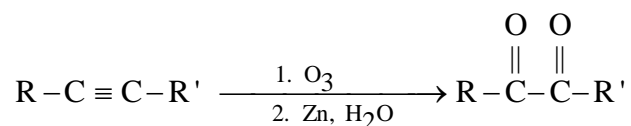
Note :   If, Zn or Pb is not used, then the product is mixture of acids.

$$R - C \equiv C - R' \xrightarrow{O_3} R - \overset{\overset{O}{\|}}{C} - OH + R' - \overset{\overset{O}{\|}}{C} - OH$$

<div align="center">mixture of acids</div>

(b) For terminal alkynes :

$$H - C \equiv CH \xrightarrow[\text{Zn/H}_2\text{O}]{O_3} OHC - CHO \quad (\text{Glyoxal})$$

$$R - C \equiv CH \xrightarrow[\text{Zn/H}_2\text{O}]{O_3} R - \overset{\overset{O}{\|}}{C} - CHO \quad (\alpha - \text{alkyl glyoxal})$$
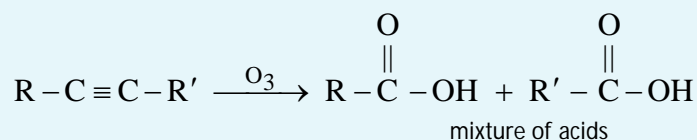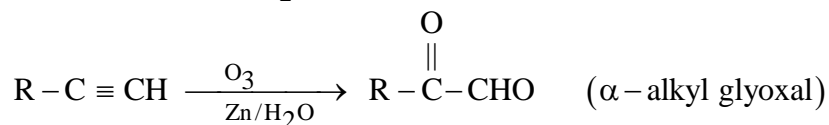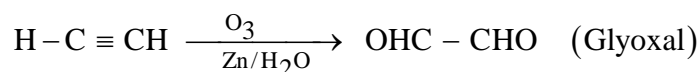
7. Polymerization Reactions of Alkynes :

Like alkenes, alkynes also undergo polymerization reactions. For example,

(a)   When acetylene is passed through red hot iron tube, it rimerises to give benzene.
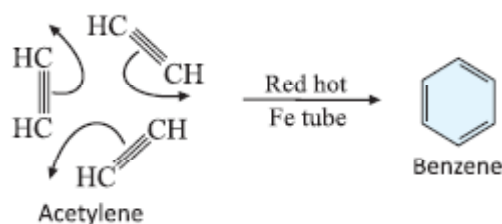
(b)   In presence of nickel cyanide as catalyst and under high pressure, four moelcules of acetyrene combine to form a tetramer called cycloocta-1, 3, 5, 7-tetraene.
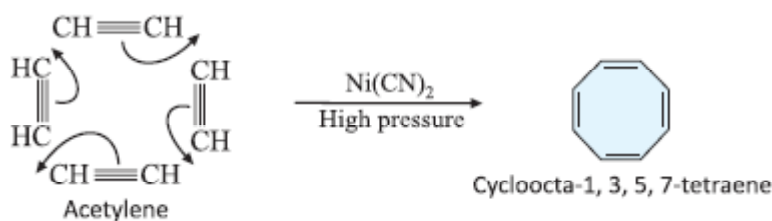
(c)   However, in presence of CuCl/NH$_4$Cl, acetylene first gives vinylacetylene and then divinylacetylene. Thus,

$$2\,HC \equiv CH \xrightarrow{\text{CuCl}/\text{NH}_4\text{Cl}} HC \equiv C - CH = CH_2 \xrightarrow[\text{CuCl}/\text{NH}_4\text{Cl}]{HC \equiv CH} H_2C = CH - C \equiv C - CH = CH_2$$

Acetylene   Vinylacetylene   Divinylacetylene
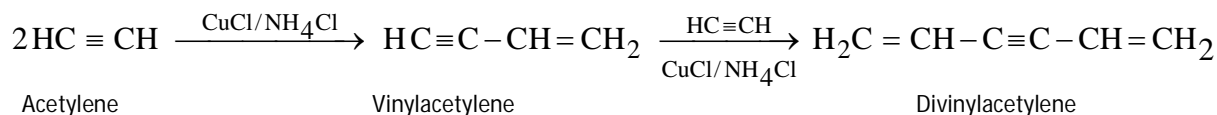
Vinylacetylene is widely used in the manufacture of chloroprene which is the starting material for the synthetic rubber neoprene.

$$CH_2 = CH - C \equiv CH + HCl \xrightarrow[\substack{\text{addition} \\ [\text{one mole}]\ \text{across}\ C = C}]{\text{Markonikov's}} CH_2 = CH - \overset{\overset{\displaystyle Cl}{|}}{C} = CH_2$$

Vinylacetylene   Chloroprene
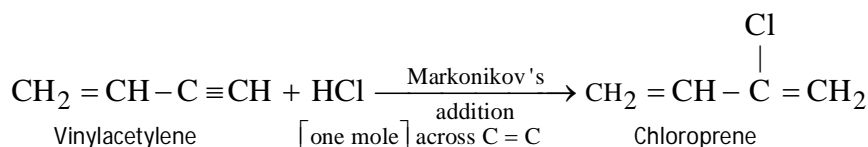
(d)   Under suitable conditions, polymerization of acetylene produces the linear polymer polyacetylene. It is a high molecular weight conjugated polyene containing the repeating unit ($-CH = CH - CH = CH-$)$_n$. Under proper conditions, this material conducts electricity. Since polyacetylenes have much higher conductance than metal conductors, these can be used to prepare lighter and cheaper batteries.

Acidic character of Alkynes :

(a)   **Formation of alkali metal acetylides :**

$$2\,HC \equiv CH + 2Na \xrightarrow{475°C} 2\,HC \equiv C^- Na^+ + H_2$$

Ethylne   Sodium acetylide
(Acetylene)

$$R - C \equiv CH \quad + \quad NaNH_2 \xrightarrow[196\ K]{\text{Liq. NH}_3} R - C \equiv C^- Na^+ + NH_3$$

(A terminal alkyne)   (An acetylide)
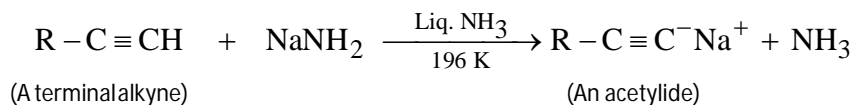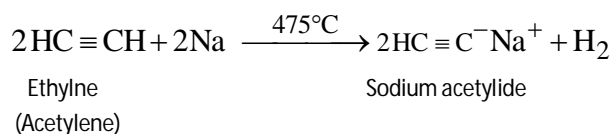
During these reactions, the acetylenic hydrogen is removed as a proton to form stable carbanions (acetylide ions). Sodium acetylide is decomposed by water regenerating acetylene. This shows that water is a stronger acid than acetylene and thus displaces acetylene from sodium acetylide.

$$HC \equiv C^- Na^+ + H_2O \longrightarrow HC \equiv CH + NaOH$$

Acetylene
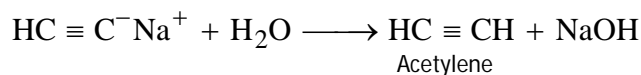
(b)   **Formation of heavy metal acetylides :**

$$CH \equiv CH + 2\left[Ag(NH_3)_2 \right]^+ OH^- \longrightarrow AgC \equiv CAg \quad + \quad 2\,H_2O + 4NH_3$$

Ethylne   Tollen's reagent   Silver acetylide
                                                                (White ppt.)

$$R - C \equiv CH + \left[Ag(NH_3)_2 \right]^+ OH^- \longrightarrow R - C \equiv C - Ag + H_2O + 2NH_3$$

Tollen's reagent   Silver acetylide
(White ppt.)

$$HC \equiv CH + 2\left[Cu(NH_3)_2 \right]^+ OH^- \longrightarrow CuC \equiv C - Cu + H_2O + 4NH_3$$

Ethyne   Copper acetylide
(Red ppt.)
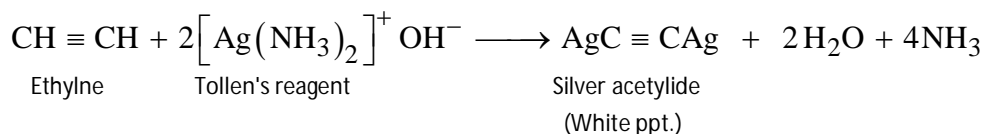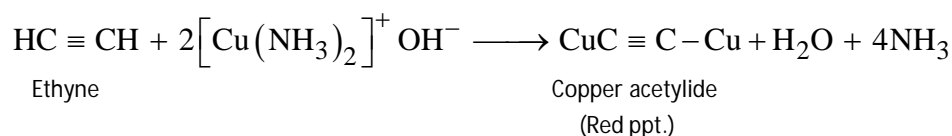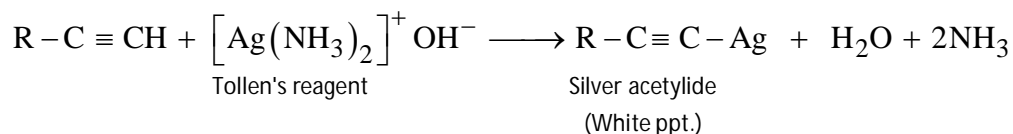
Unlike alkali metal acetylides, silver and copper acetylides are not decomposed by water. They can, however, be decomposed with dilute mineral acids to regenerate the original alkynes.

$$AgC \equiv CAg + 2HNO_3 \longrightarrow HC \equiv CH + AgNO_3$$

Silver acetylide   Acetylene

$$CuC \equiv CCu + 2HCl \longrightarrow HC \equiv CH + 2CuCl$$

Cooper acetylide   Acetylene
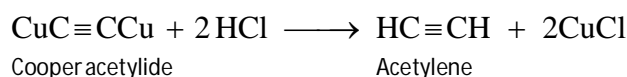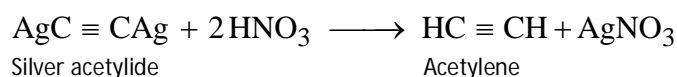
(c)   Formation of alkynyl Grignard reagents :

$$HC \equiv CH + RMgX \xrightarrow[\text{ether}]{\text{Dry}} HC \equiv CMgX + RH$$

Acetylene   Grignard reagent   Acetylenic   Alkane
Grignard reagent

$$R' - C \equiv CH + RMgX \xrightarrow[\text{ether}]{\text{Dry}} R' - C \equiv CMgX + RH$$

Terminal alkyne   Alkynyl
Grignard reagent
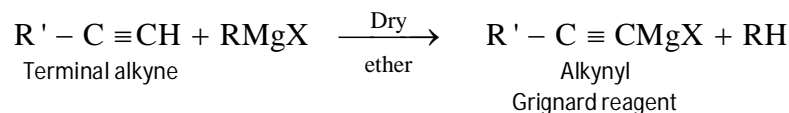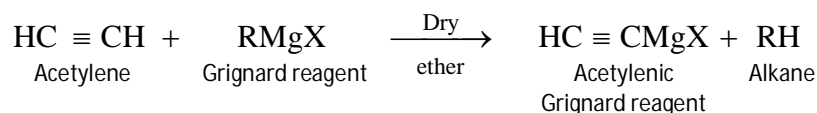
Illustration - 7   *How would convert acetylene to acetone ?*

SOLUTION :
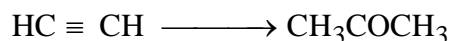
$$HC \equiv CH \longrightarrow CH_3COCH_3$$

In such question, try to visulaise formation of CH_3COCH_3. It is formed by hydration of $CH_3C \equiv CH$.

So now convert $HC \equiv CH$ to $CH_3C \equiv CH$.

$$HC \equiv CH \xrightarrow[\text{1.0 eq}]{NaNH_2} HC \equiv \overset{-}{C} - \overset{+}{Na} \xrightarrow{CH_3Br} HC \equiv C - CH_3 \xrightarrow{H_2O/H^+/Hg^{2+}} CH_3COCH_3$$

$$\left(\text{via Tautomerism} \right)$$
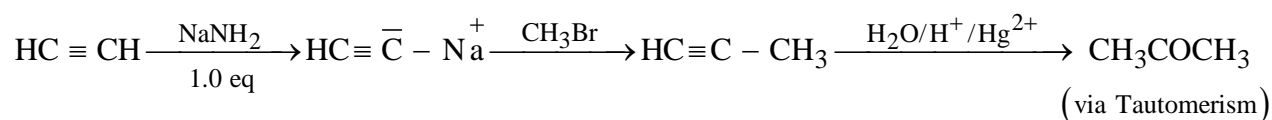
Illustration - 8

Identify A, B, C . . . .

(a) $Me-C \equiv CH \xrightarrow[\text{2. EtBr}]{\text{1. NaNH}_2} A \xrightarrow[\substack{Pd-BaSO_4 \\ quinoline}]{H_2} B \xrightarrow[Zn/H_2O]{O_3} C + D$

(b) $HC \equiv C - CH_2Br \xrightarrow[Et_2O]{Mg} A$

$A \xrightarrow{H_2O} B$

$A \xrightarrow{HC \equiv C - CH_2Br} C + D$

(c) $HC \equiv CH \xrightarrow[\text{2. EtBr (2.0 eqv.)}]{\text{1. NaNH}_2 \text{ (2.0 eqv.)}} A \xrightarrow[NH_3]{H_2, \text{ Liq. Li}} B \xrightarrow{Br_2/CCl_4} C$

SOLUTION :

(a) $Me - C \equiv CH \xrightarrow[2.]{1.} Me - C \equiv C - Et \longrightarrow$

$\underset{cis\text{-isomer}}{\underset{(B)}{\overset{Me \quad\quad Et}{\underset{H \quad\quad H}{C = C}}}} \xrightarrow[Zn/H_2O]{O_3} \underset{(C)}{MeCHO} + \underset{(D)}{EtCHO}$

(b) $HC \equiv C - CH_2Br \xrightarrow[Et_2O]{Mg} HC \equiv C - CH_2MgBr \xrightarrow{*IMPT} \underset{(A)}{BrMg - C \equiv C - CH_3}$

$\underset{(B)}{HC \equiv C - CH_3} \xleftarrow{H_2O}$

$\xrightarrow{HC \equiv C - CH_2Br}$

$\underset{(C)}{CH_3 - C \equiv C - CH_2 - C \equiv CH}$

[*IMPT : Intramolecular proton transfer]

(c) $HC \equiv CH \xrightarrow[2.]{1.} Et - C \equiv C - Et \longrightarrow$

$\underset{trans\text{-isomer}}{\overset{Et \quad\quad H}{\underset{H \quad\quad Et}{C = C}}} \xrightarrow[anti]{Br_2/CCl_4} \underset{(Meso)}{\begin{array}{c} Et \\ H \longrightarrow Br \\ H \longrightarrow Br \\ Et \end{array}}$

NOW ATTEMPT IN-CHAPTER EXERCISE-C BEFORE PROCEEDING AHEAD IN THIS EBOOK

CYCLOALKANES AND CYCLOALKENES

Section - 4

These are closed chain hydrocarbons having C_nH_{2n} as general formula. These are isomeric to alkenes.

Cyclo propane	or	C_3H_6	or		or	

Cyclo propane   or C_3H_6 or

Cyclo butane   or C_4H_8 or

Cyclo pentane   or C_5H_{10} or

Cyclo hexane   or C_6H_{12} or
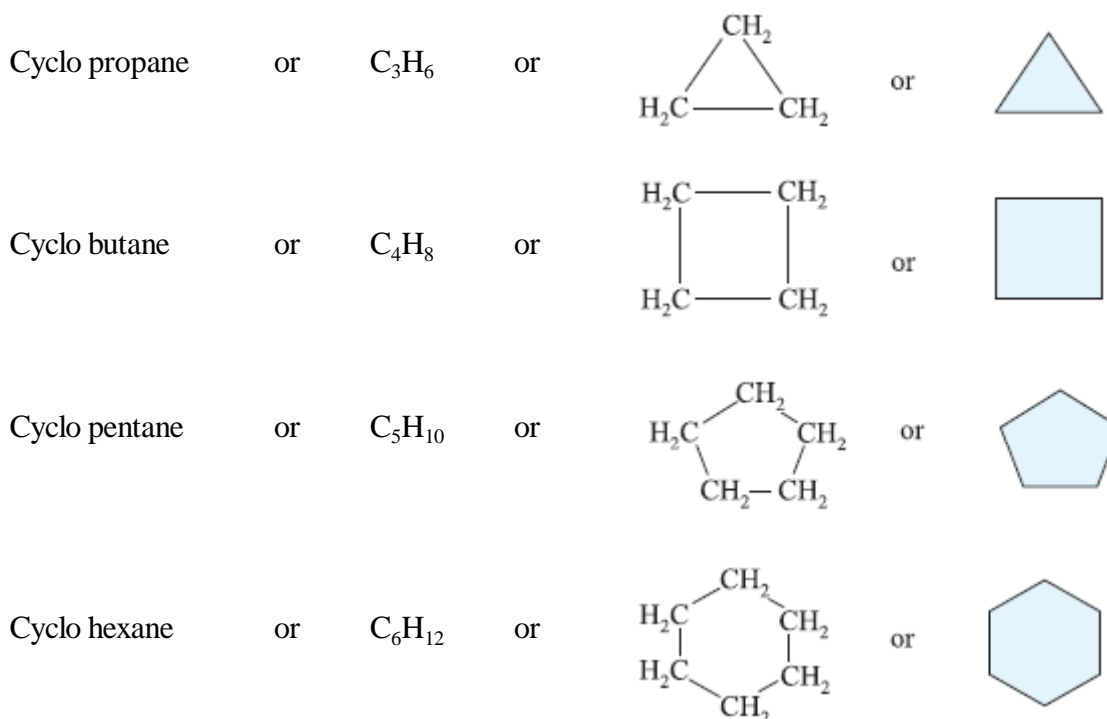
The bond angles in lower members, i.e., in cyclopropane and cyclobutane are quite different from normal tetrahedral bond angle of 109.5°. Hence these are unstable as compared to higher member such as cyclopentane and cyclohexane which have bond angles nearer to tetrahedral bond angles. The two small cycloalkanes are said to have a ring strain due to bond deformation. This is referred to as Baeyer strain theory. Due to this strain, cyclopropane and cyclobutane are highly reactive and tend to open their rings.

Cyclo propane $\xrightarrow[120°C]{H_2/Ni}$ $CH_3CH_2CH_3$

Cyclo pentane $\xrightarrow[120°C]{H_2/Ni}$ No Reaction
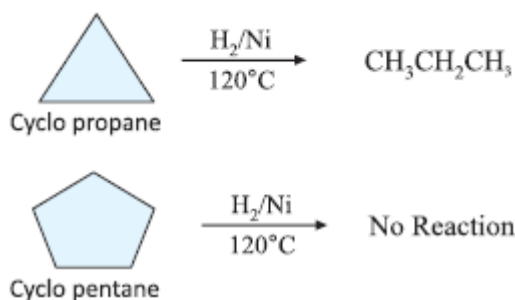
Cycloalkenes : These are isomeric to alkynes and alkadienes. Some important cycloalkenes are :

Cyclo propene   or C_3H_4 or

Cyclo butene	or	C_4H_6	or	(structure) or (square)
Cyclo pentene	or	C_5H_8	or	(structure) or (pentagon)
Cyclo hexene	or	C_6H_{10}	or	(structure) or (hexagon)

1-Methyl cyclopentene

1, 2-Dimethyl cyclohexene
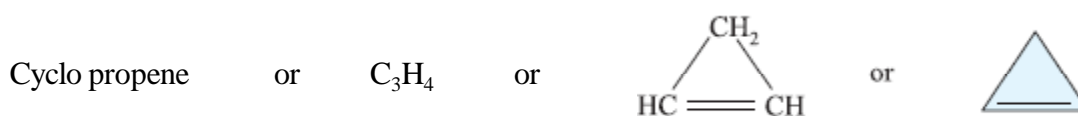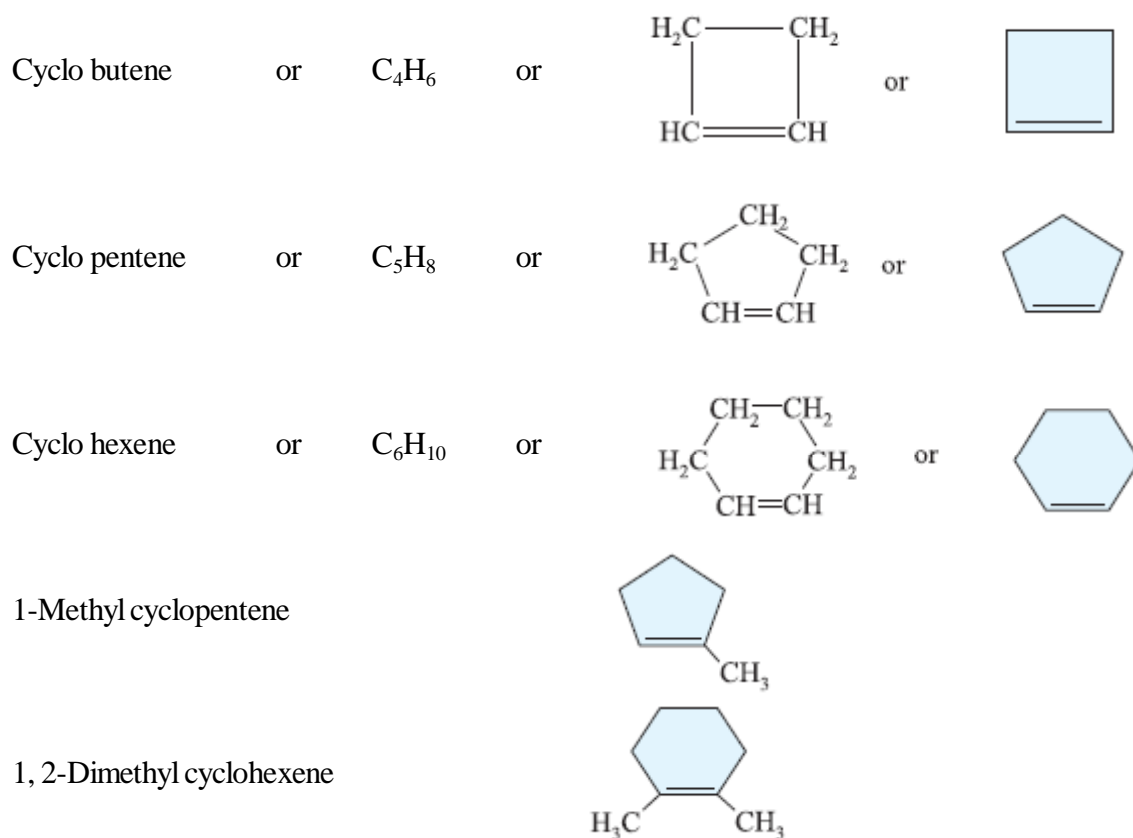
Preparation of cycloalkanes and cycloalkenes :

1. Dehalogenation of iolated dibromides :

$$BrCH_2\!-\!CH_2\!-\!CH_2Br \xrightarrow[\text{heat}]{\text{2 Na or Zn}} \triangle \; + \; 2NaBr\,(ZnBr_2)$$

$$BrCH_2\!-\!CH_2\!-\!CH_2\!-\!CH_2Br \xrightarrow[\text{heat}]{\text{2 Na or Zn}} \square \; + \; 2NaBr\,(ZnBr_2)$$
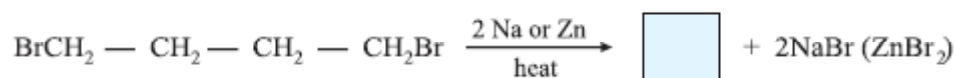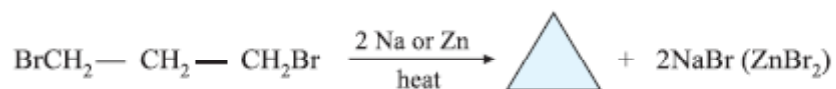
It is not a good method because of poor yield.

2. From diazomethane (CH_2N_2) :

Diazomethane or simple heating gives Carbene, $:CH_2$, which adds to the double bond of alkenes to give cyclopropane.

$$CH_2N_2 \xrightarrow{\Delta} :CH_2 + N_2$$

alkenes   carbene   cyclopropane and derivatives

cis-2-butene   cis-1, 2-Dimethyl cyclopropane

trans-2-butene   trans-1, 2-Dimethyl cyclopropane
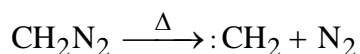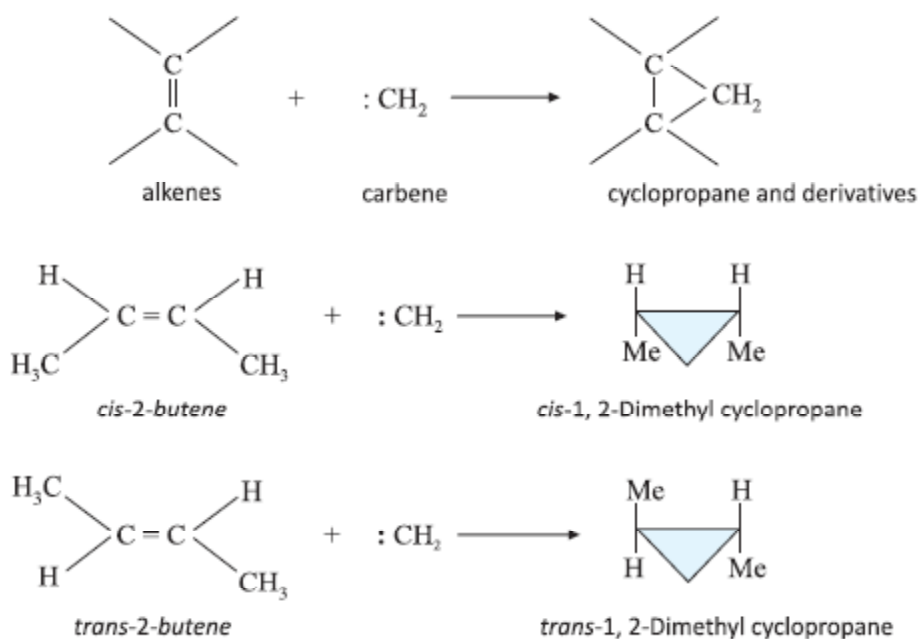
Note that the addition of $: CH_2$ (carbene) is sterospecific as 2-butene exist in *cis* and *trans* forms.

3. Simmon - Smith Reaction :

It is another method to form cyclopropane and its derivatives. Instead of diazomethane, di-iodomethane, CH_2I_2 with Zn-Cu alloy in diethyl ether is used. The rest of the reaction is same as above.
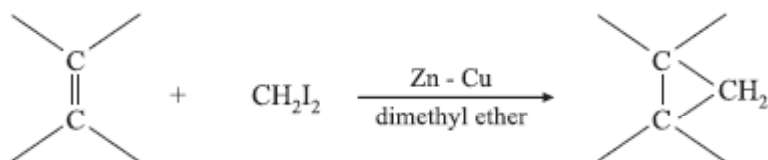
4. Heating calcium/barium salts of dicarboxylic acids :

By heating barium salts of discarboxylic acids, cyclic ketones are formed, which on Clemmensen's reduction (Zn-Hg/HCl) give cyclopentane, cyclohexanes and other higher derivatives.

Barium salt of adipic acid   Cyclopentanone   Clemmensen's Reduction   Cyclopentane

Barium salt of heptandioic acid → Cyclohexanone → Cyclohexane
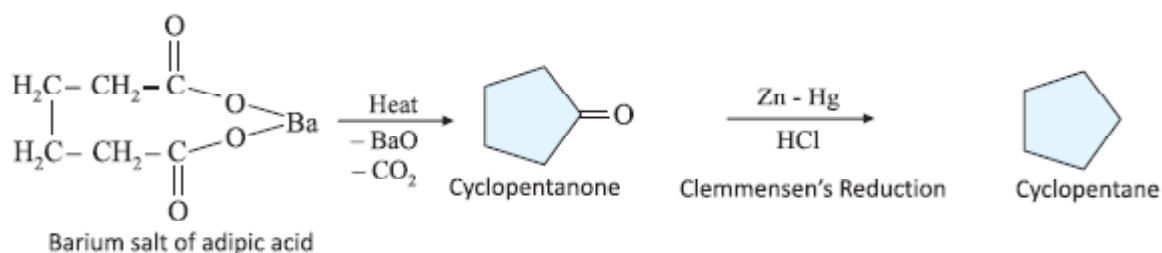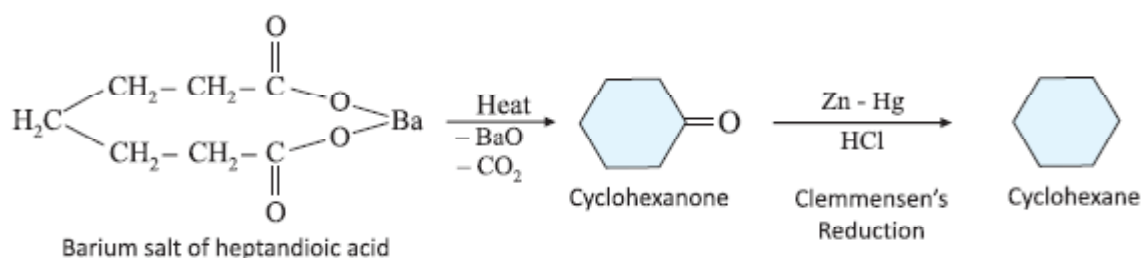
5. Hydrogenation of benzene :

Cyclohexane
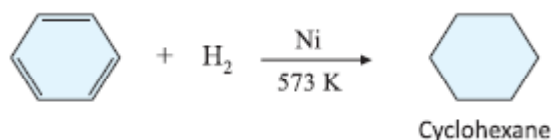
6. Diel - Alder Reaction :

It is an important reaction of conjugated dienes with double bonded compounds to form unsaturated cyclic compounds. Let us take 1, 3–Butadiene as conjugated diene and consider its reaction with some unsaturated compounds such as Ethene and Vinyl alcohol. The unsaturated compounds are called as dienophiles. This reaction proceed beacuse of formation of six membered cyclic transition state.

Cyclohexene
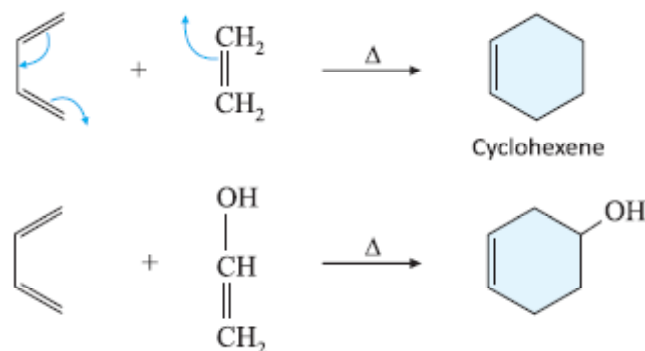
Note : (i)
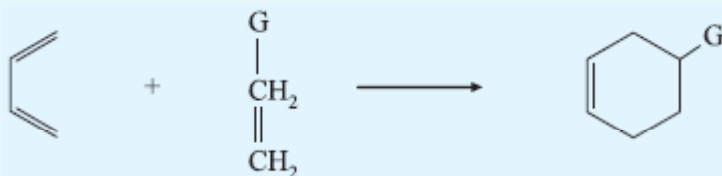
'G' is preferably an electron withdrawing group (electronegative in nature) such as $-OH$, $-NH_2$, $-CN$, $-NO_2$, etc.

(ii)   Each of the product can be hydrogenated to give a saturated compound.

Reaction of cycloalkanes :

1. Ring opening :
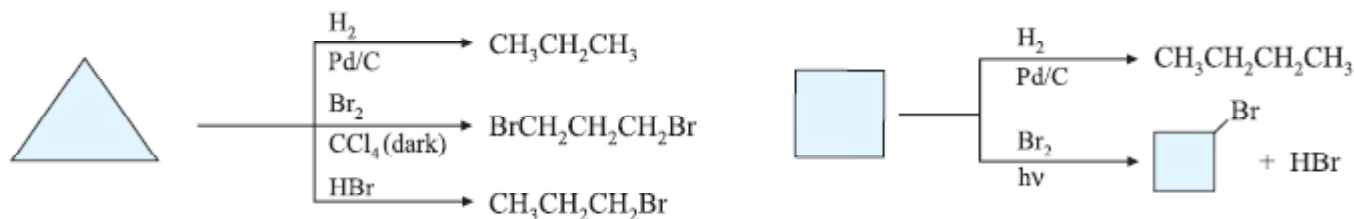
The ring of 5 carbons being stable does not open after reaction with hydrogen.

2. Chlorination :
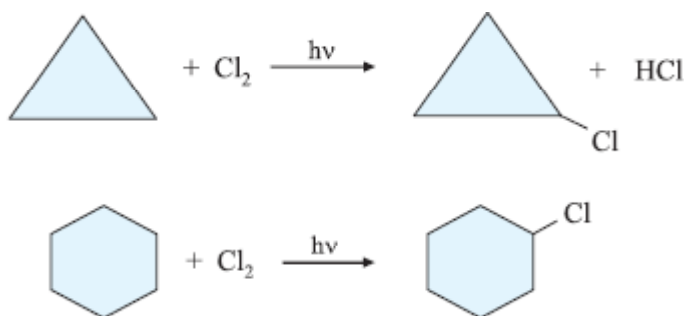
3. Oxidation :
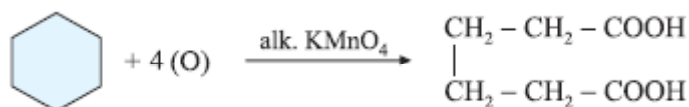
Note : Cyclobutane is opened in the presence of hydrogen and Ni. At ordinary temperatures, cyclobutanes resists the action of halogens and hydrogen halides.

Reaction of Cycloalkenes :

The cycloalkenes show the reaction of alkenes. (*Refer to the reaction of Alkenes*). For a quick review of the reactions, please go through the following page carefully. It shows all the typical reaction of alkenes taking 1 - Methylcyclopentene as the substrate.

H$_2$/Pt, Ni or Pd

Syn addition

Hydrogenation

HX(X = F, Cl, Br, I or OSO$_3$H)

Markovnikov addition

Ionic addition of HX

HBr, ROOR

Anti-Markovnikov addition

Free Radical Addition of HBr

H$_3$O$^+$/H$_2$O

Markovnikov addition

Hydration

X$_2$(X = Cl, Br)

Anti addition

Halogenation

X$_2$/H$_2$O

Anti addition, follows
Markovnikov's rule

Halohydrin Formation

Cold dil. KMnO$_4$ or

1. OsO$_4$ / 2. NaHSO$_3$

Syn Hydroxylation

KMnO$_4$,H$^+$/heat

or KMnO$_4$,OH$^-$/heat

Oxidative Cleavage

O$_3$

Zn/H$_2$O

Ozonolysis

1. Hg(OAc)$_2$/THF

2. NaBH$_4$/OH$^-$ (Markonikov's)

Oxymercuration
-demercuration

1. BH$_3$/THF

2. H$_2$O$_2$/OH$^-$

Hydroboration-oxidation
(syn & anti-Markonikov addition)

ALKADIENES   Section - 5

Alkadienes are isomers of alkynes and cycloalkenes. These are classified in three categories.

(a)   Hydrocarbons containing cumulated double bonds are called allenes or cumulated dienes.

$$CH_2 = C = CH_2 \qquad\qquad Propadiene \qquad C_3H_4$$

$$CH_2 = C = CH–CH_3 \qquad\qquad Butadiene \qquad C_4H_6$$

(b)   Those dienes which have an alternate system of double and single bonds are called conjugated dienes.

$$CH_2 = CH–CH = CH_2 \qquad 1, 3\ Butadiene$$

$$CH_2 = C–CH = CH_2$$
$$\qquad\quad |$$
$$\qquad\quad CH_3 \qquad\qquad 2\text{-Methyl-1, 3-Butadiene}$$
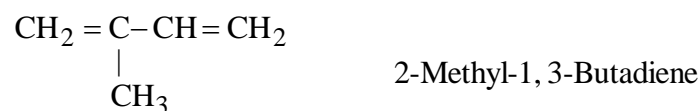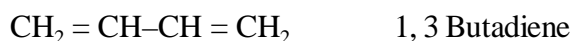
1, 3-Cyclohexadiene

(c)   In case, when two or more sp^3 hybridised carbon atoms come in between the double bonds in dienes, then they are called isolated dienes.

$$CH_2 = CH_2–\ CH_2 – CH_2 = CH_2 \qquad 1, 4\text{-Pentadiene}$$
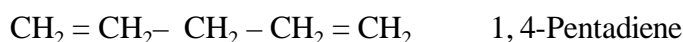
Note :   Conjugated dienes are most stable among dienes. They are stabilised due to resonance.

Preparation of Conjugate dienes :

1. From isolated dihalides

$$CH_2 - CH_2 - CH_2 - CH_2 \xrightarrow{NaNH_2} CH_2 = CH - CH = CH_2$$
$$\ \ |\qquad\qquad\qquad |$$
$$\ \ Cl\qquad\qquad\quad Cl \qquad\qquad\qquad 1, 3 \text{- Butadiene}$$

$$CH_3 - CH - CH_2 - CH_2 - CH_2 \xrightarrow{NaNH_2} CH_3 - CH = CH - CH = CH_2 + CH_2 = CH - CH_2 - CH = CH_2$$
$$\qquad\ |\qquad\qquad\qquad\ |$$
$$\qquad Cl\qquad\qquad\quad\ Cl \qquad\qquad\qquad 1, 3 \text{- Pentadiene (Major)}\qquad\qquad 1, 4 \text{- Pentadiene (Minor)}$$

2.   From isolated diols :

$$CH_3 - \underset{\underset{OH}{|}}{C}H - CH_2 - \underset{\underset{OH}{|}}{C}H_2 \xrightarrow[T=170°C]{H_2SO_4} CH_2 = CH - CH = CH_2 + CH_3 - CH = C = CH_2$$

<div align="center">1, 3 - Butadiene (Major)   1, 2 - Butadiene (Minor)</div>

$$CH_3 - \underset{\underset{OH}{|}}{C}H - CH_2 - CH_2 - \underset{\underset{OH}{|}}{C}H_2 \xrightarrow[T=170°C]{H_2SO_4} CH_3 - CH = CH - CH = CH_2 + CH_2 = CH - CH_2 - CH = CH_2$$

<div align="center">1, 3 - Pentadiene (Major)   1, 4 - Pentadiene (Minor)</div>
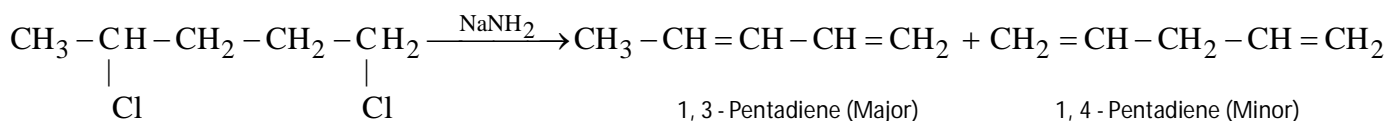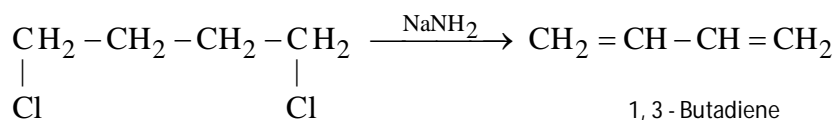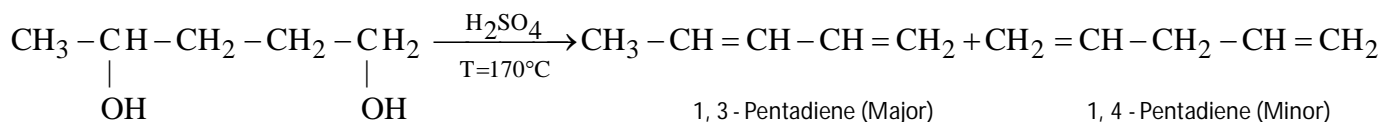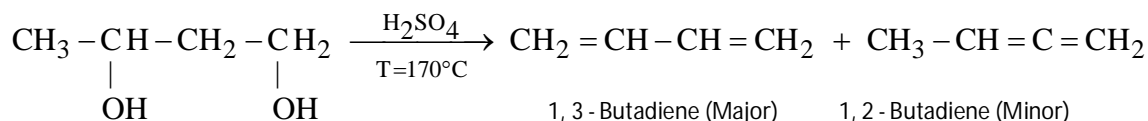
Reactions of Conjugate Dienes :

For the discussion of reactions of conjugated dienes we shall take 1, 3-Butadiene as an example.

1.   Electrophillic Addition :

1, 3-Butadiene when reacts with HCl show unusual behaviour to give mixture of two products :
3-Chloro-1-butene (1, 2-addition product) and 1-Chloro-2-butene (1, 4-addition product)

(a)   The formation of 1, 4-addition product is interesting.

$$CH_2 = CH - CH = CH_2 \xrightarrow[25°C]{HCl} CH_3 - \underset{\underset{Cl}{|}}{C}H - CH = CH_2 + CH_3 - CH = CH - CH_2Cl$$

<div align="center">(1, 2 - addition)   (1, 4 - addition)</div>
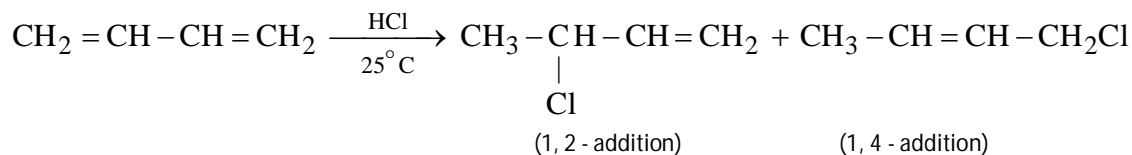
> **Note :**   Usually 1, 4-addition product is major.

(b)   Addition of HBr to 1, 3-Butadiene takes place differently at different temperatures to give 1, 2-addition and 1, 4-addition products as follows :

$$CH_2 = CH - CH = CH_2 + HBr \longrightarrow$$

(i)   At – 80°C (Low temperature) :

$$CH_3 - \underset{\underset{Br}{|}}{C}H - CH = CH_2 + CH_3 - CH = CH - CH_2Br$$
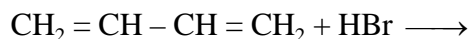
<div align="center">(1, 2 - addition)(80%)   (1, 4 - addition) (20%)</div>
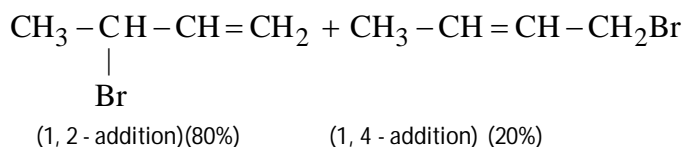
(ii)   **A 40°C (Near room temperature and above) :**

$$CH_3 - \underset{\underset{Br}{|}}{C}H - CH = CH_2 \; + \; CH_3 - CH = CH - CH_2Br$$

(1, 2 - addition)(20%)   (1, 4 - addition) (80%)
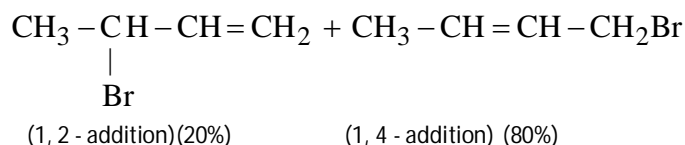
> **Note :**   At high temperatures, in case of HBr, 1, 2-addition product rearranges to give 1, 4-addition product.

(c)   Addition of Br_2 to 1, 3–Butadiene also gives a mixture of 1, 2-addition and 1, 4-addition products.

(i) $CH_2 = CH - CH = CH_2 \xrightarrow[-15°C]{Br_2} \underset{\underset{Br}{|}}{C}H_2 - \underset{\underset{Br}{|}}{C}H - CH = CH_2 \; + \; \underset{\underset{Br}{|}}{C}H_2 - CH = CH - CH_2Br$

$\left(1, 3 \text{ - Butadiene}\right)$ (1, 2 -addition) (54%)   (1, 4 - addition) (46%)

(ii) $CH_2 = CH - CH = CH_2 \xrightarrow[T > 27°C]{Br_2} 1, 4 - \text{addition is major}$
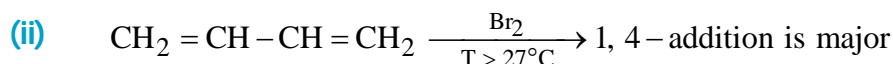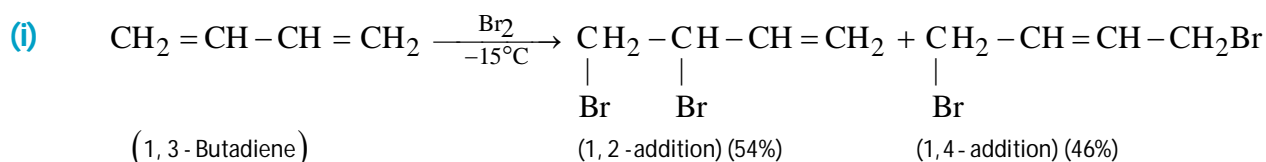
2.   Free radical addition :

In presence of perioxides, both 1, 2-addition product and 1, 4-addition products are formed. Consider addition of $BrCCl_3$ in presence of perioxide.

$$CH_2 = CH - CH = CH_2 + BrCCl_3 \longrightarrow Cl_3C - CH_2 - \underset{\underset{Br}{|}}{C}H - CH = CH_2 \; + \; Cl_3C - CH_2 - CH = CH - CH_2Br$$

(1, 2 -addition)   (1, 4 - addition)
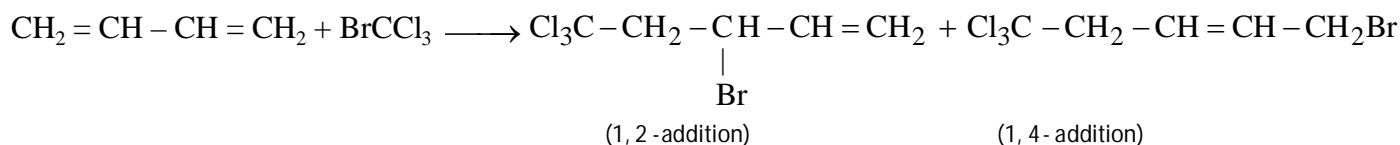
> **Note :**   Temperature dependency of products is similar to that HBr addition. Also refer to Diel - Alder reactions (diense with alkenes) in cycloalkenes.

3.   Reduction :

Catalytic hydrogenation of conjugated dienes in presence of H_2/ Li gives a mixture of 1, 2-addition and 1, 4-addition product with the 1, 4-addition products being major.

$$CH_2 = CH - CH = CH_2 \xrightarrow{H_2/Li} \overset{\overset{H}{|}}{C}H_2 - \overset{\overset{H}{|}}{C}H - CH = CH_2 \; + \; \overset{\overset{H}{|}}{C}H_2 - CH = CH - \overset{\overset{H}{|}}{C}H_2$$

Buta - 1,3 - diene   But - 1 - ene (Minor)   But - 2 - ene (Major)
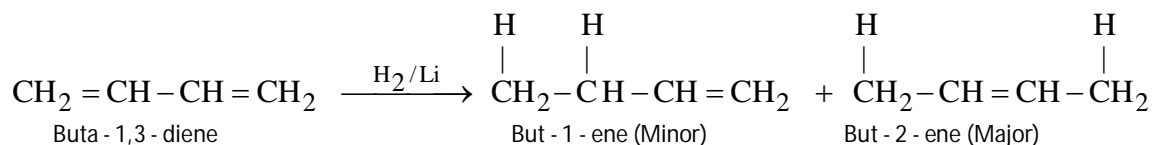
However, the chemical reduction of 1, 3-Butadiene with sodium in alcohol gives mainly the 1, 4-addition product, i.e., But-2-ene.

$$CH_2 = CH - CH = CH_2 \xrightarrow{\text{Na/alcohol}} CH_3 - CH = CH - CH_3$$

1, 3-Butadiene　　　　　　　　　　　　　　　　　　　But-2-ene
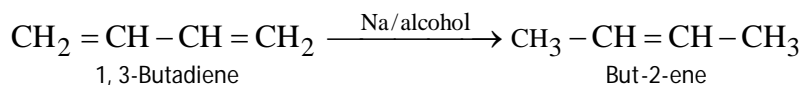
Under these conditions the isolated double bonds are not reduced. This suggests that dienes are much more reactive than simple alkenes.

4.　Polymerization :

$$n\left(CH_2 = CH - CH = CH_2\right) \xrightarrow{\text{Peroxides}} \left(-CH_2 - CH = CH - CH_2 -\right)_n$$

Buta-1, 3-diene　　　　　　　　　　　　　　　Polybutadiene
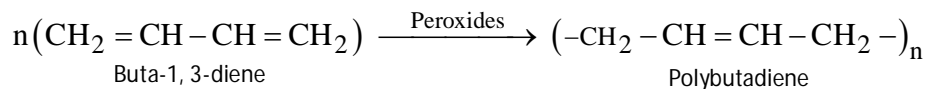
Since each repeating unit in polybutadiene contains a double bond, it may have either *cis* or *trans*-configuration. Actually the polybutadiene polymer obtained by free-radical polymerisation has *trans*-configuration.

$$n\left(\begin{array}{c} CH_3 \\ | \\ CH_2 = C - CH = CH_2 \end{array}\right) \xrightarrow{\text{Peroxides}} \left(\begin{array}{c} H_3C \qquad\quad CH_2- \\ \diagdown \qquad \diagup \\ C = C \\ \diagup \qquad \diagdown \\ -H_2C \qquad\quad H \end{array}\right)_n$$

2-Methylbuta-1, 3-diene　　　　　　　　　　　Major Product
(Isoprene)　　　　　　　　　　　　　　　　(Gutta Percha)

$$n\left(\begin{array}{c} Cl \\ | \\ CH_2 = C - CH = CH_2 \end{array}\right) \xrightarrow{\text{Peroxides}} \left(\begin{array}{c} Cl \\ | \\ -CH_2 - C = CH - CH_2 - \end{array}\right)_n$$

2-Chlorobuta-1, 3-diene　　　　　　　　　Polychloroprene
(Chloroprene)　　　　　　　　　　　　　　(Neoprene)
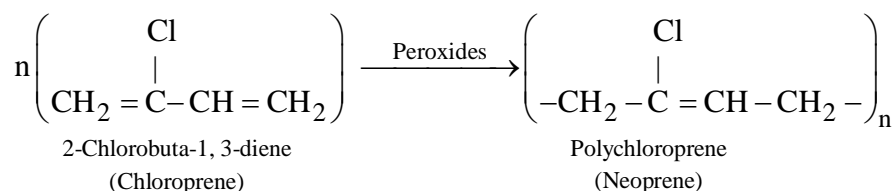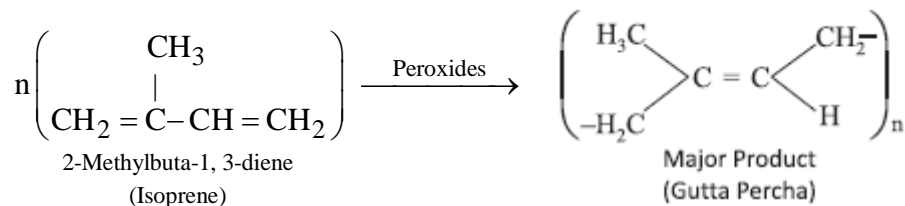
Neoprene is an important substitute for natural rubber and is superior to natural rubber in being more resistant to oil, gasoline and other organic solvents.

Illustration - 9 *Isomers A, B, C, and E have a common molecular formula C_4H_6. Identify A, B, C……as per given instructions.*

(a) *A reacts with RMgBr to give a hydrocarbon.*

(b) *B reacts with Br_2 to give a mixture of two products.*

(c) *C, an alicyclic compound, when oxidised by hot acidic $KMnO_4$, gives a dicarboxylic acid whose sodium salt on electrolysis gives an alkene, D. Also identify D.*

(d) *E is an alicyclic compound which is oxidized by hot $KMnO_4$ to give 3-Oxo-1-butanoic acid.*

SOLUTION :

C_4H_6 : can be alkyne, or alkadiene, or cycloalkene

(a) A should be terminal alkyne as it react with Grignard reagent.

(A) $CH_3CH_2C \equiv CH^{\delta+} \xrightarrow[]{\overset{\delta-}{R\,MgBr}} RH + CH_3CH_2C \equiv C-MgBr$
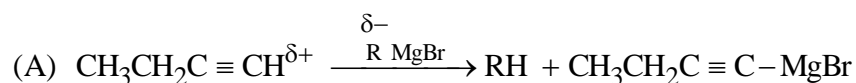
(b) B should be a conjugated diene as it gives a mixture of products.

$$\underset{(B)}{CH_2 = CH - CH = CH_2} \xrightarrow{Br_2} \underset{\underset{(1,\,2\text{ - addition})}{\overset{|\quad\;\;|}{Br\quad Br}}}{CH_2 - CH - CH = CH_2} + \underset{\underset{(1,\,4\text{ - addition})}{\overset{|\qquad\qquad\;\;|}{Br\qquad\qquad Br}}}{CH_2 - CH = CH - CH_2}$$

(c)
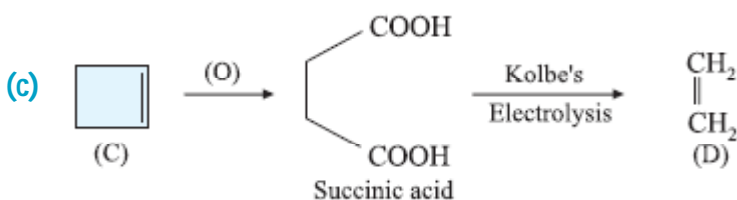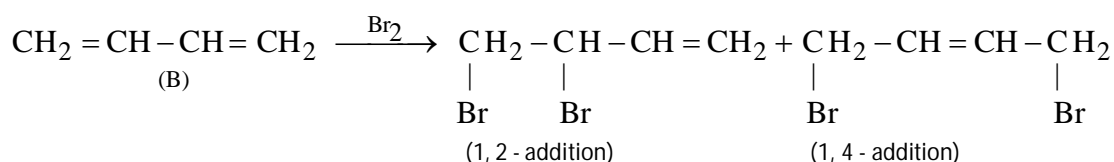
D is clearly ethene as it is the only lakene formed by Kolbe's electrolysis.

(d)
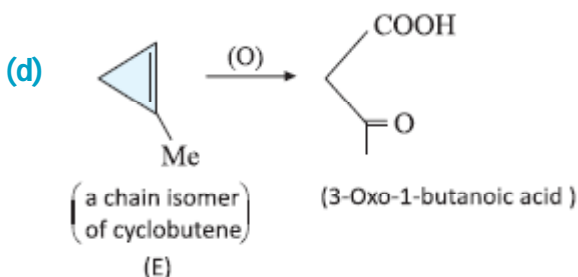
Illustration - 10 *Give the products.*

(a) $\xrightarrow{[O]}$

(b)

SOLUTION :

(a)
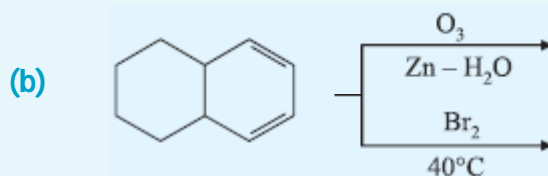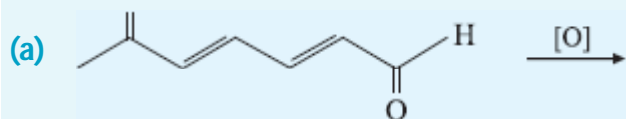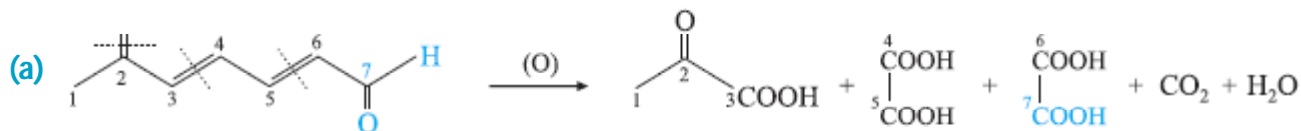
Note that aldehyde group is oxidised to acidic group
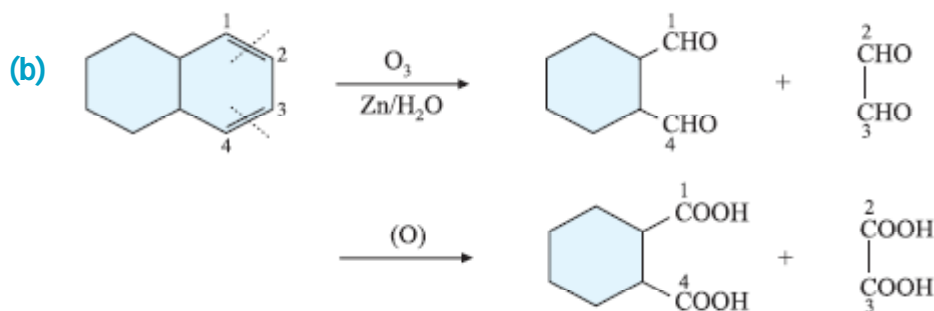
(b)

AROMATIC HYDROCARBONS

Benzene : [C_6H_6]

Structure :

Its molecular formula is C_6H_6. This implies unsaturation in benzene. It shows addition reactions : addition of 3 molecules of Hydrogen, 3 moles of Cl_2 and 3 moles of Ozone (like alkenes).

This leads to idea of three double bonds. However, benzene fails to give unsaturation test (i.e., Baeyer's test or decolouration of bromine water). Benzene also gives substitution reactions like halogenation, nitration etc. (like alkanes). On addition of H_2, benzene forms cyclohexane (a cyclic hydrocarbon) C_6H_{12}. Kekule (1865) proposed following structure the basis of the structure of cyclohexane. But this structure fails to explain ozonolysis of Xylene [$C_6H_4 - (CH_3)_2$], a derivative of benzene. So benzene is found to be a resonance hybrid of two Kekule structures :

Kekule structures   Resonance hybrid
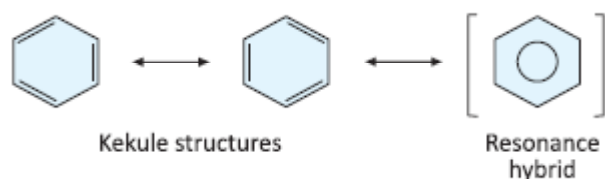
This is supported by ozonolysis of o-Xylene, which gives a mixture of Glyoxal, Methyl glyoxal, Dimethyl glyoxal which can not be explained by either of Kekule structures.

Now benzene is considered as resonance hybrid of two Kekule structures. Resonance imparts stability to the benzene due to delocalisation of π electrons over entire benzene ring . Since π electrons are not concentrated in any specific region, addtion reaction (electrophillic) are not common is benzene. However, in benzene electrophillic substitution reactions are common as they are stabilized by resonance stabilisation of intermediate Carbonium ion. When a group is introduced in benzene nucleus (ring), only one product (monosubstitued) is obtained. On the other hand, when a group of electrophillic nature is introduced in a mono-substituted benzene, three different isomers are possible.

Ortho (o)   Meta (m)   Para (p)
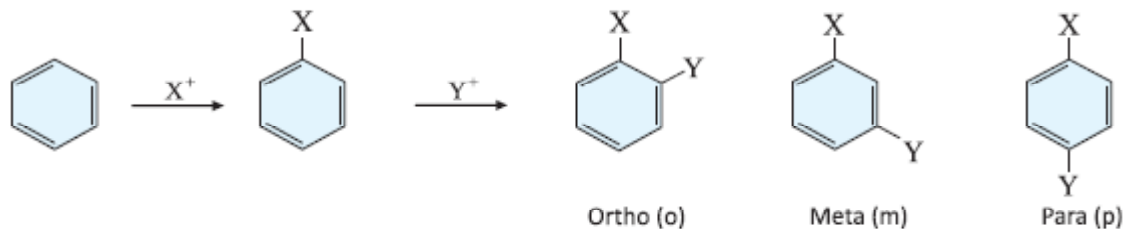
In the above sequence, nature of X (group over mono-substituted benzene) is responsible for the formation of either 'm' or 'o' & 'p' derivatives.

Directive (orienting) influence of groups :

(a) **o and p directing groups :** These groups direct the incoming group predominantly to the 'o' & 'p' position. Some important groups are :

$$-NH_2 ; -NHR ; \quad -\ddot{O}H ; \quad -\ddot{O}R ; \quad \ddot{X} ; -R$$

All of these groups exerts +M effect over benzene and tends to increase electron-density over benzene and make benzene strongly nucleophillic towards electrophiles. These groups are called activating groups. -I effect (elctronegative or electron withdrawing nature) of these groups is weaker as compared to +M effect. Halogens exerts +M effect over benzene but their -I effect is very powerful. Though they are o and p directing (+ M effect) but are de-activating in nature and hence it is difficult to carry out electrophillic substitution in halo benzenes. Alkyl group (R) are o and p directing due to hyperconjugation (to be discussed later).

(b) **m-directing groups :** These groups direct the incoming groups predomintly to m-positions. Some of the important groups are :

$$\overset{O}{\underset{\parallel}{-C}}-OH ; -\overset{OH}{\underset{\underset{O}{\parallel}}{S}}-O ; \overset{R}{\underset{\mid}{C}}=O ; -\overset{H}{\underset{\mid}{C}}=O ; -NO_2 ; -CCl_3$$
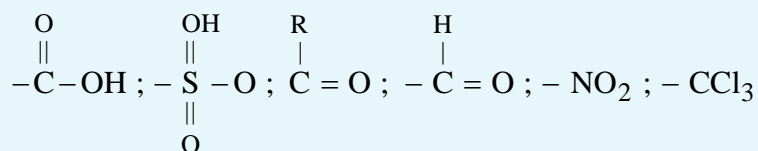
All m-directing groups, (except –CCl$_3$) either possess a positive charge or the key atom of substituents has an electronegative atom linked by a multiple bond. The benzene nucleus containing these groups undergo strong –M, –I, effect such that the displacement of electron takes place away from the benzene ring. These groups tends to deactivate the benzene ring and hence makes it less nucleophillic towards electrophiles. These are called as de-activating groups. Benzene having these groups will have greater difficulty in electrophillic substitution reactions.

Preparation of Benzene :

1.   Decarboxylation of Sodium Benzoate :

2.   From Chlorobenzene :
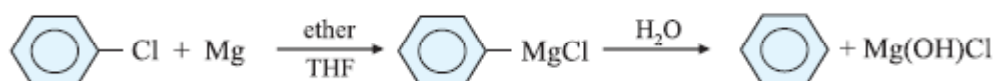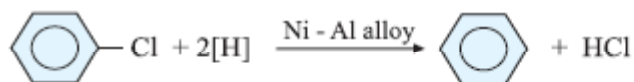
3. From Phenol :
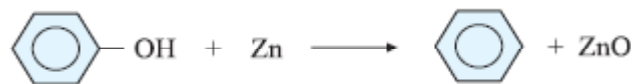
4. From Sulphonic Acid :

5. Synthesis :

$$3C_2H_2 \xrightarrow{\text{Red hot Fe tube}} C_6H_6$$
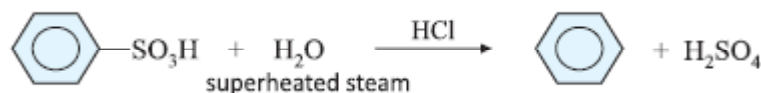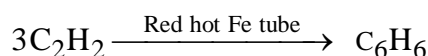
6. From Benzene Diazonium Chloride :

7. Manufacture :

(a) **n-hexane :**

$$CH_3(CH_2)_4 CH_3 \xrightarrow[600°C, \text{ pressure}]{Al_2O_3 - Cr_2O_3}$$
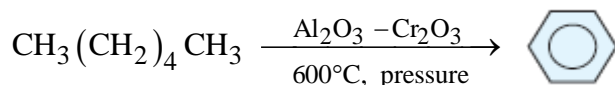
This is known as Hydroforming or catalytic Reforming or aromatisation

(b) **Coal Tar :**

$$\text{Dry distillation} \xrightarrow{} \text{COAL-TAR} \xrightarrow[\text{Distillation}]{\text{fraction}} \text{Ligt-oil-fraction} \xrightarrow{}$$
of wood   80 – 170°C
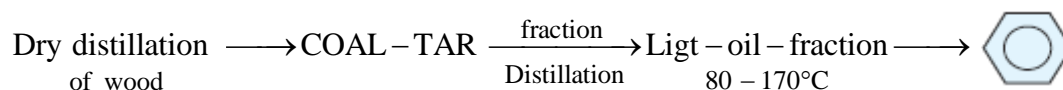
Physical properties of Arenes :

1. Benzene and its homologues containing upto eight carbon atoms are colourless liquids with characteristic smell.

2. Due to large hydrophobic hydrocarbon part, arenes are not soluble in water but are soluble in organic solvents.

3. The melting points and boiling points of arenes increase with increase in the molecular size due to a corresponding increase in the magnitude of van der Waal's forces of attraction. Amongst isomeric arenes, i.e., o-, m- and p-Xylenes, the p-isomer is most symmetrical, has the highest melting point.

Reaction of Benzene :

When benzene is treated with bromine in carbon tetrachloride in the dark or with aqueous potassium in the dark or with aqueous potassium permanganate or with dilute acids, none of the expected reactions (addition reactions) occurs. Benzene does add hydrogen in the presence of finely divided nickel, but only at high temperature and under high pressures.

Benzene does react with bromine except in the presence of catalyst such as ferric bromide. The interesting aspect of this reaction is that benzene show substitution not addition (like alkenes).

Substitution :

$$C_6H_6 + Br_2 \xrightarrow{\text{FeBr}_3} C_6H_5Br + HBr$$
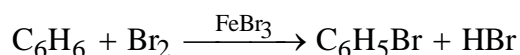
Addition : Benzene does not show addition reaction of Br_2 or H_2 at all under normal conditions.

When benzene reacts with bromine, only one monobromobenzene is formed. That is, only one compound with the formula C_6H_6Br is found among the products. Similarly, when benzene is chlorinated, only one monochlorobenzene results.

Two possible explanations can be given for these observations. The first is that only one of the six hydrogen atoms in benzene is reactive toward these reagents. The second is that all six hydrogen atoms in benzene are equivalent, and replacing any one of them with a substituent results in the same product. From the concept of Resonance we know all six carbon atom form equivalent C – C and C – H bonds. Hence this is the correct explanation.

Structure of Benzene

The fact that the bond angles of the carbon atoms in the benzene ring are all 120° strongly suggests that the carbon atoms are sp^2 hybridized. If we accept this suggestion and construct a planar six-membered ring from sp^2 carbon atoms, a representation like and shown in figure emerges. In this model, each carbon is sp^2 hybridized and has a p-orbital available for overlap with p-orbitals of its neighbouring carbons. If we consider favaourble overlap of these p-orbitals all around the ring, the result is the model shown in figure.

(a)   Six sp^2-hybridized carbon atoms are joined in a ring (each carbon also bears a hydrogen atom). Each carbon has a p-orbital with lobes above and below the plane of the ring. Fig.(1)

Fig. (1)
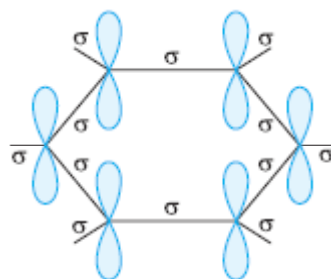
(b)   Overlap of the p-orbitals forming $pi(\pi)$ bonds around the ring results in the delocalisation of $pi(\pi)$ electrons on the ring. [Refer to Fig.(2), (3), (4)]

Fig. (2)

Fig. (3)

Fig. (4)

(electron cloud)   (Resonance hybrid)
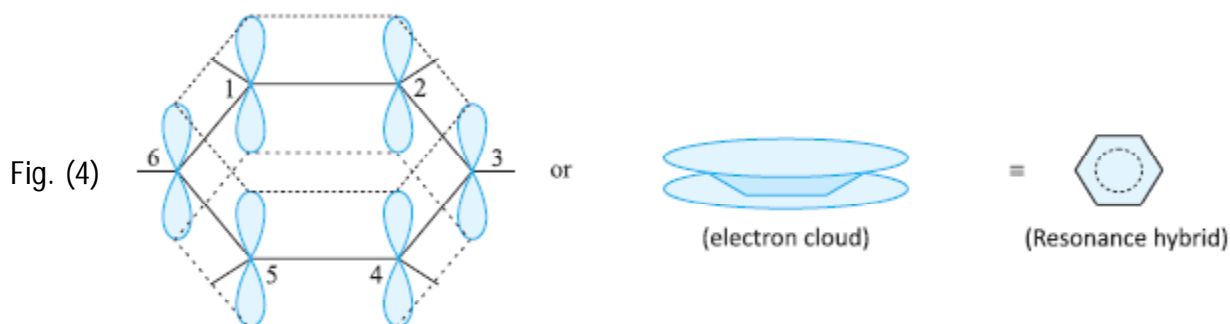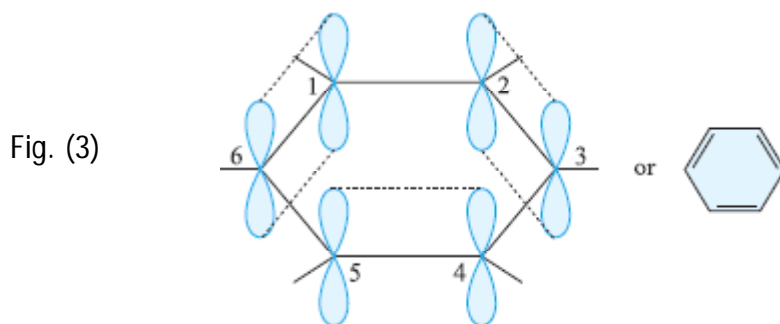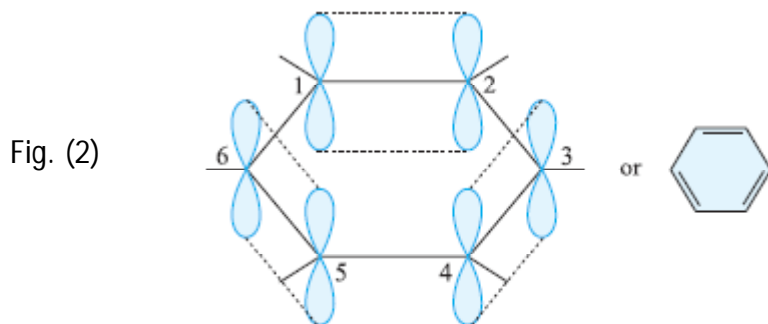
The six π electrons are thus delocalised and can move freely about the six carbon nuclei, instead of any two as shown in figure (4). The delocalised π electron cloud is attracted more strongly by the nuclei of the carbon atoms than the electron cloud localised between two carbon atoms. Therefore, presence of delocalised π electrons in benzene makes it more stable than the hypothetical cyclohexatriene. X-Ray diffraction data reveals that benzene is a planar molecule. It also indicates that all the six C – C bond lengths are of the same order (139 pm) which is intermediate between C – C single bond (154 pm) and C – C double bond (133 pm). This absence of pure double bond in benzene accounts for the reluctance of benzene to show addition reactions under normal conditions, thus explaining the unusual behaviour of benzene.

1.   Addition of Hydrogen (H_2) :

2.   Ozonolysis :

$$\text{Benzene} + 3O_3 \xrightarrow{\text{Zn/H}_2\text{O}} 3\left[\text{OHC} - \text{CHO}\right]$$
Glyoxal
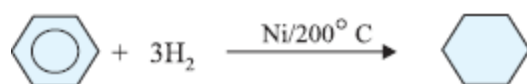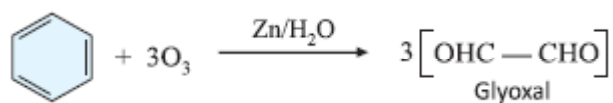
3.   Oxidation :

Benzene is unreactive towards even strong oxidising agents such as : $KMnO_4/K_2Cr_2O_7$. However in drastic conditions, it can be oxidised slowly to CO_2 and H_2O. It can be burned (i.e., combustion) to give luminous and smoky flame.

(a)   Controlled oxidation with air :

Benzene on oxidation with air at 773 K in presence of V_2O_5 as catalyst gives Maleic anhydride.

$$\text{Benzene} + \frac{9}{2}O_2 \xrightarrow[-2CO_2, \ -H_2O]{V_2O_5, \ 773 \ K} \begin{bmatrix} \text{CHCOOH} \\ \| \\ \text{CHCOOH} \\ \text{Maleic acid} \end{bmatrix} \xrightarrow[-H_2O]{\Delta} \begin{matrix} \text{CHCO} \\ \| \quad \quad \diagdown O \\ \text{CHCO} \diagup \end{matrix}$$
Maleic anhydride
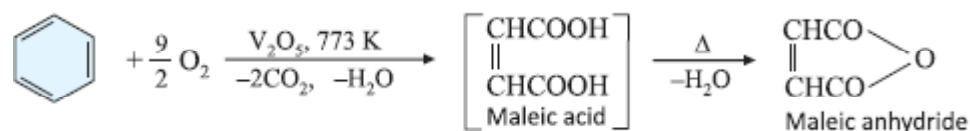
(b)   Oxidation of alkyl benzene :

$$\text{C}_6\text{H}_5-\text{R} \xrightarrow[\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}^+]{(O)} \text{C}_6\text{H}_5-\text{COOH}$$
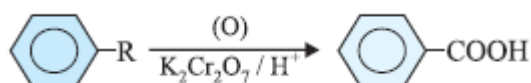
Note :   If R is a 3° alkyl group, then it resists oxidation the benzene ring is destroyed.

3.   Substitution Reactions :

Most important reactions of benzene are electrophillic substitution reactions. These are also denoted as S_E reactions.

Aromatic carbocation
(Arenium ion)

Resonance stabilisation of intermediate carbocation

Resonance hybric

$$+ \ HCl + AlCl_3$$
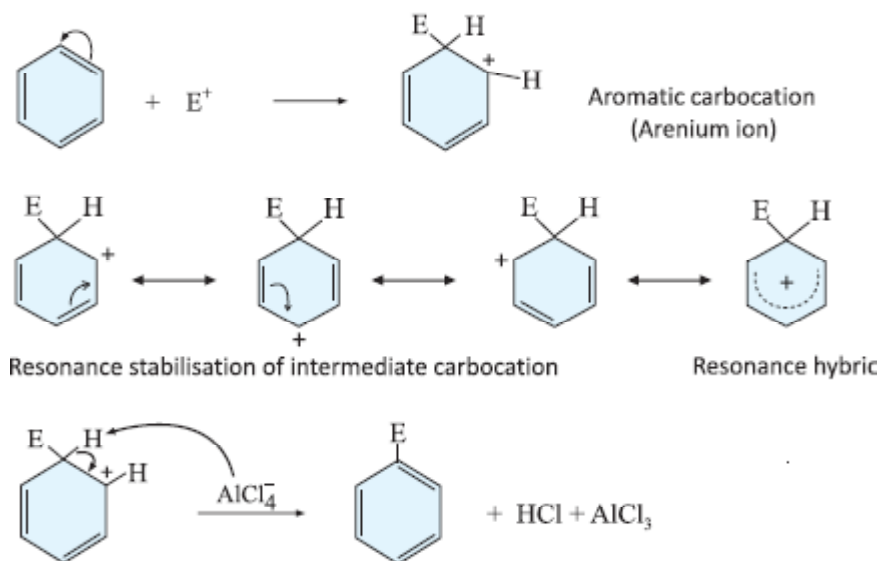
Elecrophiles :

Cl^+ (Chloronium ion), $\overset{+}{N}O_2$ (Nitronium ion), SO_3 (Sulphur trioxide), $\overset{+}{R}$ (Carbonium ion), $R-C \equiv \overset{+}{O}$ (Acylium ion).

(a)   Halogenation :

$$FeCl_3 + Cl_2 \longrightarrow FeCl_4^- + Cl^+$$
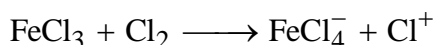
Note :   **(i)**   In iodination, oxidising agents like HNO_3 or HIO_3 are used to oxidise HI, a reducing agent.
        (ii)   In presence of sunlight and absence of halogen carriers (i.e., $AlCl_3$, $FeBr_3$, etc), benzene adds three molecules of chlorine to form Benzene hexachloride (BHC) or Gammexane.

$$C_6H_6 + 3Cl_2 \xrightarrow{h\nu} C_6H_6Cl_6$$
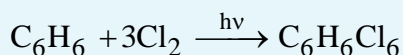
It may be noted that this is an addition reaction, not a substitution reaction.

(b)   Nitration :

$$\underset{\substack{\text{Base} \qquad \text{Acid} \\ \text{(Nitrating mixture)}}}{HNO_3 + H_2SO_4} \longrightarrow HSO_4^- + \underset{\substack{| \\ H}}{H\overset{+}{O}-NO_2} \longrightarrow NO_2^+ + H_2O$$

(c)   Sulphonation :

$$H_2S_2O_7 \longrightarrow \underset{\text{electrophile}}{SO_3} + H_2SO_4$$
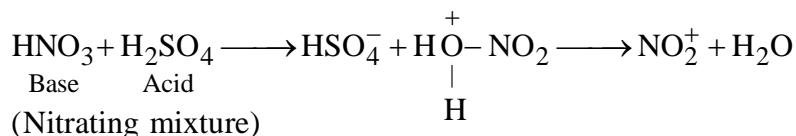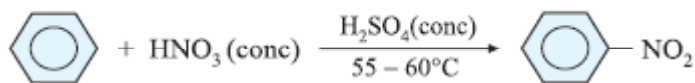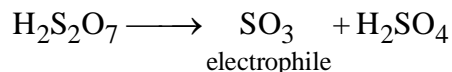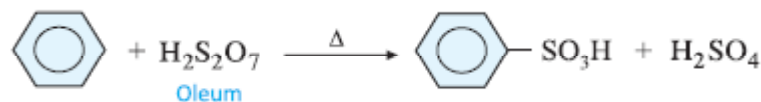
(d)   Introduction of alkyl and acyl groups in presence of Catalysts : $AlCl_3$, $FeCl_3$, $SbCl_3$ (acting as Lewis acids) or protonating agents like HF, H_2SO_4, H_3PO_4 etc. These are known as Friedal Craft reactions.

(i)   Alkylation :

$$RCl + AlCl_3 \longrightarrow AlCl_4^- + \underset{\text{Electrophile}}{R^+} \quad \text{(alkyl carbonium)}$$
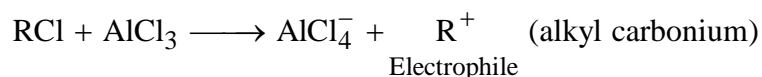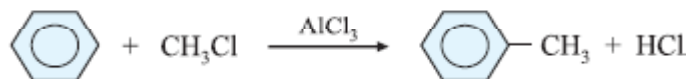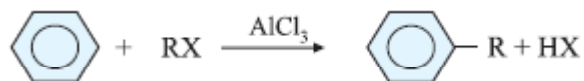
Note :   The above reaction can be achieved with :

(a)   An alcohol in HF or dil H_2SO_4 **(b)**   An alkenne in HF or dil. H_2SO_4 (at low temperature)
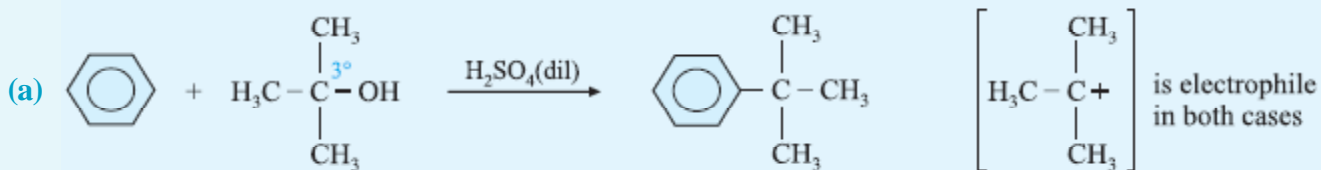
Obseve that $3°$ carbon is attached to the ring.

While during alkylation, we expect formation of polyalkylated products as alkyl groups are *o-* and *p*-directing and activating

---

(ii)   Acylation :

$$RCOCl + AlCl_3 \longrightarrow \overset{\overset{\textstyle O}{\textstyle \|}}{R-C} + AlCl_4^-$$
<center>+</center>
<center>Acylium ion is Electrophile</center>
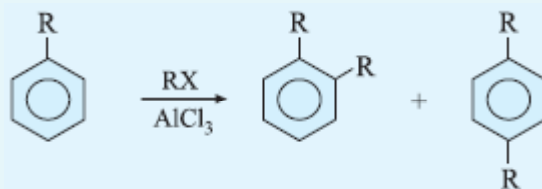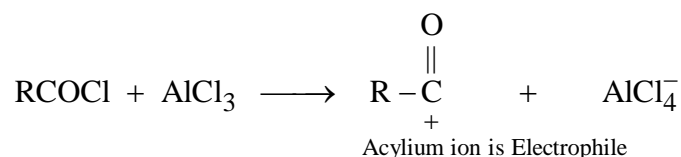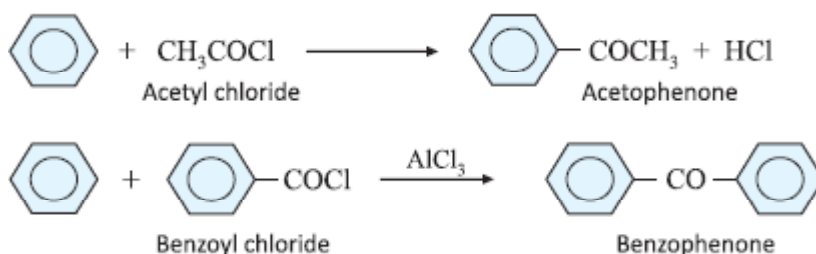
The above two reaction are called as Acctylation and Benzoylation respectively.

Some Friedal Craft acylation are shown below :
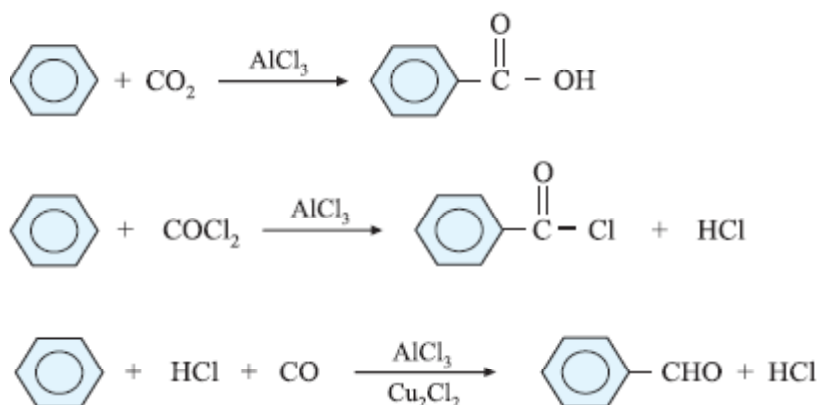
The above reaction is also known as Gatterman - Koch reaction.

Note : **(i)** Aryl and vinylic halides cannot be used in Friedal craft reactions as they do not form carbocations easily.
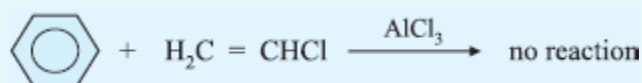
(ii) In substituted benzenes, Friedal Craft reactions gives poor yield when electron withdrawing (de-activating) groups are present on the ring. These include :

$$-NO_2, \ CN^-, \ -COOH, \ -\overset{\overset{\displaystyle O}{\displaystyle \|}}{C}-R, \ -CCl_3, \ -SO_3H$$
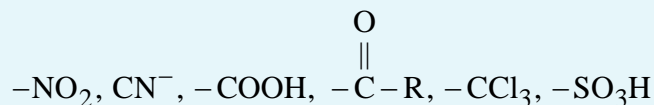
(iii) In Friedal craft alkylation. most stable carbocation (from alkyl halide or alkene) determines the final substitution product.
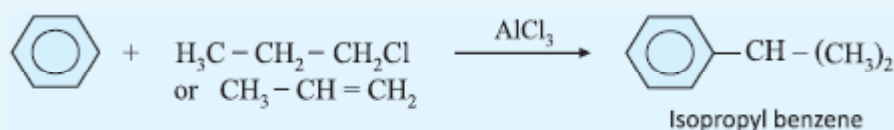
It does not give n–propyl benzene since $CH_3 - \overset{+}{C}HCH_3$, being a 2° carbocation is more stable than $CH_3CH_2\overset{+}{C}H_2$ (1°).

$$CH_3CH_2CH_2Cl \xrightarrow{AlCl_3} \underset{1°}{CH_3CH_2\overset{+}{C}H_2} \xrightarrow[Shift]{H^- \text{ (hydride)}} \underset{2°}{CH_3 - \overset{+}{C}H - CH_3}$$
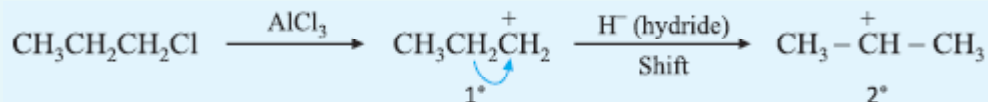
* The detailed mechanism of SE reaction will be discussed later in the chapter "Organic Concepts".

(iv)   Intramolecular Friedal Craft reactions of β- & -γ alkyl alkanoic acid or alkanoyl chlorides give cyclic products.

α - tetralone

+ HCl

4.   Dehydrogenation :

Phenyl radical

$$2C_6H_5^{\bullet} \longrightarrow C_6H_5 - C_6H_5 \quad \left[\text{} \right]$$

Diphenyl (biphenyl)

Toluene : $- CH_3$
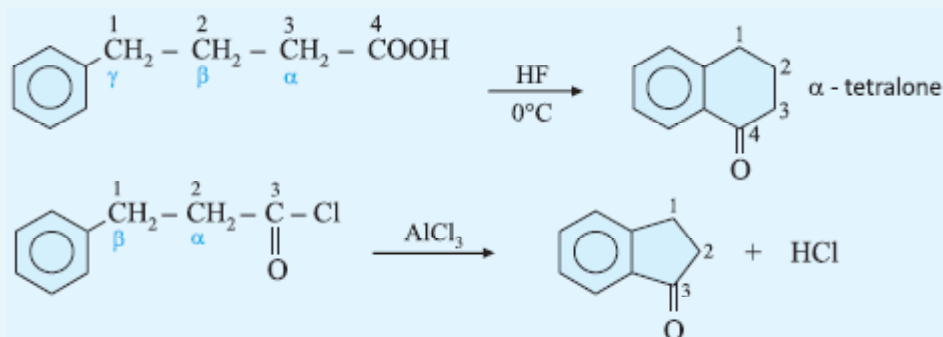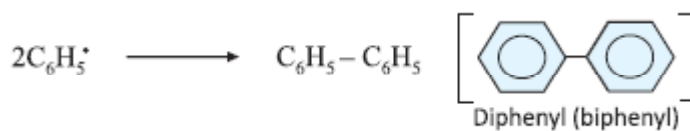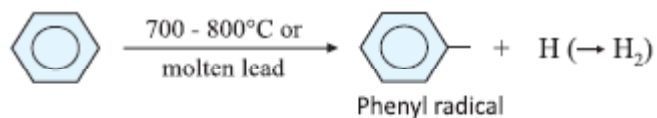
Preparation of Toluene :

1.   Friedal craft alkylation :

2. From dialkyl cuprates :

$$\left(CH_3\right)_2 CuLi \ + \ C_6H_5I \ \longrightarrow \ C_6H_5-CH_3 \ + \ LiI \ + \ CH_3Cu$$

Reactions :

1. Oxidation :

(a)

Benzoic acid

(b)

Benzaldehyde
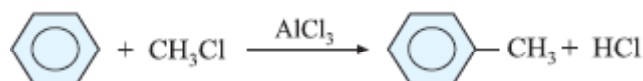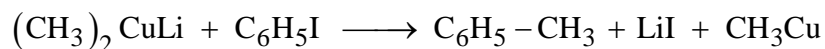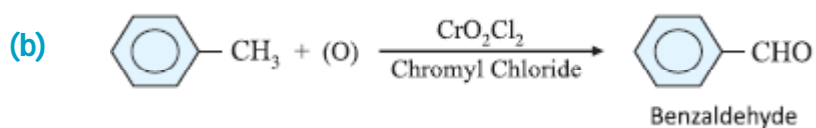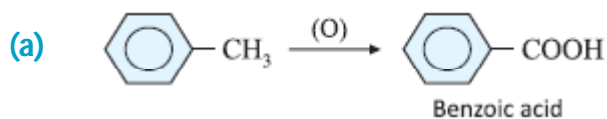
This is also known as Etard reaction.

2. Substitution :

(a) **Side chain substitution :**

(b) CH_3 group being *o* and *p* directing directs incoming electrophile to *o* and *p* position :
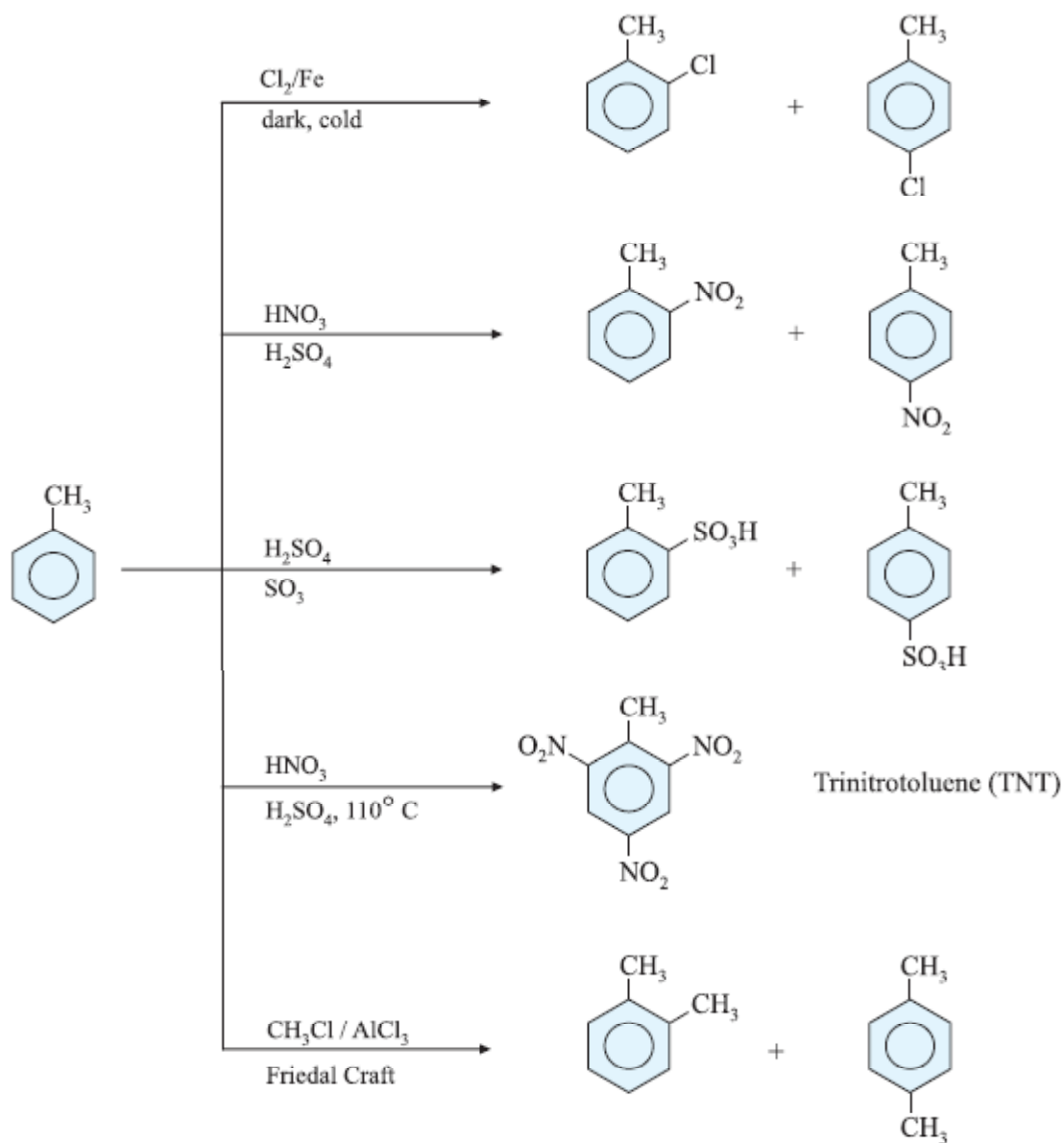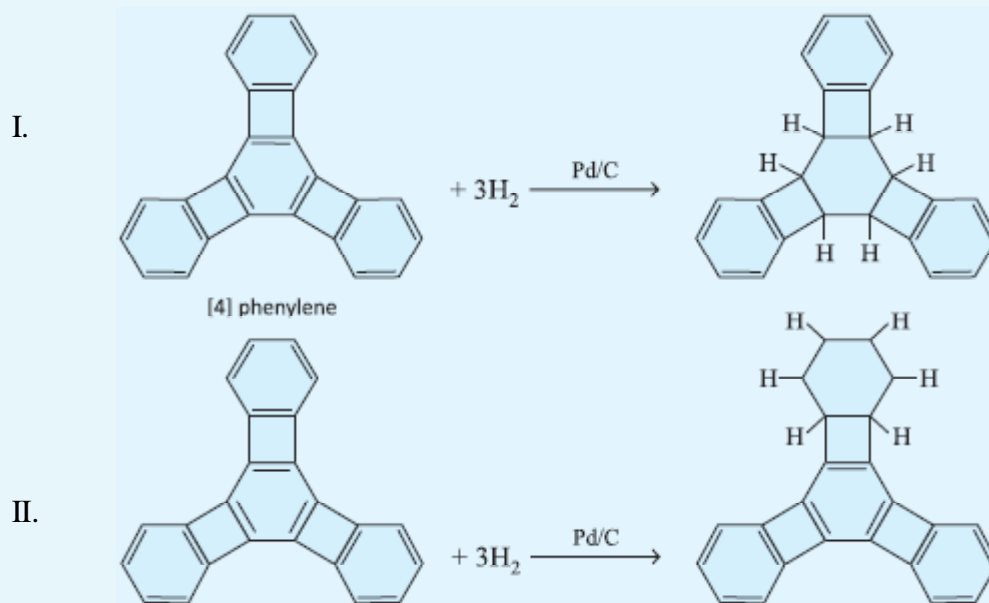

3. Addition Reactions :

Methyl Cyclohexane
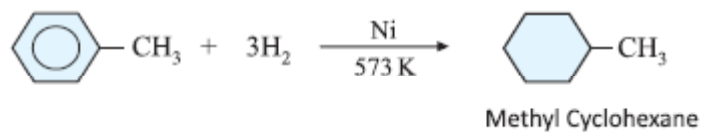
Illustration - 11 *One of the benzene ring of [4] phenylene undergoes catalytic hydrongation readily under conditions usually used for ordinary alkenes, but the other benzene ring do not. Identify which of these two reaction correctely represent product of hydrogenation of [4] phenylen ?*
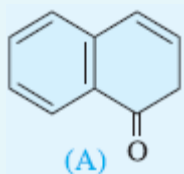
I.

[4] phenylene

$+ 3H_2 \xrightarrow{\text{Pd/C}}$

II.

$+ 3H_2 \xrightarrow{\text{Pd/C}}$

(A) *Only I*   **(B)** *Only II*   **(C)** *Both I and II*   **(D)** *None*

SOLUTION

Reaction I correctly represent product of hydrogenation of [4]-phenylen beacuse of loss in anti-aromatic characters of all four memebered rings.

Illustration - 12 *Which is the major product of the following intramolecular F.C. acylation reaction ?*

(A)　　　(B)　　　(C)　OH　　　(D)
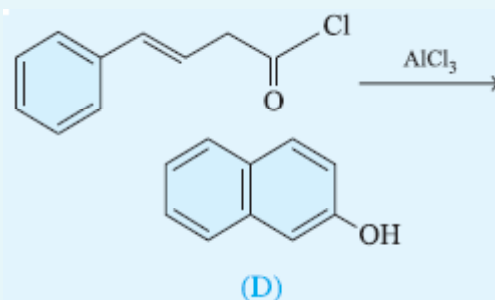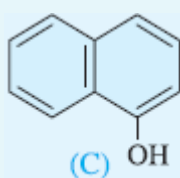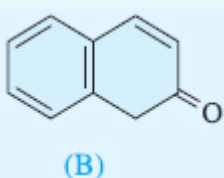
SOLUTION

Enolic form is more stable than keto form due to more aromatic characters in enolic form.
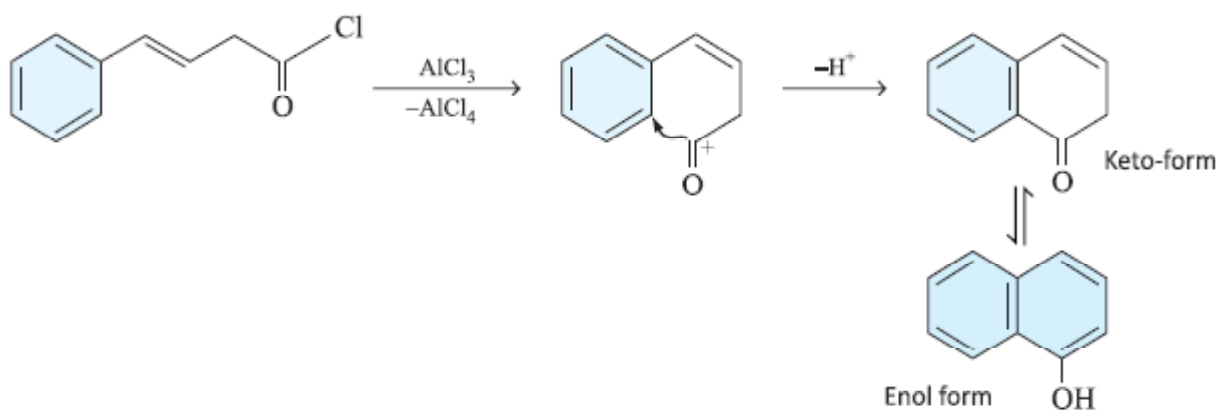
NOW ATTEMPT IN-CHAPTER EXERCISE-F BEFORE PROCEEDING AHEAD IN THIS EBOOK

SUBJECTIVE SOLVED EXAMPLES

Example - 1 *Give the structure of A, B and C (explanation are not required) :*

(i) *A (C_4H_8) which adds on HBr in the presence and in the absence of peroxide to give same product, C_4H_9Br*

(ii) *B (C_4H_8) which when treated with H_2O/H_2SO_4 gives $C_4H_{10}O$ which cannot be resolved into optical isomers.*

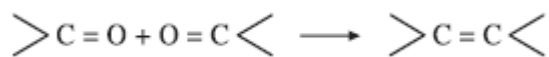**(iii)** *C (C_6H_{12}), an optically active hydrocarbon which on catalytic hydrogenation gives an optically inactive compound C_6H_{14}.*

SOLUTION :

(i) A : $CH_3CH = CHCH_3$ symmetric alkenes give same product.

(ii) B : $CH_3 - \underset{\underset{CH_3}{|}}{C} = CH_2 \xrightarrow[H^+]{H_2O} CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}} - CH_3$; optically inactive (No chiral centre)

(iii) C : $CH_3 - \underset{\underset{C_2H_5}{|}}{\overset{\overset{H}{|}}{C^*}} - CH = CH_2$ (active) $\xrightarrow[\Delta]{H_2/Pt} CH_3 - \underset{\underset{C_2H_5}{|}}{\overset{\overset{H}{|}}{C}} - C_2H_5$

(* : Chiral centre)

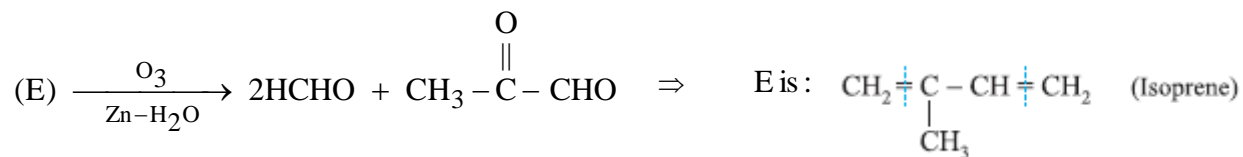optically inactive (No chiral centre)

Example - 2 *An organic compound E (C_5H_8) on hydrogenation gives compound F (C_5H_{12}). Compound E on ozonolysis gives formaldehyde and 2-ketopropanal. Deduce the structure of compound E.*

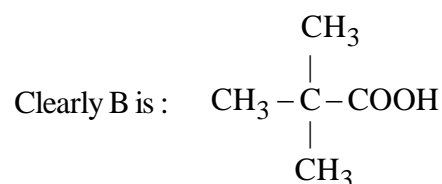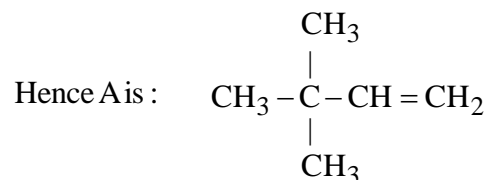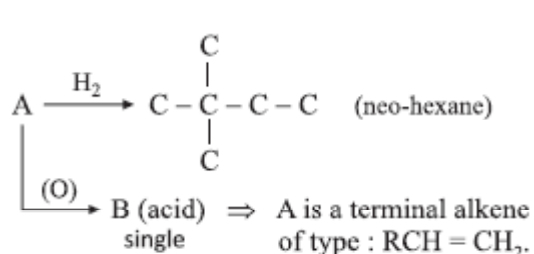**SOLUTION :** In such questions, by working backwards we join :

$$\begin{array}{c}>\end{array}C = O + O = C\begin{array}{c}<\end{array} \longrightarrow \begin{array}{c}>\end{array}C = C\begin{array}{c}<\end{array}$$

Note : Since 2-ketopropanal has two keto groups, hence there must be 2 moles of HCHO.

(E) $\xrightarrow[Zn-H_2O]{O_3}$ 2HCHO + $CH_3 - \overset{\overset{O}{||}}{C} - CHO$ $\Rightarrow$ E is : $CH_2 \vdots C - CH \vdots CH_2$ (Isoprene) with CH_3 branch
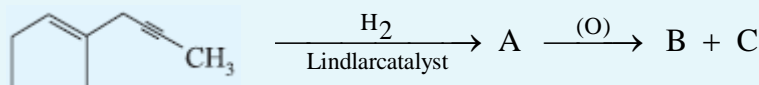
Example - 3   *The hydrocarbon, A adds one mole of hydrogen in the presence of a platinum catalyst to form neo-hexane. When A is oxidised vigorously with $KMnO_4$, a single carboxylic acid, B is isolated. Give the structures of A and B.*
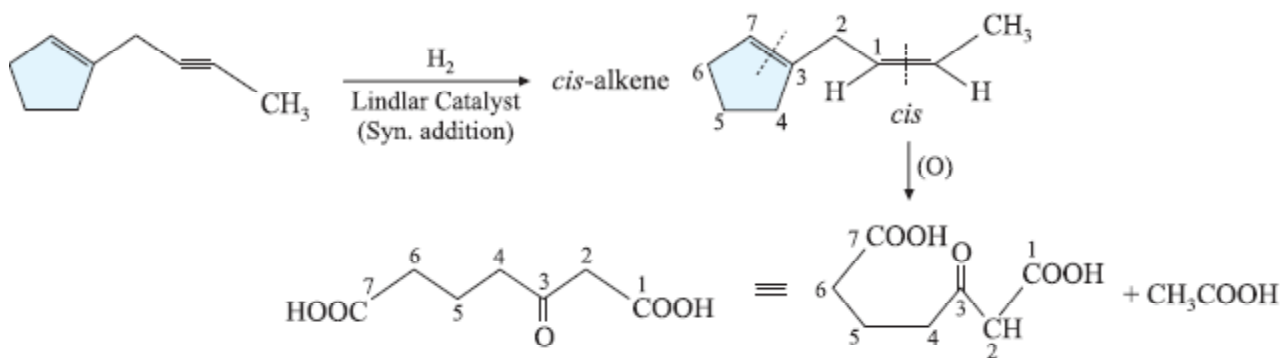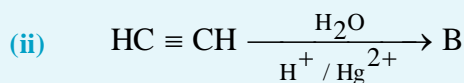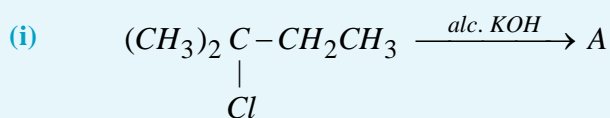
SOLUTION :

$$A \xrightarrow{H_2} C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-C-C \quad \text{(neo-hexane)}$$

$$A \xrightarrow{(O)} \underset{\text{single}}{\text{B (acid)}} \Rightarrow \begin{array}{l}\text{A is a terminal alkene}\\ \text{of type : } RCH = CH_2.\end{array}$$

Hence A is :
$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH = CH_2$$

Clearly B is :
$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - COOH$$

Example - 4   *What are product A, B and C in the following rection ?*

$$\xrightarrow[\text{Lindlarcatalyst}]{H_2} A \xrightarrow{(O)} B + C$$

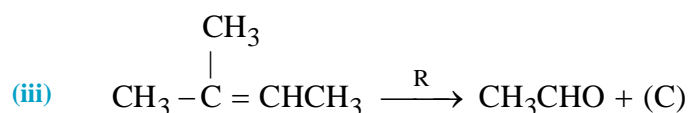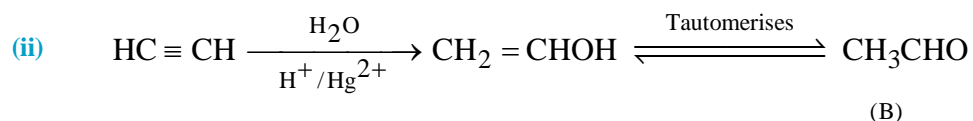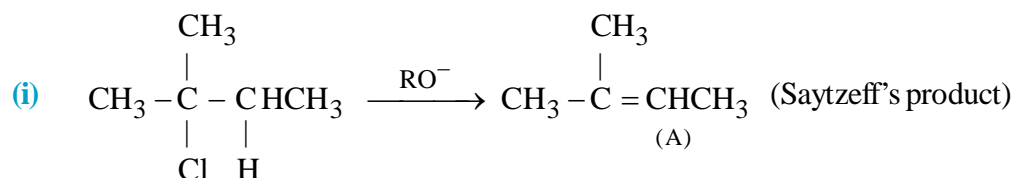**SOLUTION :**   Visualise the structure of given compound as follows :

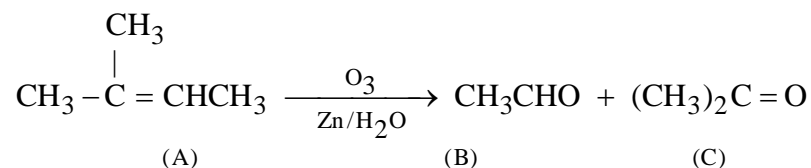**Example - 5**   *Identify the products A, B and C and the reagent R in the following reactions :*
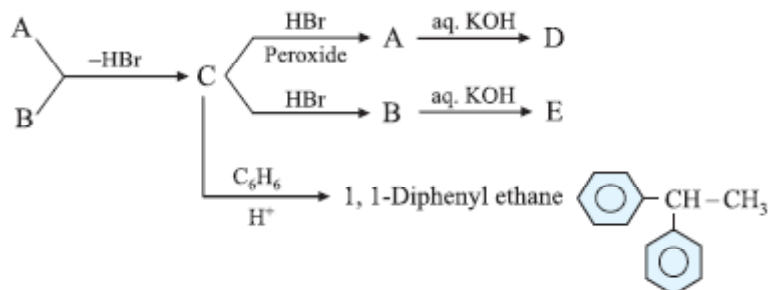
(i) $(CH_3)_2\, C - CH_2CH_3 \xrightarrow{alc.\ KOH} A$
$\qquad\qquad \underset{Cl}{|}$

(ii) $HC \equiv CH \xrightarrow[H^+ / Hg^{2+}]{H_2O} B$

(iii) $A \xrightarrow{R} B + C$

SOLUTION :

(i)
$$CH_3 - \underset{\underset{H}{\overset{\displaystyle |}{\overset{\displaystyle Cl}{|}}}}{\overset{\overset{\displaystyle CH_3}{|}}{C}} - CHCH_3 \xrightarrow{RO^-} CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CHCH_3 \quad \text{(Saytzeff's product)}$$
(A)

(ii)
$$HC \equiv CH \xrightarrow[H^+/Hg^{2+}]{H_2O} CH_2 = CHOH \underset{\text{Tautomerises}}{\rightleftharpoons} CH_3CHO$$
(B)

(iii)
$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CHCH_3 \xrightarrow{R} CH_3CHO + (C)$$

R is clearly O_3/Zn-H_2O and (C) is acetone (CH_3COCH_3)

$$\underset{(A)}{CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CHCH_3} \xrightarrow[Zn/H_2O]{O_3} \underset{(B)}{CH_3CHO} + \underset{(C)}{(CH_3)_2C = O}$$
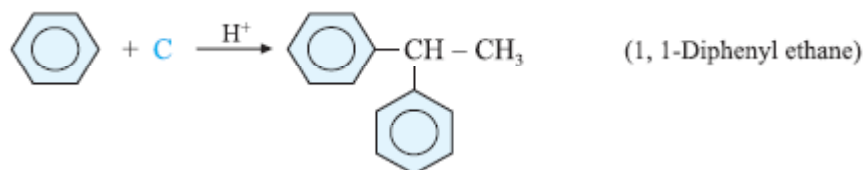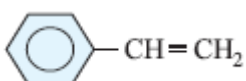

Example - 6 *De-hydro-bromination of two compounds A and B gives the same compound C. C regenerates A and B when reacts with HBr in the presence and absence of peroxide respectively. The hydrolysis of A and B gives isomeric products D and E respectively. C when reacts with benzene in presence of H^+ ions gives 1, 1-Diphenylethane. Identify the compounds A to E.*
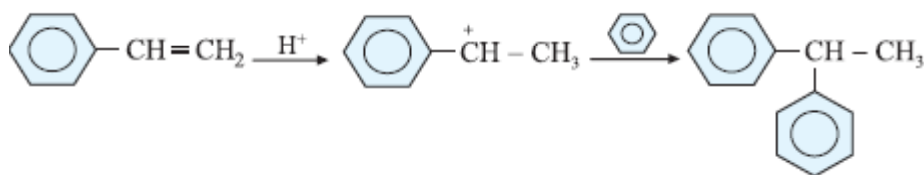
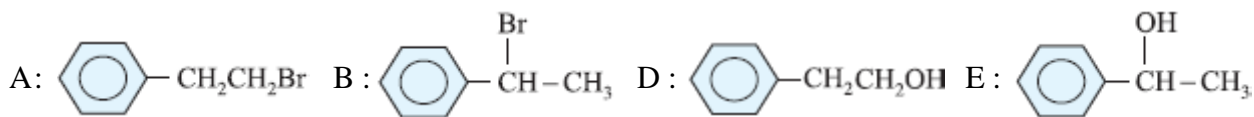**SOLUTION :** Visualizing the flow chart of the question as follows.

Recall Friedal Craft alkylation

$$CH_2 = CH_2 + HF + \bigcirc \longrightarrow \bigcirc - CH_2CH_3$$

$$\bigcirc + C \xrightarrow{H^+} \bigcirc - CH - CH_3 \qquad (1, 1\text{-Diphenyl ethane})$$

$\Rightarrow$ C is an alkene containing a – C = C – bond, hence C is vinyl benzene.   C : $\bigcirc - CH = CH_2$

$$\bigcirc - CH = CH_2 \xrightarrow{H^+} \bigcirc - \overset{+}{C}H - CH_3 \longrightarrow \bigcirc - CH - CH_3$$

As per given reactions in question :

A: $\bigcirc - CH_2CH_2Br$ B : $\bigcirc - \overset{Br}{\overset{|}{CH}} - CH_3$ D : $\bigcirc - CH_2CH_2OH$ E : $\bigcirc - \overset{OH}{\overset{|}{CH}} - CH_3$

Example - 7   *An organic compound A, C_5H_9Br de-colourises bromine water and alk. $KMnO_4$. It gives B, $C_5H_{11}Br$ when treated with H_2, Pd-carbon in methanol. The reaction of A with $NaNH_2$ gives C with the evolution of NH_3. C does not react with sodium but reacts with Lindlar catalyst to give D. It also reacts with Na/liquid NH_3 to give E. Both D and E are isomers. Identify the compounds A to E with proper reasoning.*
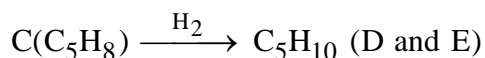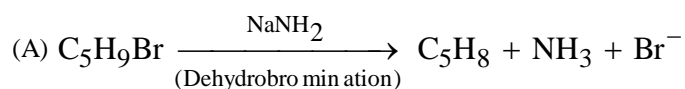
SOLUTION :

Visualizing the flow chart of the question as follows :

$$A\ (C_5H_9Br) \quad \xrightarrow[CCl_4]{Br_2} \text{ decolourised} \quad \Rightarrow \quad \text{A is an unsaturated compound.}$$

$$\xrightarrow[KOH]{KMnO_4} \text{ decolourised} \quad \Rightarrow \quad \text{A is an unsaturated compound.}$$

$$\xrightarrow[\text{Pd-C/MeOH}]{H_2} C_5H_{11}Br\ (B) \quad \Rightarrow \quad \text{A contains one } - C = C - \text{ bond.}$$

$$A \xrightarrow{\text{NaNH}_2} C + NH_3$$

$$C \xrightarrow{\text{Na}} \text{No reaction}$$

$$C \xrightarrow{\text{Lindlar Catalyst}} D$$

$$C \xrightarrow[\text{Liq. NH}_3]{\text{Na}} E \quad (D, E \text{ are isomers})$$
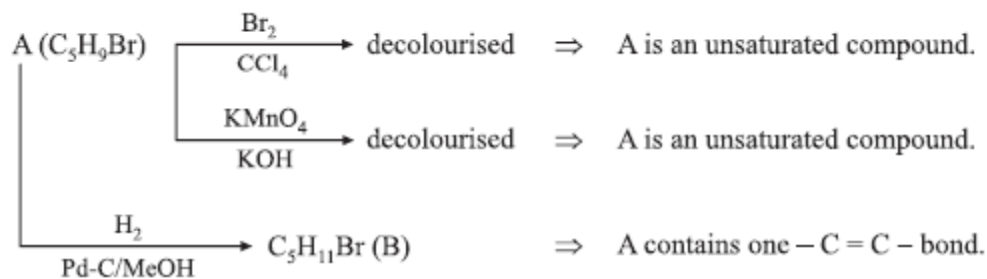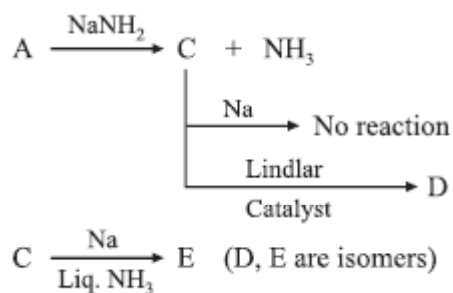
Since D and E are isomers obtained by partial hydrogenation of 'C' (C : an alkyne) from two different reagents, D and E must be geometric isomers with molecular formula C_5H_{10}. "*Check this as follows*"
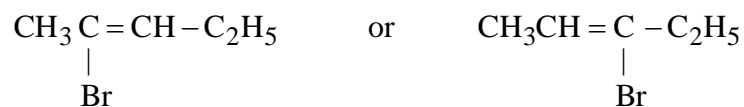
$$\text{(A) } C_5H_9Br \xrightarrow[\text{(Dehydrobro min ation)}]{\text{NaNH}_2} C_5H_8 + NH_3 + Br^-$$

$$C(C_5H_8) \xrightarrow{H_2} C_5H_{10} \ (D \text{ and } E)$$

The alkene with molecular formula, C_5H_{10} showing geometric isomerism is only 2-Pentene

$$[CH_3CH = CHC_2H_5]$$
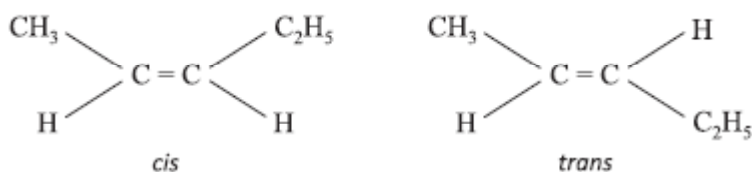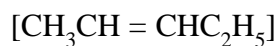
Hence the compound (C) is 2-Pentyne (Non-terminal alkynes do not react with Na).

A can be :

$$CH_3 \underset{\underset{Br}{|}}{C} = CH - C_2H_5 \qquad \text{or} \qquad CH_3CH = \underset{\underset{Br}{|}}{C} - C_2H_5$$
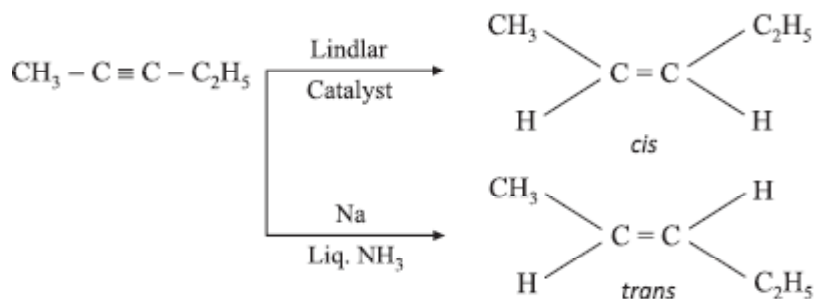
Both will give 2-Pentyne with $NaNH_2$.

Accordingly B can be :

$$CH_3 \underset{\underset{Br}{|}}{CH} - CH - C_2H_5 \qquad \text{or} \qquad CH_3CH_2 - \underset{\underset{Br}{|}}{C}HC_2H_5$$
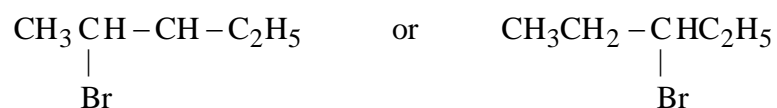
NOW ATTEMPT OBJECTIVE WORKSHEET BEFORE PROCEEDING AHEAD IN THIS EBOOK

My Chapter Notes