

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 : $[C_nH_{2n+2}]$

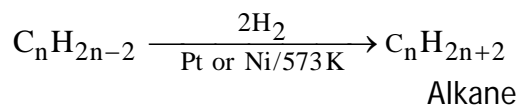
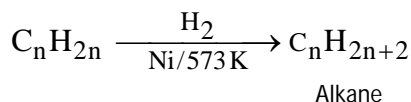
Alkanes form a homologous series, represented by a general formula : C_nH_{2n+2} . These have a tetrahedral structure around carbon atom or one can say that all the carbon atoms in alkanes show sp^3 type of hybridisation. The important members of alkanes are: Methane (CH_4), Ethane (CH_3CH_3), Propane

($CH_3CH_2CH_3$), 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)

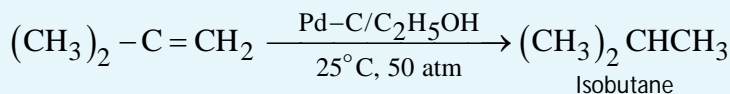
Preparation of Alkanes :

1. Reduction of Alkenes and Alkynes :



This is known as Sabatier-Sandern's reaction.

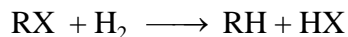
Note : For the reduction of alkenes, and alkynes $Pd - carbon/Ethanol$ at $25^\circ C$ (50 atm) is generally used.



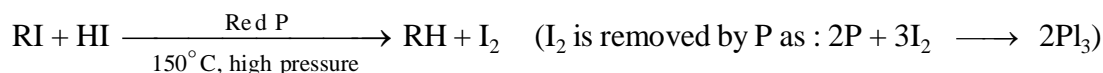
2. From Alkyl Halides :

(a) By reducing Alkyl Halides :

Reducing agents : $\text{Zn} + \text{CH}_3\text{COOH}$; $\text{Zn} + \text{HCl}$; $\text{Zn} + \text{NaOH}$; $\text{Zn}-\text{Cu}$ Couple ; $\text{Al}-\text{Hg}$ amalgam.

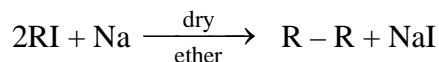


Alkyl iodides are reduced by HI in red P under high temperature and pressure.



(b) Wurtz Reaction :

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

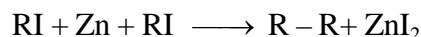


If we start with $\text{R}'\text{I}$ and RI , we get mixture of alkanes. Hence it is not good method for unsymmetric alkanes.

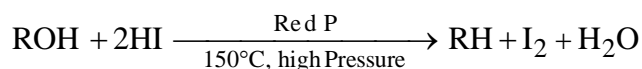
Note : Methane cannot be formed by this method.

Order of reactivity of alkyl halides $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$.

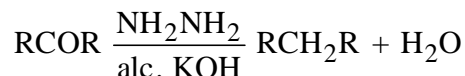
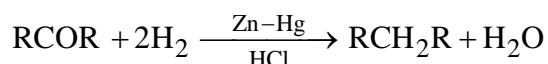
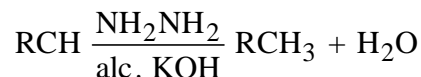
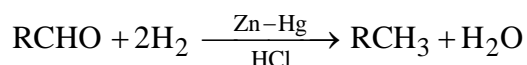
(c) Frankland Reaction :



3. Reduction of Alcohols :



4. Reduction of Aldehyde and Ketones :

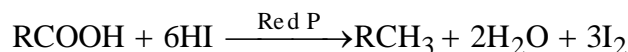


This is known as **Clemmensen's Reduction**.

This know as **Woff-Kishner's Reduction**.

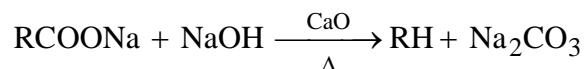
5. From Carboxylic Acids :

(a) Reduction :

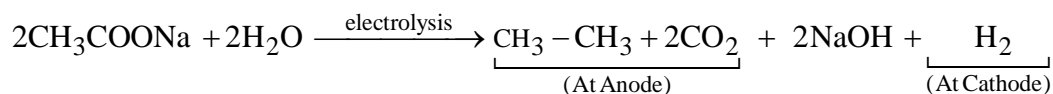
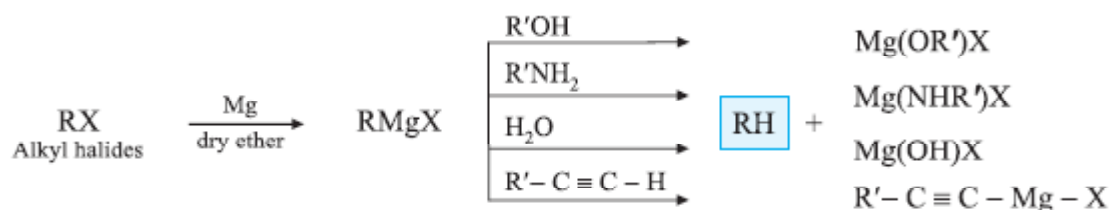


(b) Decarboxylation :

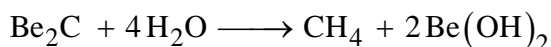
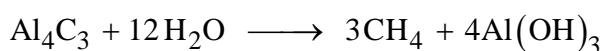
It is obtained by heating sodium salts of carboxylic acids with sodalime (NaOH - CaO).



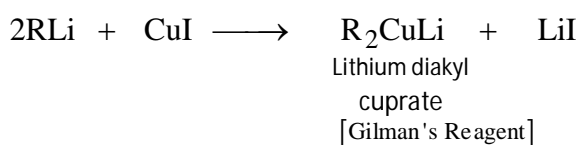
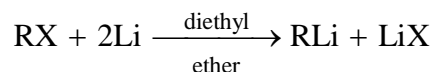
Note : In the product there is one carbon less than parent compound. So this reaction is an important method to reduce a carbon atom in organic synthesis (known as Step-down method).

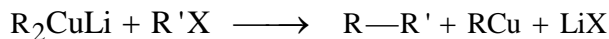
(c) Kolbe's Electrolysis :**6. From Grignard Reagent** (Alkyl magnesium halides, RMgX) :

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

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

Note : Only Methane is formed by this reaction.

8. Through formation of Lithium Dialkylcuprates :



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 :

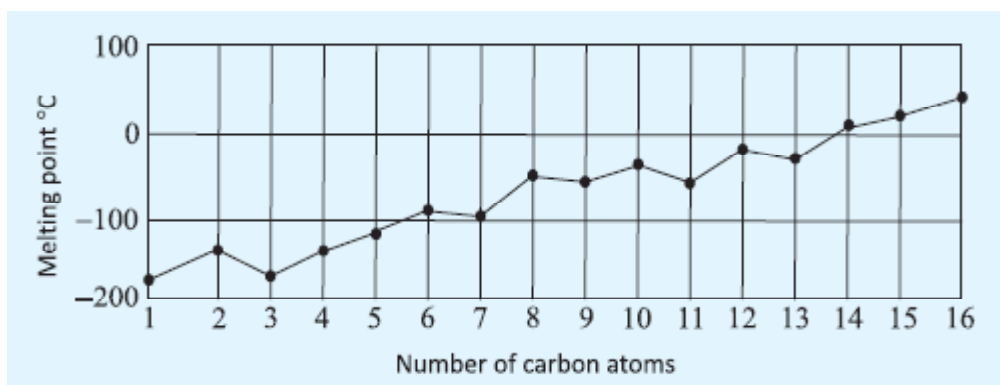
The physical properties of alkanes such as boiling point, density and solubility depend upon the intermolecular forces of attraction. The magnitude of these forces of attraction depend upon the surface area of contact between adjacent molecules. Greater the surface area, stronger are the forces of attraction.

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

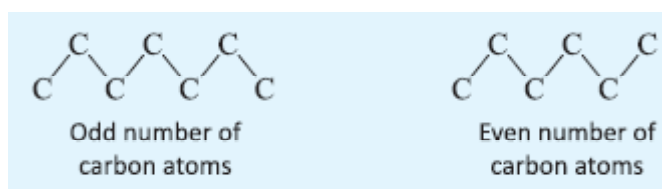
$CH_3CH_2CH_2CH_2-CH_3$	$ \begin{array}{c} CH_3 \\ \\ CH_3 - CH - CH_2CH_3 \end{array} $	$ \begin{array}{c} CH_3 \\ \\ CH_3 - C - CH_3 \\ \\ CH_3 \end{array} $
n-Pentane B.P. = 309 K	Isopentane B.P. = 301 K	Neopentane B.P. = 282.5 K

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)

- 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_3	184.4	101.0	0.5462
Propane	$\text{CH}_3\text{CH}_2\text{CH}_3$	230.9	85.3	0.5824
n-Butane	$\text{CH}_3(\text{CH}_2)_2\text{CH}_3$	272.4	134.6	0.5788
Isobutane	$(\text{CH}_3)_2\text{CH}-\text{CH}_3$	261.0	114.7	-
n-Pentane	$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$	309.1	143.3	0.6264
Isopentane	$(\text{CH}_3)_2\text{CH}-\text{CH}_2-\text{CH}_3$	300.9	113.1	-
Neopentane	$(\text{CH}_3)_3\text{C}-\text{CH}_3$	282.5	256.4	-

- 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 ether, Benzene, Carbon tetrachloride, etc.
- 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 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) in presence of UV light. The substitution reaction is explained by **free radical mechanism**.



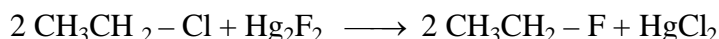
The bromination is same as chlorination but it is relatively slow and high temperature favours it.

The iodination is reversible reaction : $\text{CH}_4 + \text{I}_2 \rightleftharpoons \text{CH}_3\text{I} + \text{HI}$

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



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,



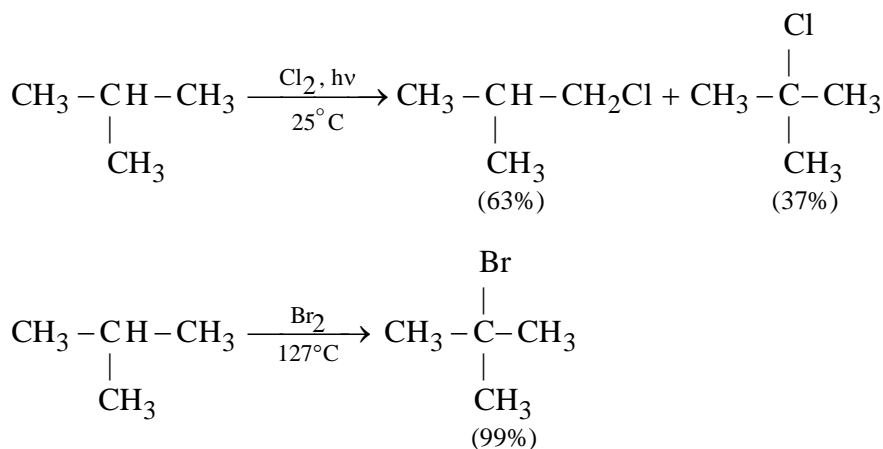
The above reaction is known as **Swarts reaction**.

Ease of halogenation : $3^\circ \text{H} > 2^\circ \text{H} > 1^\circ \text{H} > \text{CH}_4$

Reactivity of X_2 : $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

The reactivity decreases with the electronegativity of the halogens.

Consider halogenation in Isobutane.



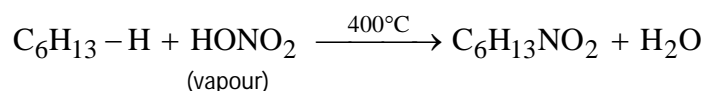
The above reactions show that Bromine is *less reactive* toward alkanes (in general) than chlorine. But bromine shows greater ability to identify among different types of hydrogen atom (i.e., primary, secondary and tertiary). It gives exclusive replacement of tertiary hydrogen atom. Chlorine, on the 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 peroxide, ROOR is used as an indicator.

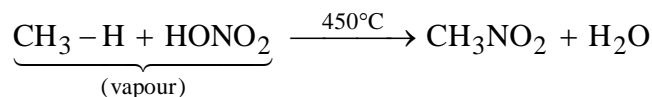
➤ During monochlorination, number of monochlorinated products formed are equal to number of different types of hydrogen atoms in the alkane.

2. Nitration:

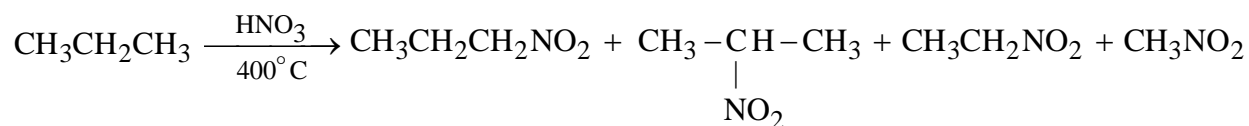
Lower members do not react with conc. HNO_3 at ordinary temperatures but long chain members on heating with HNO_3 yield nitro-alkanes.



However, when a mixture of vapour of an alkane and nitric acid is heated at $400 - 450^\circ\text{C}$, nitroalkane is formed readily. By this process lower as well as higher alkanes can be converted into nitroalkanes.

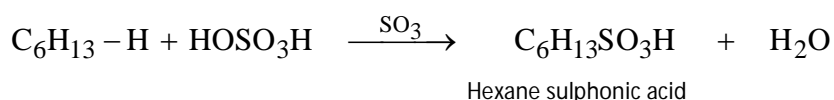


In alkanes having two or more carbon atoms, there is always a possibility that the C - C bonds may break at high temperature and a mixture of nitro alkanes is formed.



3. Sulphonation :

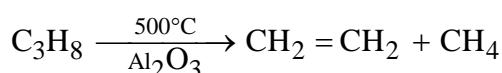
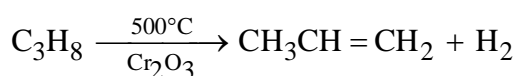
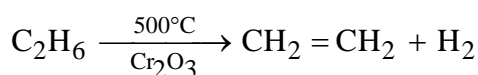
Lower alkanes do not undergo sulphonation but higher member (from hexane onwards) are sulphonated slowly when treated with fuming sulphuric acid at about 400°C.



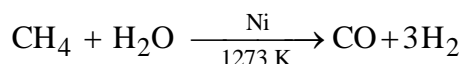
However lower members such as Propane, Butane, Pentane, etc., react with SO_3 in vapour phase to form Sulphonic acids.

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, Vanadium, Molybdenum, etc., and the rupture of C – C bonds is catalysed by Silica, Alumina, Zinc oxide, etc.

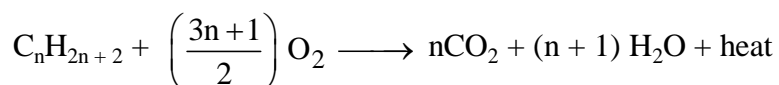
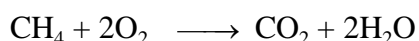


5. Reaction with Steam :



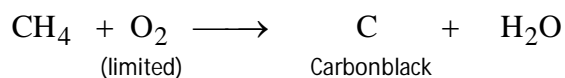
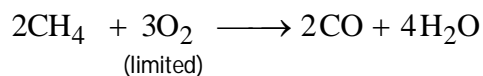
6. Combustion :

(a) Complete Combustion :



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

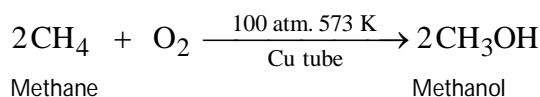
- (b) **Incomplete Combustion :** If the combustion of alkanes is carried out in limited supply of air or oxygen, CO is produced along with unburnt carbon in the form of carbon black or soot.



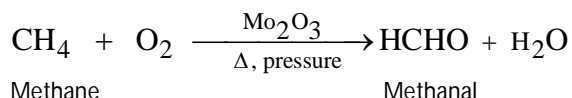
Carbon black is used in the preparation of black inks, paints, polishes etc.

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

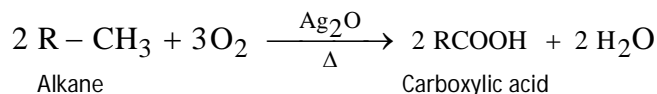
- (i) When a mixture of methane and oxygen (9 : 1 by volume) at a pressure of 100 atm. is passed through a copper tube at 573 K, methanol is formed.



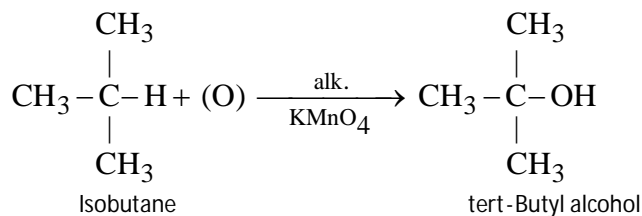
- (ii) When a mixture of methane and oxygen under pressure is passed over heated molybdenum oxide, it is oxidised to methanal.



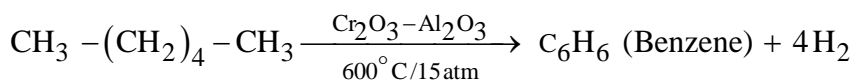
- (iii) Higher alkanes on oxidation in presence of silver oxide give carboxylic acids.



- (iv) In presence of oxidising agents such as KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ etc.



7. Aromatisation :



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,

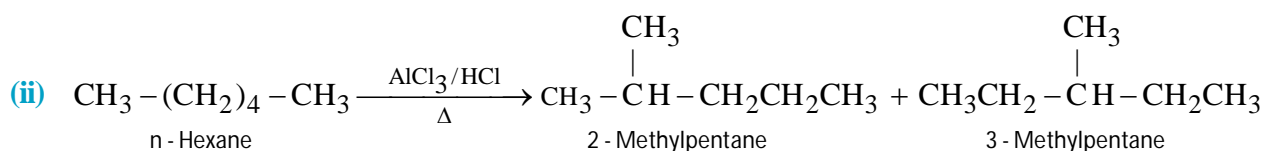
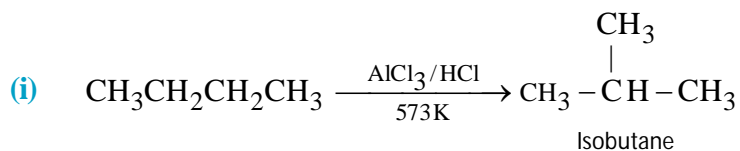
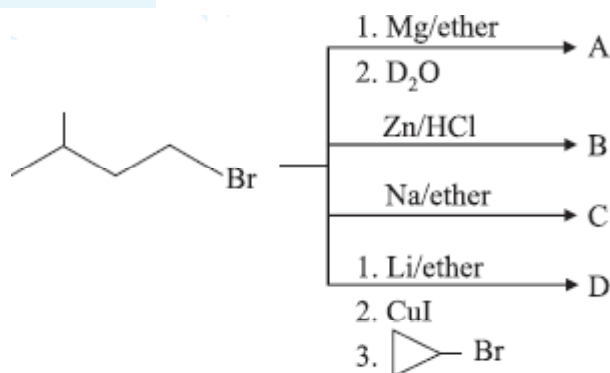
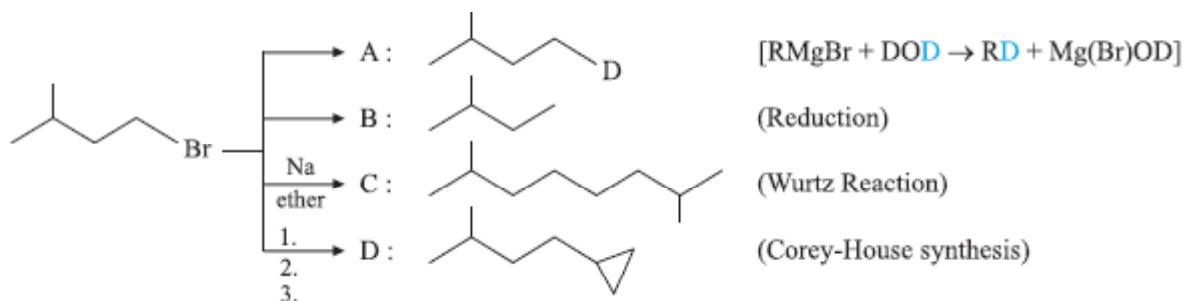


Illustration - 1

Identify A, B, C, D.



SOLUTION :



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 sp² type of hybridisation. The important members of alkenes are: Ethene (CH₂=CH₂), Propene (CH₃CH=CH₂), 1-Butene (CH₃CH₂CH=CH₂) and its isomers, 2-Butene (CH₃CH=CHCH₃) and Iso-butene $\left(\begin{array}{c} \text{CH}_3 - \text{C} = \text{CH}_2 \\ | \\ \text{CH}_3 \end{array} \right)$.

Generally, alkenes are also represented as :

1. Terminal alkenes RCH = CH₂, R₂C = CH₂
2. Non-terminal alkenes RCH = CHR, R₂C = CHR, R₂C = CR₂ (where R : alkyl radical)

Preparation of Alkenes :

1. Dehydration of Alcohols :

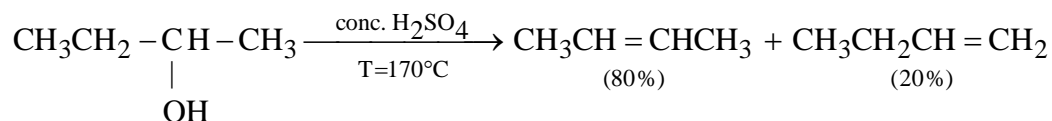
The dehydration of alcohols is generally carried out in either of two ways :

- (a) Heating the alcohol with conc. H₂SO₄ or H₃PO₃ to temperature as high as 170°C.
- (b) Passing the vapours of alcohol over alumina (Al₂O₃) at 350 – 400°C.



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

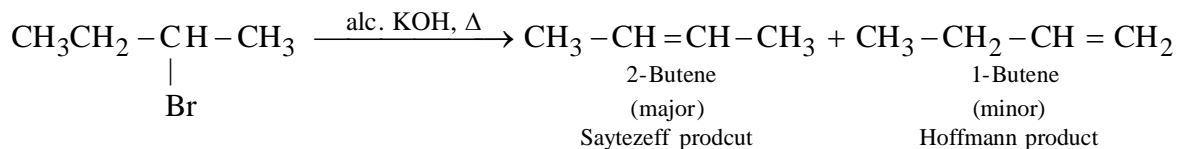
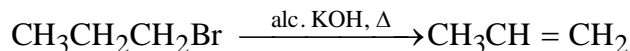
Dehydration is governed by Saytzeff or Zaitsev rule i.e., the greater is number of alkyl groups attached to doubly bonded 'C' atoms, the more stable is the alkene.



Order of Stability : R₂C = CR₂ > R₂C = CHR > R₂C = CH₂ > RCH = CHR > RCH = CH₂ > CH₂ = CH₂

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 :

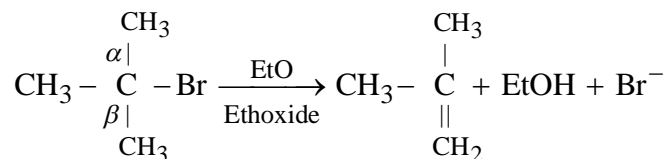


The formation of less substituted alkene in an elimination reaction is called as a **Hoffmann Elimination** and that of more substituted alkene as a Zaitsev Elimination or **Saytzeff's elimination**.

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

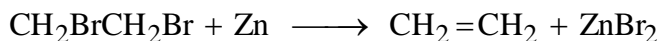
Ease of dehydrohalogenation for different halogens is in the order : Iodine > Bromine > Chlorine.

We can also use alkoxide ion, RO^- , which acts as a strong base. The alkoxide ion abstracts a proton from β -carbon. Then dehydrohalogenation is known as β -elimination or 1, 2-elimination.

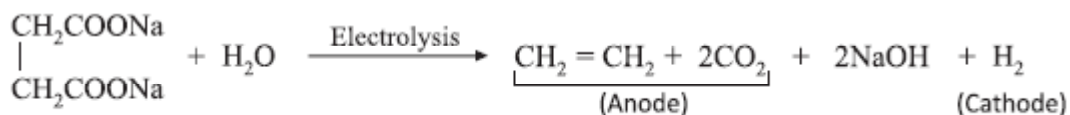


- Note :**
- (i) In case of 1° RX, alkoxide ($\text{R}'\text{O}^-$) does nucleophilic substitution to form ethers [$\text{R}'-\text{O}-\text{R}$].
 - (ii) By using alc. KOH [KOH / ROH], 1°, 2°, 3° alkyl halides give elimination products.

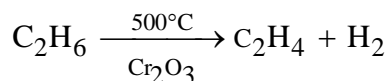
3. By dehalogenation of Vicinal Halides :

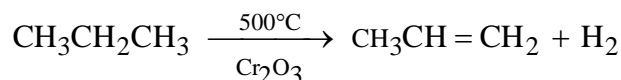


4. Electrolysis of aqueous solution of sodium salts of dicarboxylic acids : (only for Ethene)



5. Cracking of Alkanes :



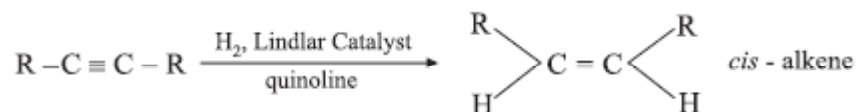


6. Partial Hydrogenation of Alkynes :

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

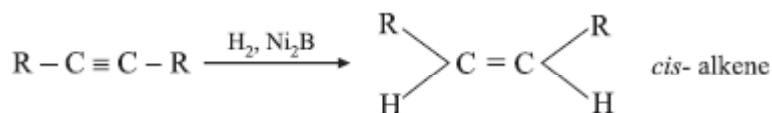
Note : Reaction that produce a particular stereoisomers of the product is called as stereoselective reaction.

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

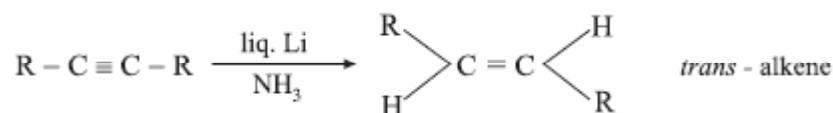


This is also called as **syn addition**, as two H-atoms are added to the same side.

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



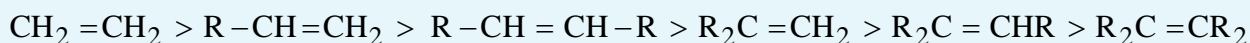
- (b) Using Lithium (or Sodium) in NH_3 (or in ethyl amine) at low temperature, gives *trans* alkene.



This is also called as **anti addition**, as two H-atoms are added to the opposite side of the bond.

Stability of Alkenes :

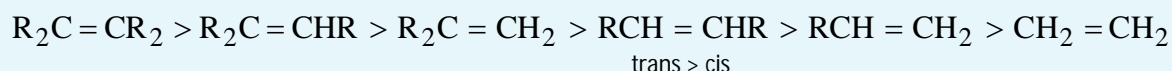
The reactivity of different types of alkenes in decreasing order is as follows : (As per heat of hydorgenation)



The heat of hydrogenation is always exothermic and experimentally it has been found that :

Stability of alkene $\propto \frac{1}{\text{Heat of hydrogenation}}$ (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 :



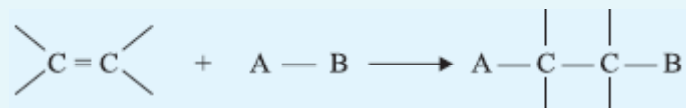
Physical Properties of Alkenes :

- Physical state and smell :** The first three members of the family, i.e., Ethene, Propene and Butene are colourless gases. The next eleven members ($\text{C}_5 - \text{C}_{15}$) are liquids while the higher ones are solids. Except Ethene which has a pleasant smell, all other alkenes are odourless.
- 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 alkanes.
Amongst isomer of alkenes, *trans*-alkenes have higher melting points than their corresponding *cis*-isomers.
- 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.
- 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.
- 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.

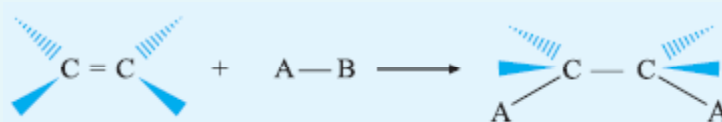
Compound	M.P. (°C)	B.P. (°C)	Density (g/mL)
Ethene	-169	-104	0.384
Propene	-185	-47	0.514
1-Butene	-	-6.3	0.595
cis-2-Butene	-139	3.7	0.621
trans-2-Butene	-106	0.9	0.604
1-Pentene	-165	30	0.641
2-Methyl-1-butene	-138	31	0.650

Reaction of Alkenes :

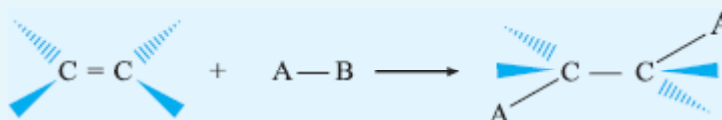
Alkenes undergo mainly addition reactions.



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

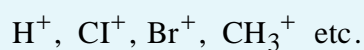


The opposite of *syn-addition* is an *anti-addition*. An anti-addition puts the parts of AB on opposite faces of reactants.



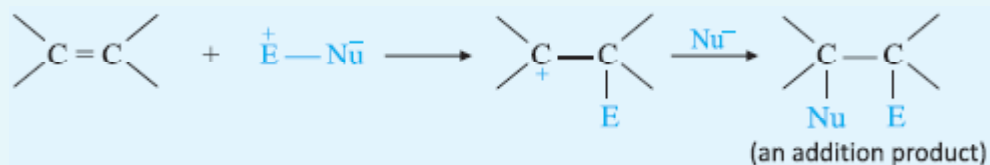
The addition reaction of alkenes are usually **electrophilic addition**.

Electrophile (E⁺) : An electron loving species looking for electron rich regions such as localised pi (π) electron in alkenes and alkynes. Important Electrophiles :



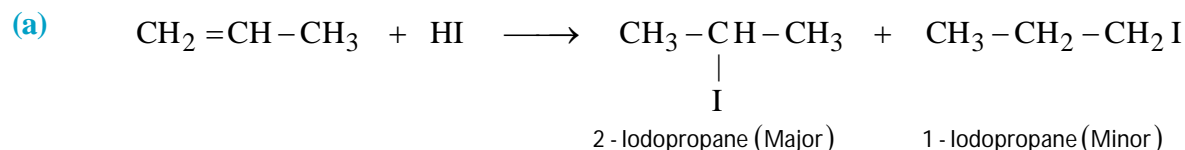
Nucleophile (Nu) : A nucleus loving (electron rich) species looking to attack the electrophilic sites.

Important Nucleophiles : X⁻, OH⁻, OR⁻, CH₃⁻ etc.

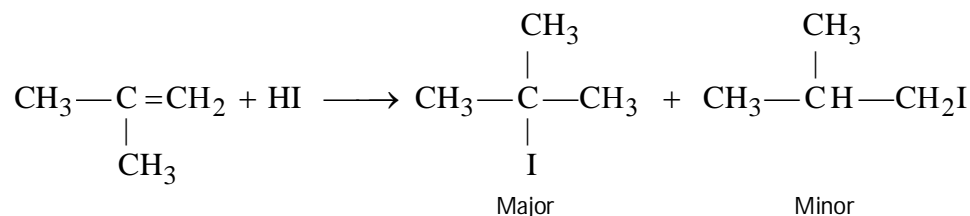


1. Addition of hydrogen halides (HX) :

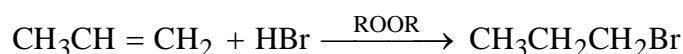
The addition of HX to alkene is an electrophilic addition reaction. The reactivity order follows : $\text{HI} > \text{HBr} > \text{HCl}$. The addition follows **Markonikov's rule**. It states that in the addition of HX to an alkene, the hydrogen atom adds to the carbon atom of the double bond that has 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.



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

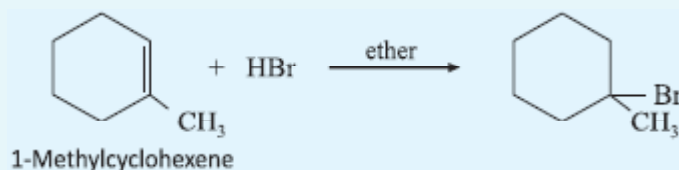


Anti Markonikov's addition : When addition of HBr takes place in presence of peroxides ($\text{R}-\text{O}-\text{O}-\text{R}$ or benzoyl peroxide), addition occurs in an anti-markonikov's manner, i.e., Br is added to the carbon having large number of H-atom.



In presence of peroxides, **free radical addition** occurs in an anti-Markonikov's fashion unlike the electrophilic addition in above case (i.e., Markonikov's addition).

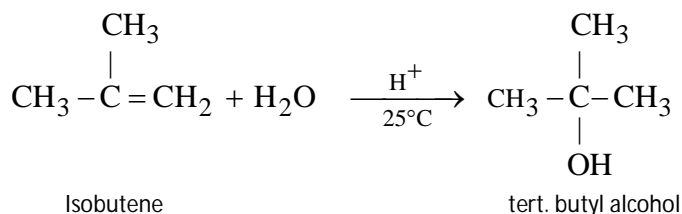
Note : (i) Addition of HX in cycloalkenes also follows Markonikov's addition.



(ii) Addition of HCl and HI in presence of peroxide follows Markonikov's rule.

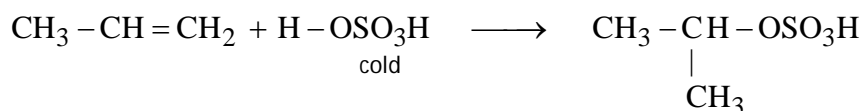
2. Addition of H₂O :

The acid catalysed addition of H₂O produces alcohols and follows Markonikov's addition. The acids used to catalyse the reaction are H₂SO₄ or H₃PO₄ (phosphoric acid).

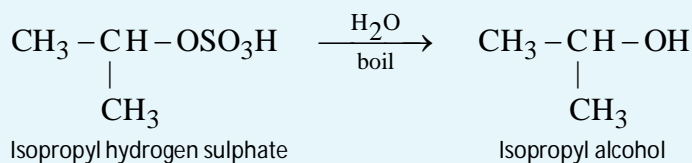


3. Addition of H₂SO₄ (cold and concentrated) :

Alkene react with cold concentrated H₂SO₄ to give alkyl hydrogen sulphates following Markonikov's addition.

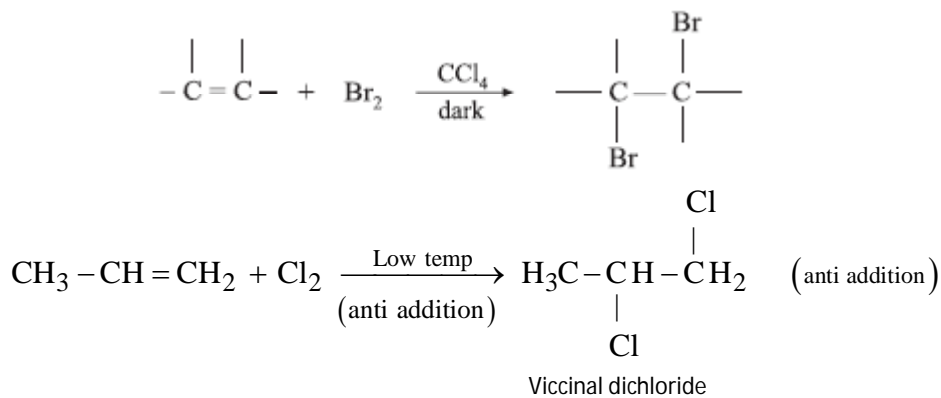


Note : Alkyl hydrogen sulphates when boiled with water give alcohols. It is an irreversible reaction.

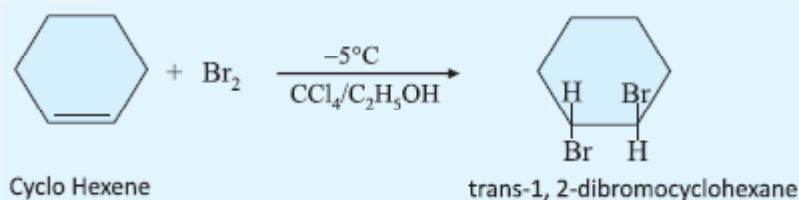


4. Addition of Halogens (Cl₂, Br₂, I₂) :

Alkenes decolourises Bromine water (Br₂ in CCl₄) following addition of Br₂ across double bond. This serves as a test of unsaturation. It follows *anti-addition*.

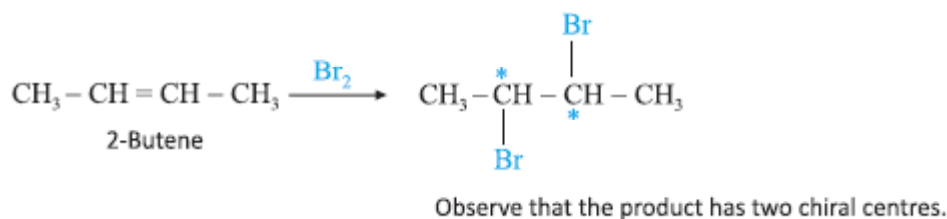


Note: (i) The addition of Br_2 to cycloalkenes also follows anti-addition.

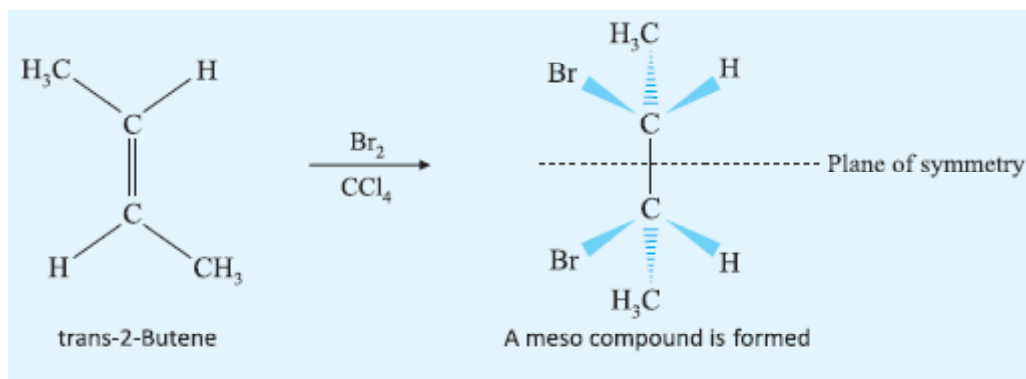


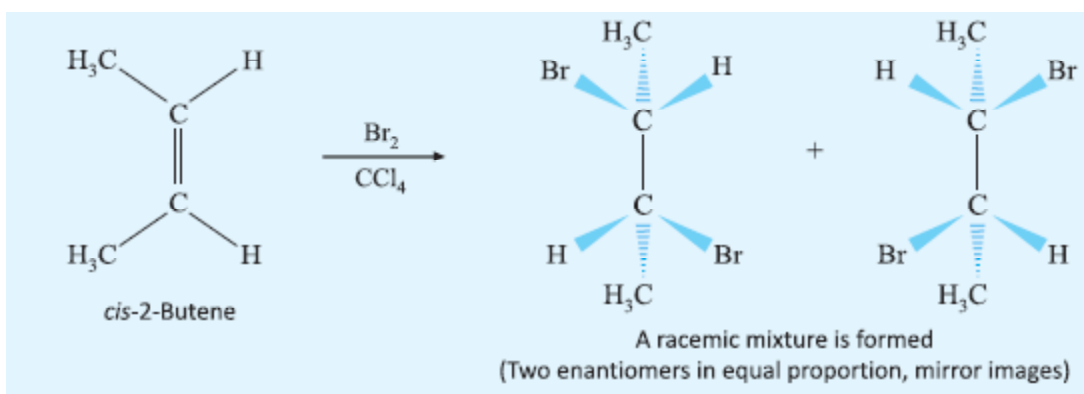
(ii) The addition of halogens to alkene is an anti-addition and provides an illustration for a **stereoselective** and **stereospecific** reaction. For example, cyclohexene gives *trans*-1, 2-Dibromocyclohexane (geometric isomer) is an example of stereoselective reaction. Consider addition of Br_2 to *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”.



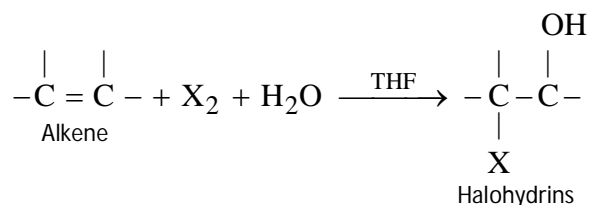
The above reaction, it is visualised as follows and remember the nature of product(s) : (Refer to the next page)





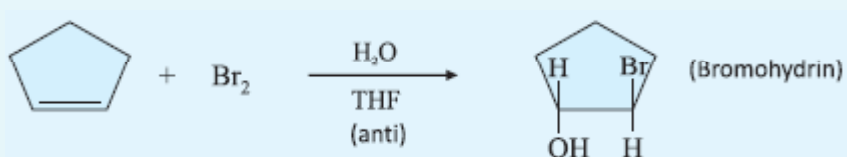
5. Addition of halogen in aqueous solution :

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

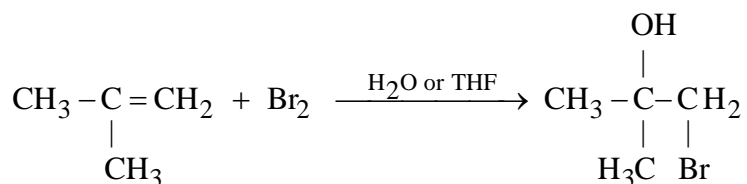
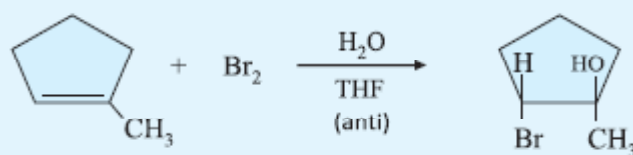


The above reaction follows Markovnikov's rule. It is an *anti-addition* reaction.

Note : (i) The cycloalkenes also reacts with aqueous Br_2 to give anti-addition products.



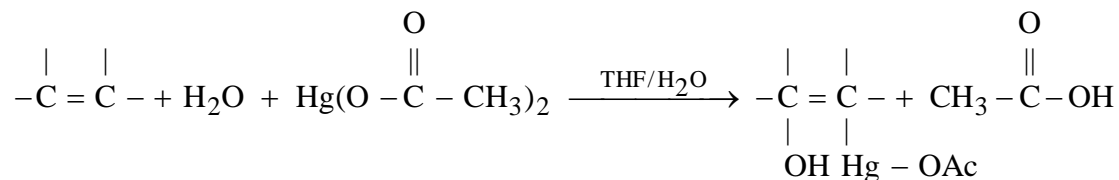
(ii) In case of unsymmetrical alkene, halogen is added to the carbon atom with greater number of H-atom, (i.e., Markonikov's addition).



6. Oxymercuration - Demercuration :

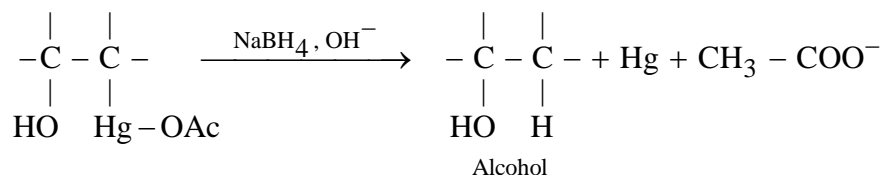
An important method of formation of alcohols from alkenes. It occurs in two steps.

- (i) Alkenes react with mercuric acetate $\text{Hg}(\text{CH}_3\text{COO})_2$ or represented as, $\text{Hg}(\text{OAc})_2$ in a mixture of THF and water to give a mercury compound.

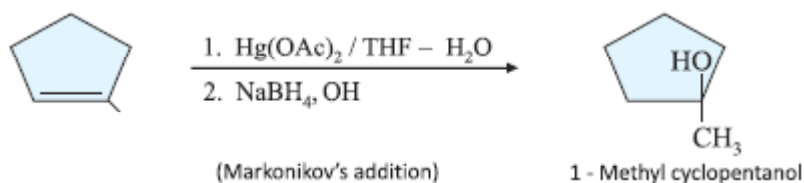
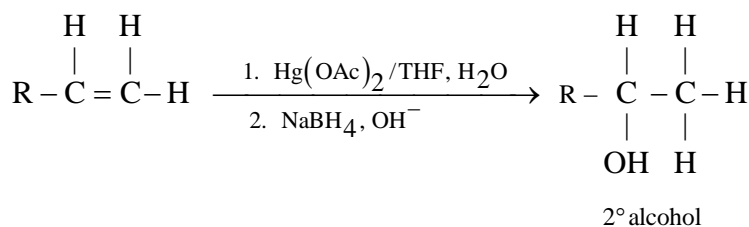


This step is known as Oxymercuration.

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



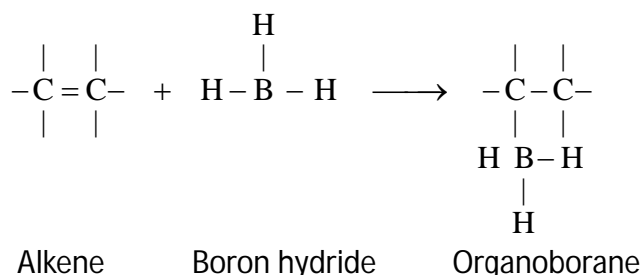
The above reaction occurs in accordance with Markonikov's addition. The 'H' becomes attached to the carbon atom of the double bond with greater number of hydrogen atom.



Note : Observe that in the final product, **OH** comes from H_2O and **H** comes from $\text{NaBH}_4/\text{OH}^-$.

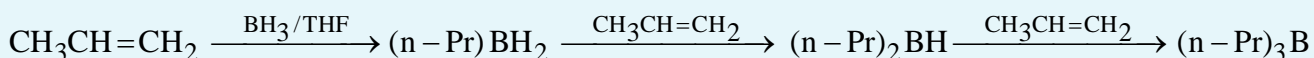
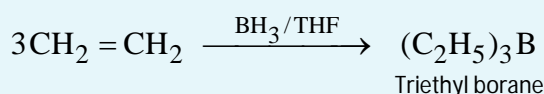
7. Hydroboration - Oxidation :

Hydrocratation-oxidation serves as an important method for synthesis of alcohol (1° & 2°). It can be represented as :



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.



(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.

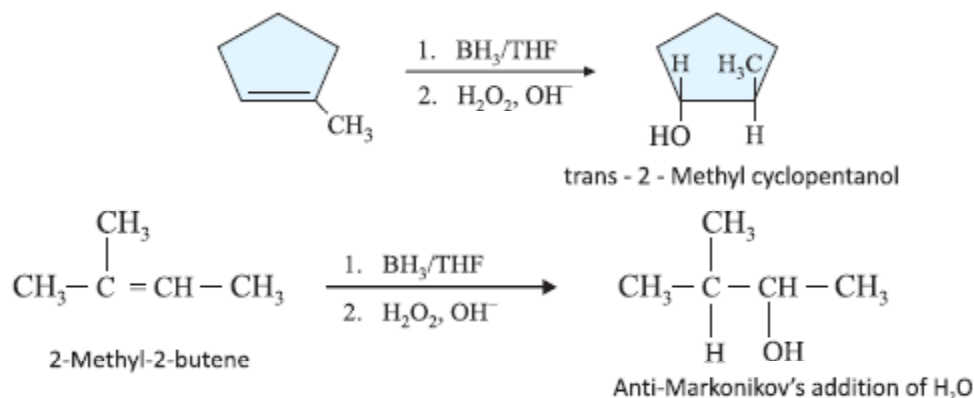
The organoboranes formed are oxidised and hydrolysed to alcohols by the addition of hydrogen peroxides in an aqueous base.



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

Consider hydroboration and oxidation in 1-Methyl cyclopentene. It show syn-addition and anti-Markonikov's addition of H_2O to alkene.

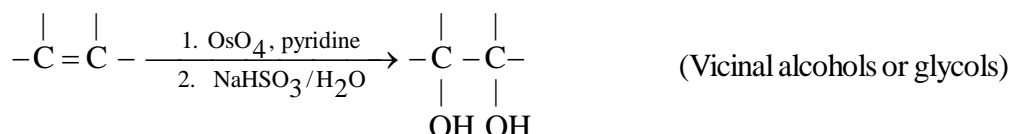
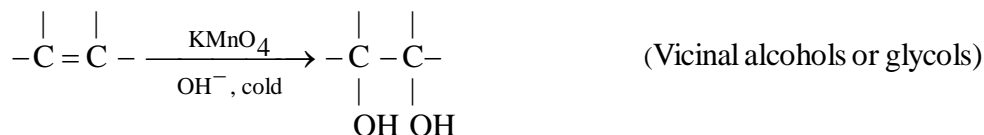
Note: Observe that in the final product, OH comes from $\text{H}_2\text{O}_2/\text{OH}^-$ and H comes from BH_3 .



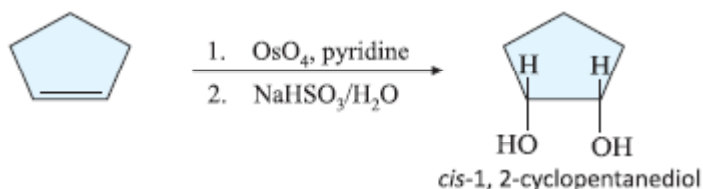
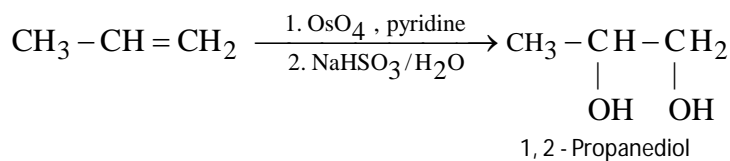
Note: Compare the alcohols formed above with those formed by Oxymercuration-Demercuration.

8. Hydroxylation of alkenes (Oxidation by cold alkaline KMnO_4):

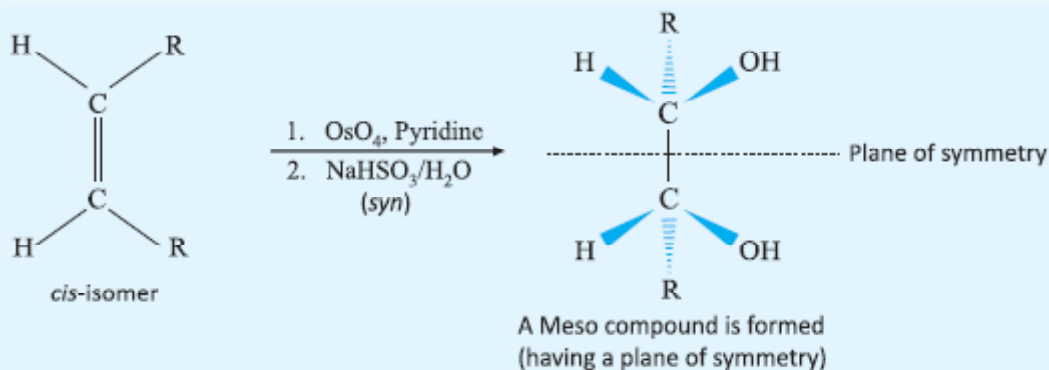
The hydroxylation of alkene is brought about by alkaline KMnO_4 or osmium tetroxide (OsO_4) to give 1, 2-diols (or glycols).

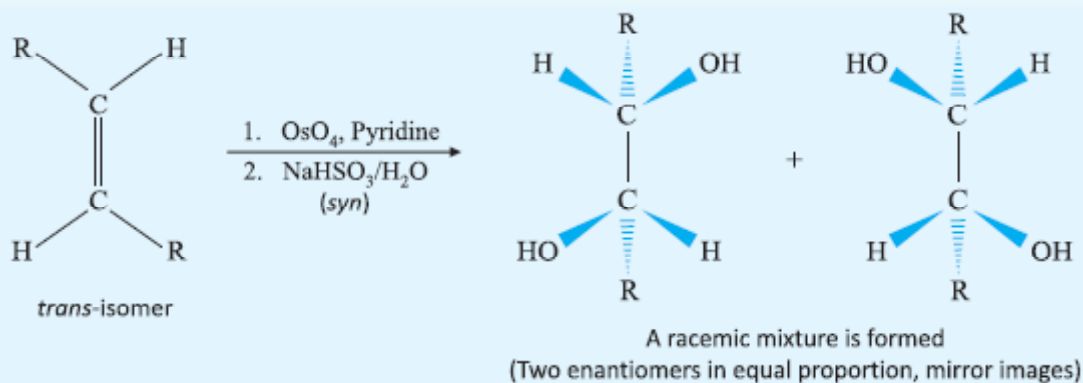


It represents *syn-addition*.



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.

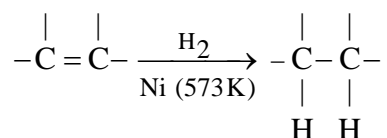




9. Hydrogenation :

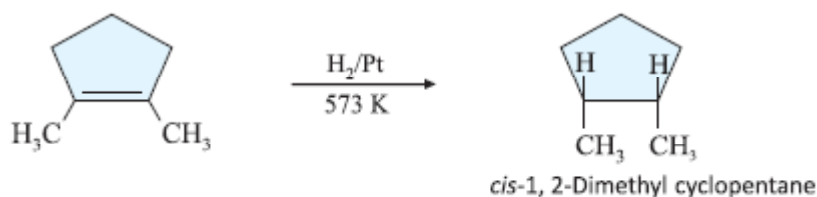
The hydrogenation of alkenes is a *syn-addition*, carried out by many reagents such as :

Na in liquid NH_3 and alcohol ; H_2 , $\text{PtO}_2/\text{CH}_3\text{COOH}$; H_2/Ni at 573 K ; H_2/Pd -Carbon in ethanol.



This reaction also follows *syn-addition* rule.

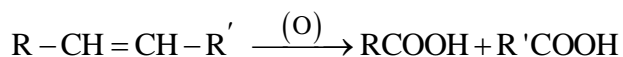
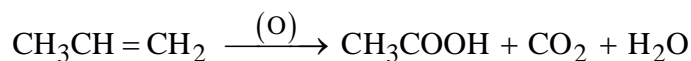
Consider hydrogenation in 1, 2-Dimethyl cyclohexene.

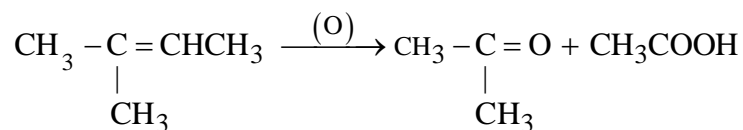


10. Oxidation of Alkenes :

(a) Oxidation by hot. conc. KMnO_4 :

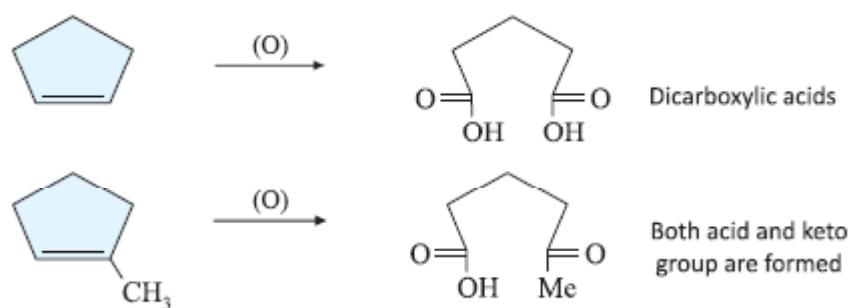
It gives acids or ketones depending upon structure of alkenes. The terminal alkenes gives acids (ketones) and CO_2 , whereas non-terminal alkenes gives mixture of acids and ketones.



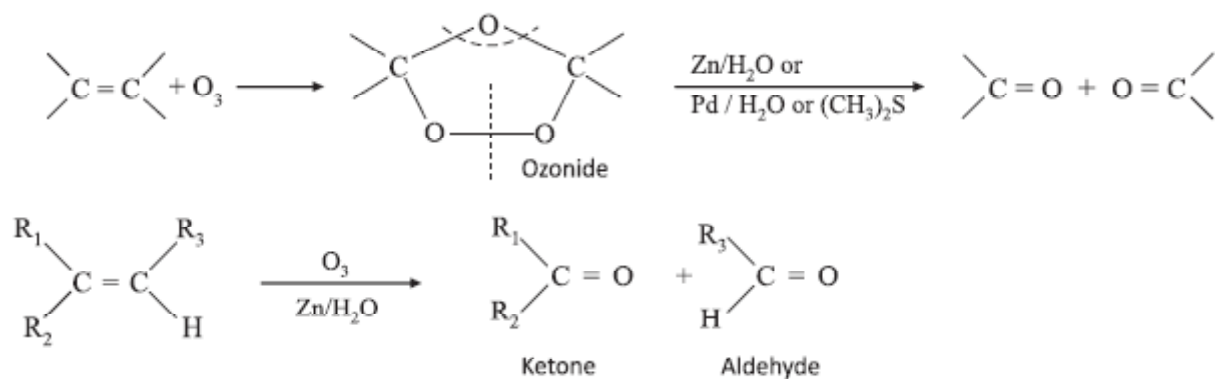


Note: Observe that the dialkylated side of double bond gives corresponding ketone.

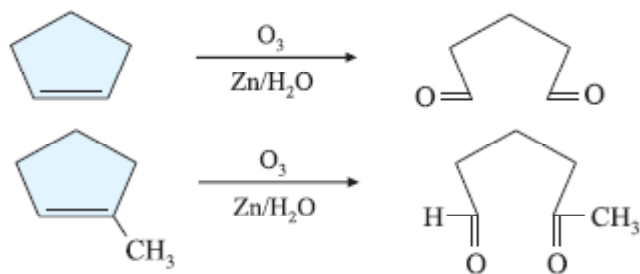
Oxidation of cycloalkenes leads to the ring opening and gives dicarboxylic acids or keto acids.



(b) By Ozone (ozonolysis) :

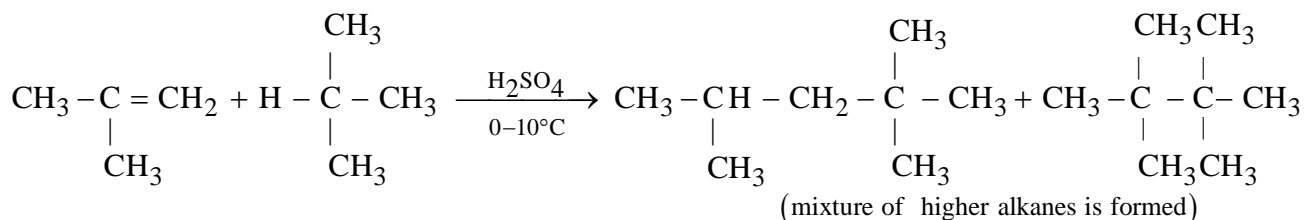


Consider the ozonolysis of cycloalkenes :

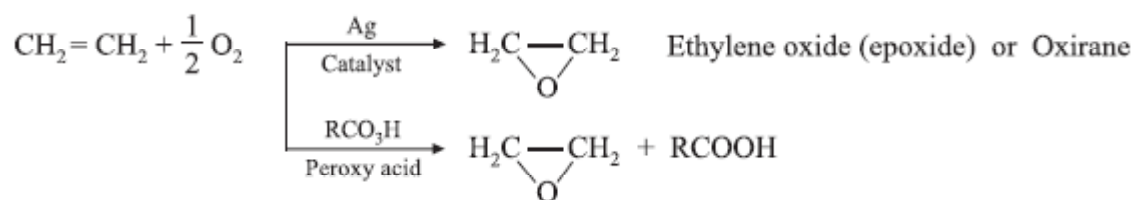


Note : In ozonolysis, observe that we are using $\text{Zn}/\text{H}_2\text{O}$ or $\text{Pb}/\text{H}_2\text{O}$ or $(\text{CH}_3)_2\text{S}$ which reduces the nascent oxygen (O) given by ozonide. This is referred to as Reductive Ozonolysis. If $\text{Zn}/\text{H}_2\text{O}$ is not used, the product aldehyde is oxidised to acid.

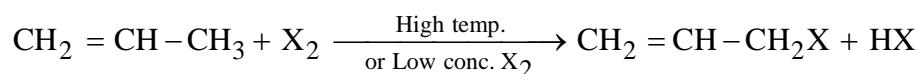
11. Alkylation :



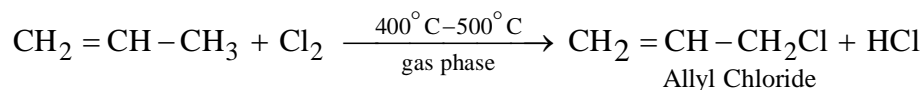
12. Addition of oxygen :



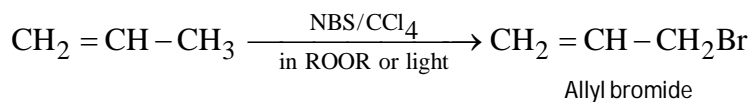
13. Substitution in alkenes : (Partial Oxidation)



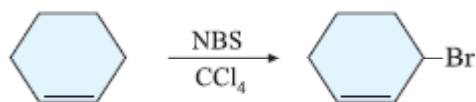
Here, halogen replaces one of the hydrogen atoms of the methyl group. These hydrogen are allylic hydrogen atom and hence the substitution is called as *allylic substitution*.



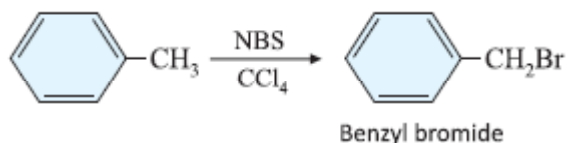
Propene undergoes allylic bromination when it is treated with N-bromo succinimide (NBS) in CCl_4 in presence of peroxides or light.



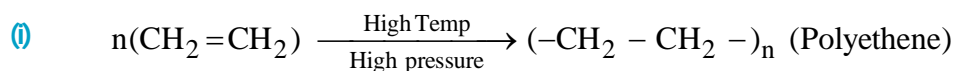
The mechanism is free radical substitution initiated by Br^\bullet (bromide free radical) to give intermediate allyl radical which is stable. Consider allylic substitution in cyclohexene using NBS in CCl_4 .



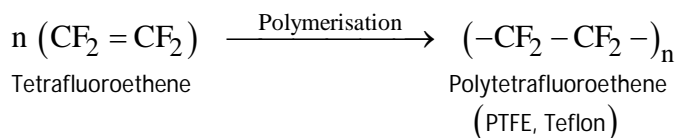
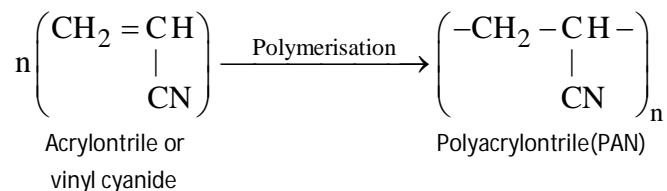
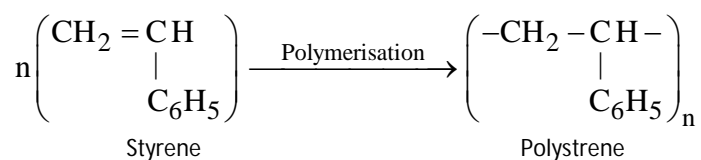
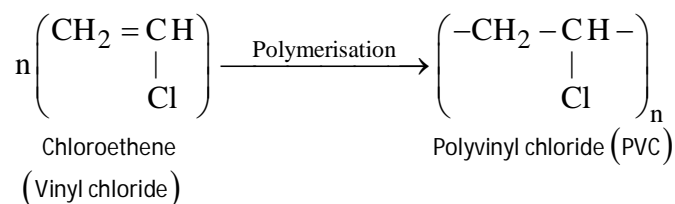
Another interesting aspect of this reaction is that it also occurs in alkyl benzenes.



14. Polymerisation :



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



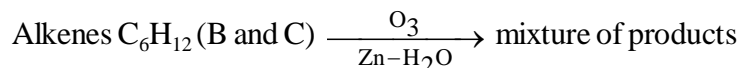
Polyvinyl chloride (PVC) is used for making plastic bottles, syringes, etc. Polyacrylonitrile is used for making Orlon and Acrilan fibres used for making clothes, carpets and blankets.

Illustration - 2

Compound A ($C_6H_{13}Cl$) on treatment with hot alcoholic potassium hydroxide gave a mixture of two isomeric alkenes B and C, having formula C_6H_{12} . The mixture of (B) and (C), on ozonolysis, furnished four compounds :

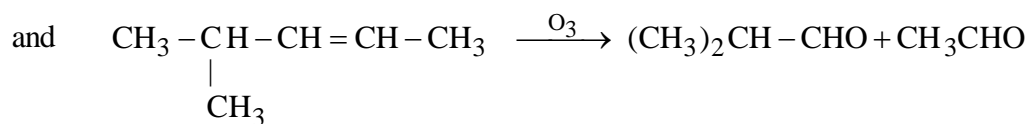
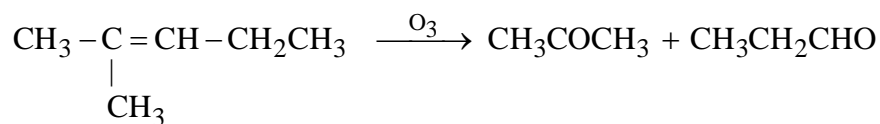


What are the structures of A, B and C ?

SOLUTION :

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 :



The structure of A must be :

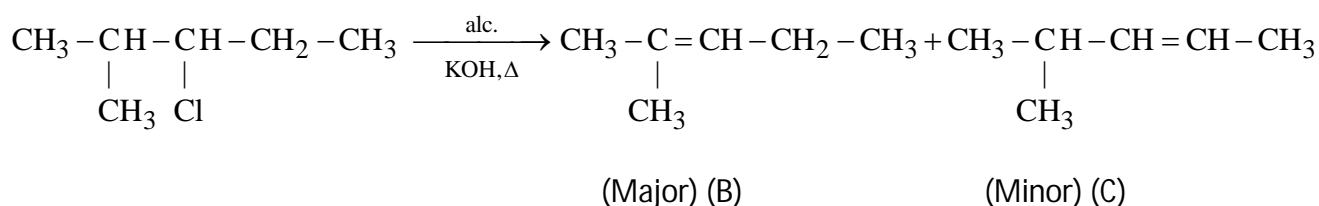


Illustration - 3

Give the structure of the major organic products from 3-Ethyl-1-pentene under each of the following reaction conditions :

- (A) HBr in the presence of peroxide (B) $\text{Br}_2/\text{H}_2\text{O}$ (C) $\text{Hg}(\text{OAc})_2/\text{THF}/\text{H}_2\text{O}$, $\text{NaBH}_4/\text{OH}^-$

SOLUTION :

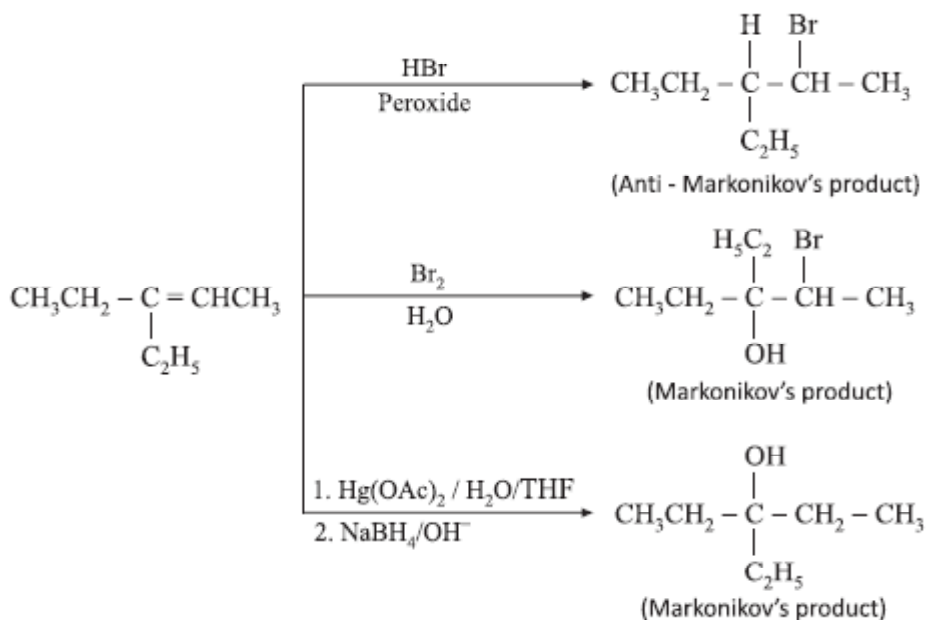
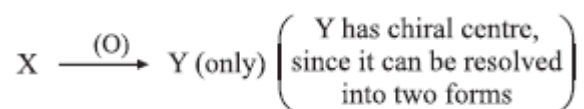
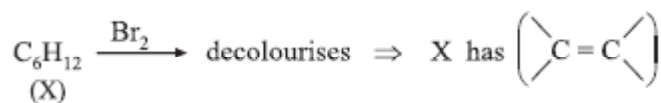


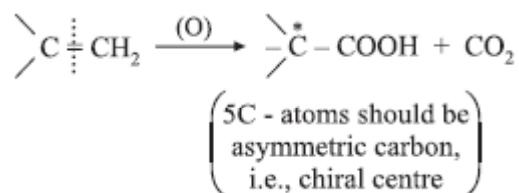
Illustration - 4

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.

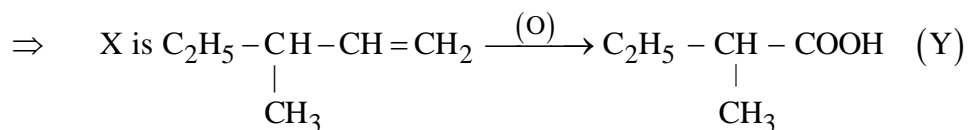
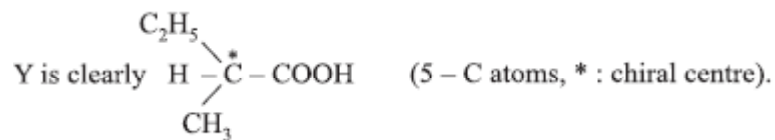
SOLUTION :



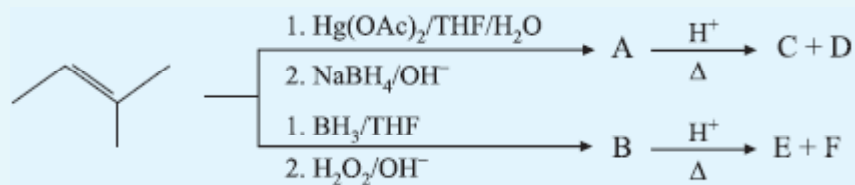
X is terminal alkene as it gives only Y.



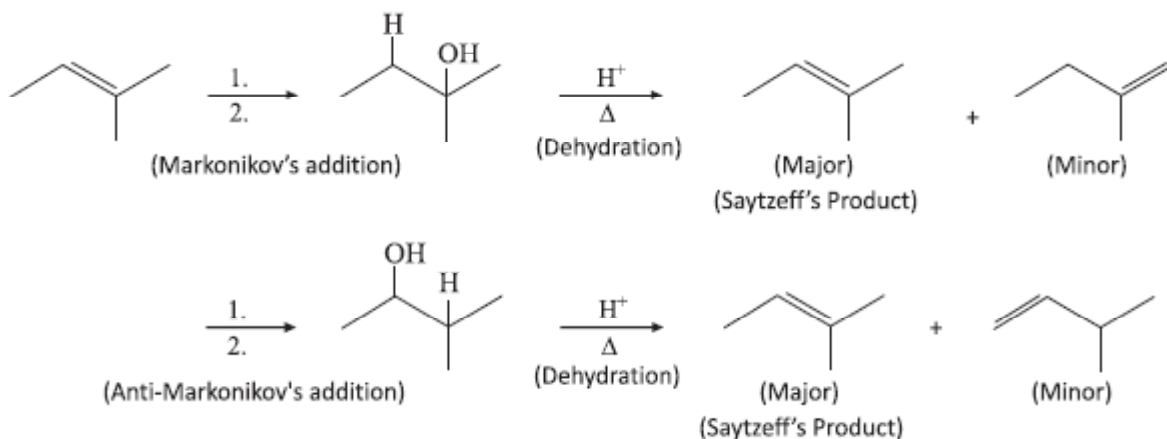
Visualise the structure of Y (having a chiral centre) :

**Illustration - 5**

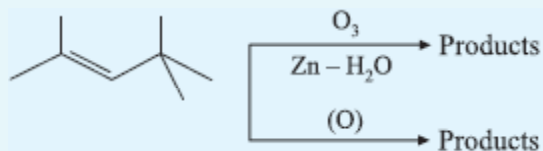
Identify A, B, C, D,



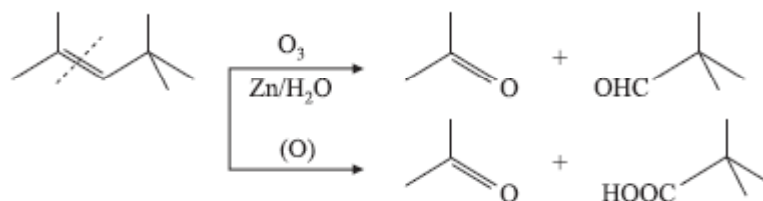
SOLUTION :

**Illustration - 6**

Identify the products



SOLUTION :



Note that the dialkylated site in alkene give the same producer (Ketone) on oxidation and ozonolysis.

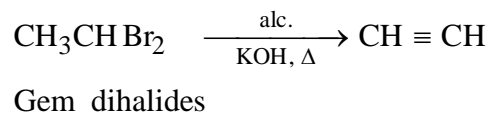
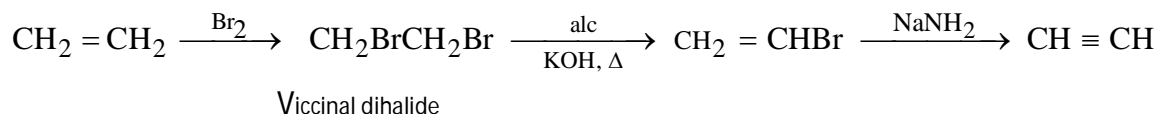
Alkynes form a homologous series, represented by a general formula : C_nH_{2n-2} . These have one $C \equiv C$ bond or one can say that two carbon atoms (adjacent) in alkynes show sp type of hybridisation. The important members of alkynes are: Ethyne ($CH \equiv CH$), Propyne ($CH_3C \equiv CH$), 1-Butyne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

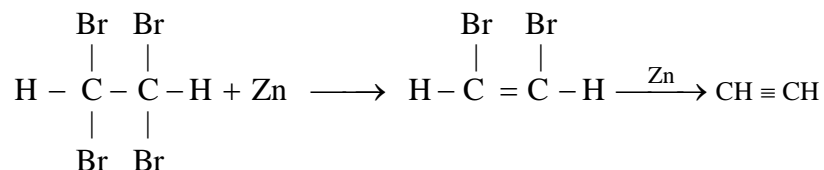
Preparation of Alkynes :

1. Dehydrohalogenation of Dihalides : (Gem and Vicinal)



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 :

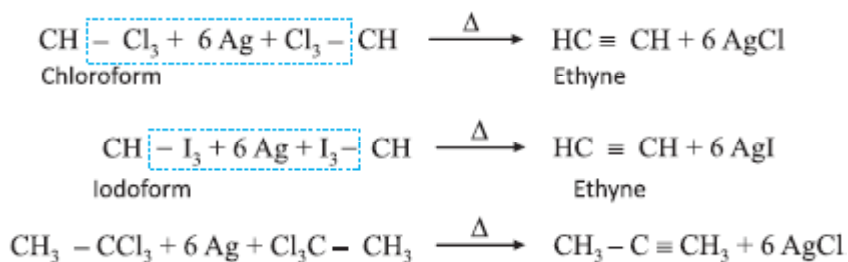


3. By dehalogenation of haloform :

Trihaloderivative of methane is known as haloform (CHX_3).

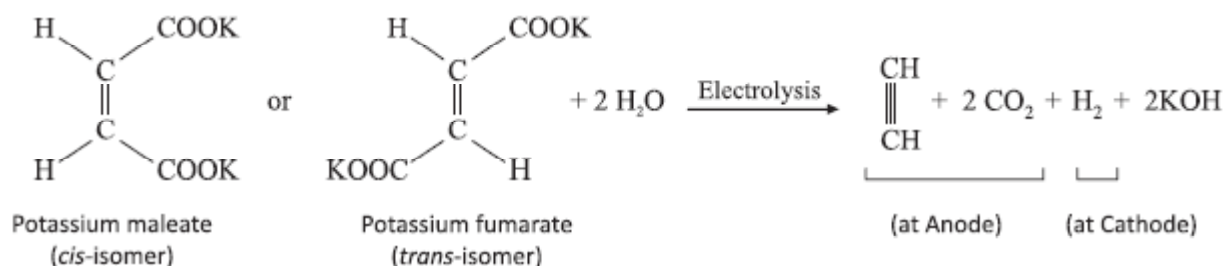
Chloroform and Iodoform on heating with silver powder undergo dehalogenation to form ethyne.

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



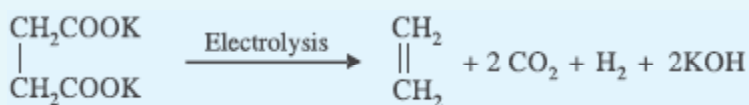
4. Kolbe's electrolytic reaction :

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



This reaction is called Kolbe's electrolytic reaction.

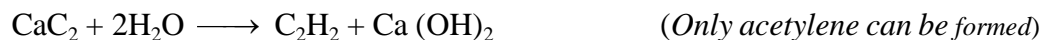
Note : On electrolysis of aqueous solution of Potassium succinate, we get Ethylene (C_2H_4) as a product at anode.



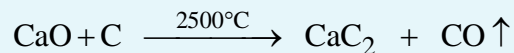
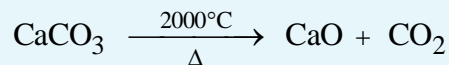
5. From Graphite :



6. From calcium carbide :



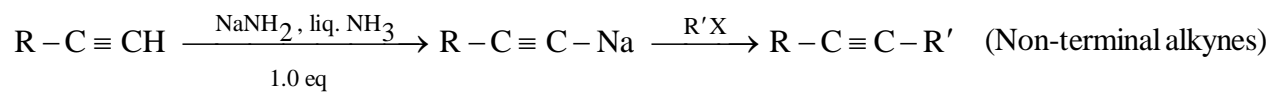
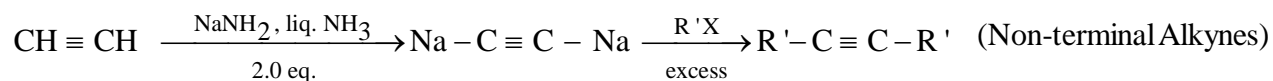
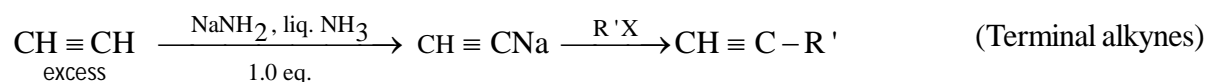
Note: (i) Calcium carbide is formed as follows :



(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 :



Note: R' can only be 1° and 2° alkyl or cycloalkyl groups only.

Physical Properties of Alkynes:

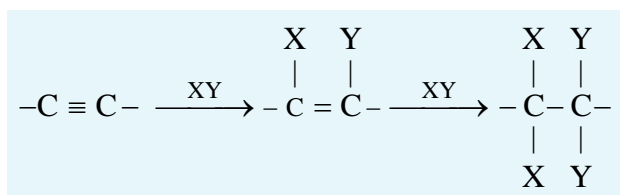
- Physical state:** The first three members of this family (Ethyne, Propyne and Butyne) are colourless gases, the next eight are liquids while the higher ones are solids.
- Smell:** All the alkynes are odourless. However acetylene has garlic smell due to the presence of phosphine as impurity.
- Melting 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

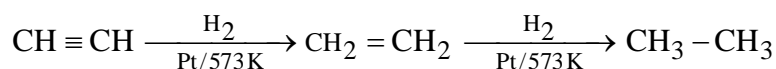
- Solubility :** Alkynes like alkanes and alkenes being non-polar are insoluble in water but readily dissolve in organic solvents such as petroleum ether, benzene, carbon tetrachloride etc.
- Density :** Densities of alkynes increase as the molecular size increases. However, they are all lighter than water since their densities lie in the range $0.69 - 0.77 \text{ g/cm}^3$.

Reactions of Alkynes :

1. Electrophillic Addition Reactions :

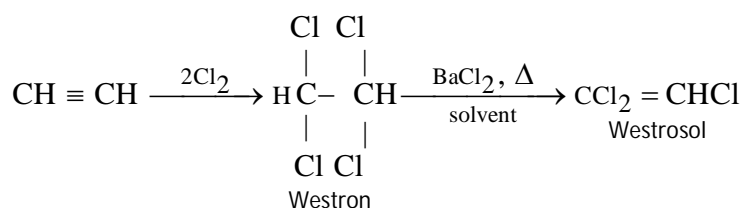


(a) **Addition of Hydrogen :**

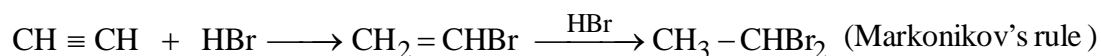


Read hydrogenation of alkynes in the preparation of alkenes.

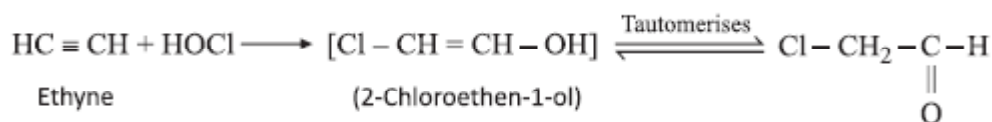
(b) Addition of Halogens : (X = Cl, Br, I)



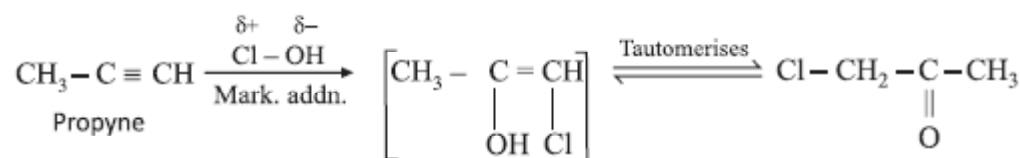
(c) **Addition of Halogen acids : (HX)**



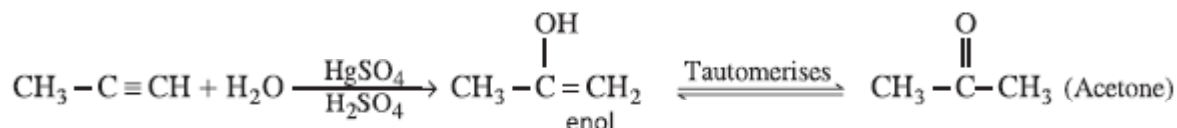
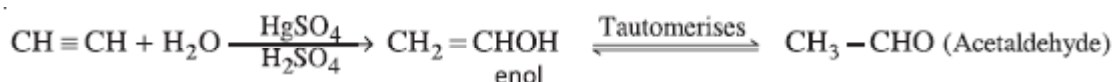
(d) **Addition of Hypohalous acids(HOX) :**



Similarly,

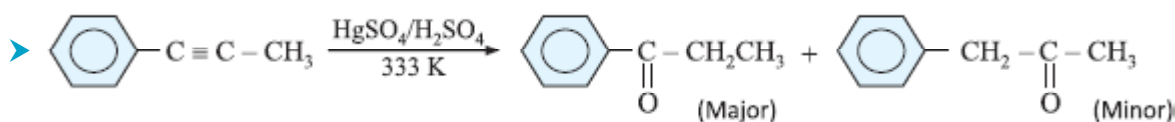
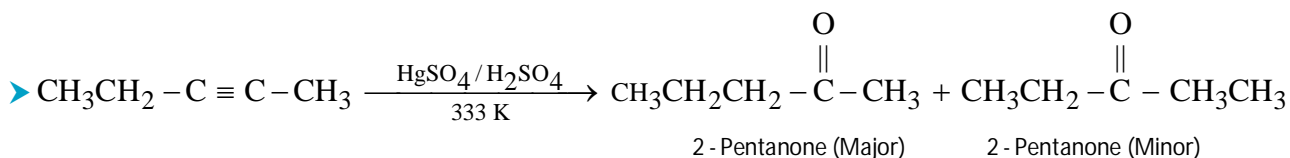


(e) Addition of water (H_2O) in presence of acid :



Note : The addition of water to alkynes also follows Markonikow's rule. The hydrogen atom becomes 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.

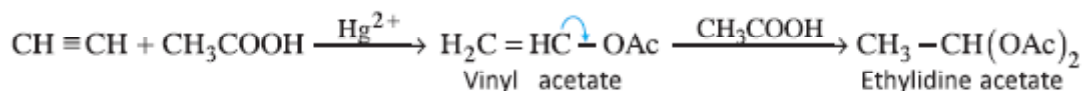


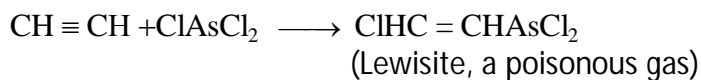
(f) Addition of HCN :



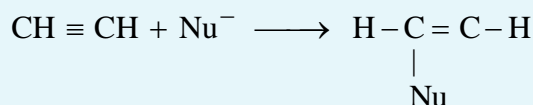
Note : Acrylonitrile is used in manufacture of BuNa-S rubber and Orlon fibre.

(g) Addition of Acetic acid (CH_3COOH) :



(h) Addition of Arsenic trichloride (AsCl_3) :

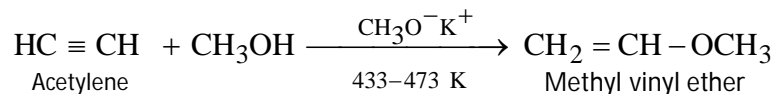
2. Nucleophilic Addition reactions :



(Vinyl carbanion)

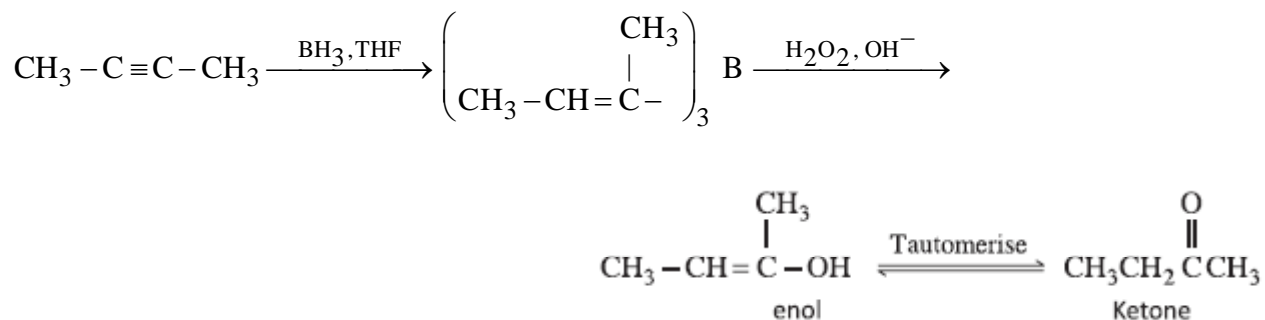
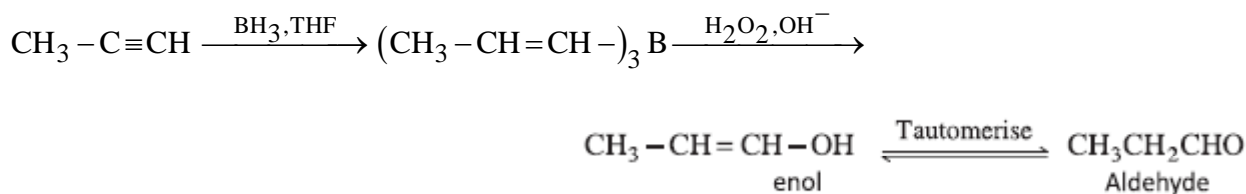
Vinyl Carbanion is formed which is more stable than vinyl carbonium ion.

Addition of Methanol :

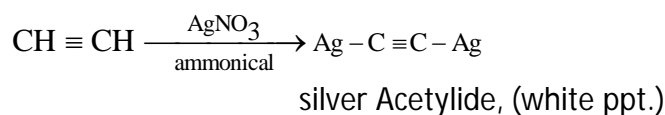


Methyl vinyl ether is used for making polyvinyl ether plastics.

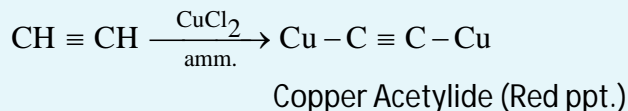
3. Oxidative - Hydroboration



4. Acetylide Formation :

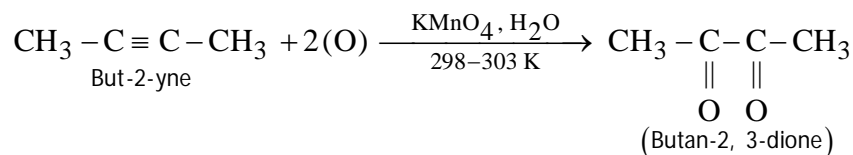


Note : This reaction shows the acidity of terminal alkynes and serves as a test for terminal alkynes.



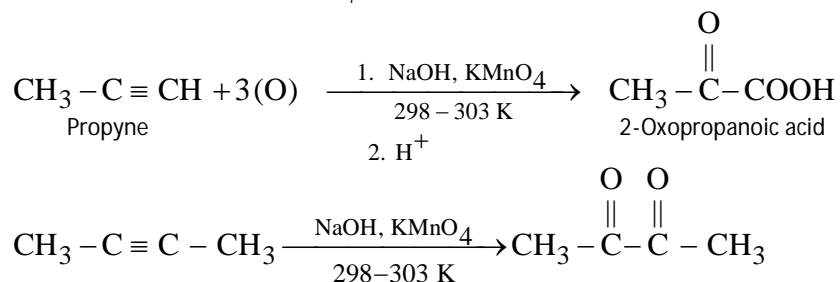
5. Oxidation of Alkynes :

(a) Oxidation in Neutral KMnO_4 :



(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, $\equiv \text{CH}$ part is oxidised to $-\text{COOH}$ group while in case of non-terminal alkynes, $\equiv \text{CR}$ part is oxidised to $\text{R} - \text{C} = \text{O}$ group, For example :

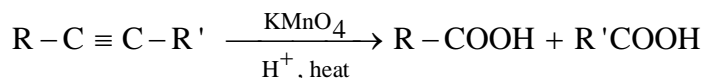


Acetylene, however, under these conditions gives oxalic acid probably due to further oxidation of the initially formed glyoxal.



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**.

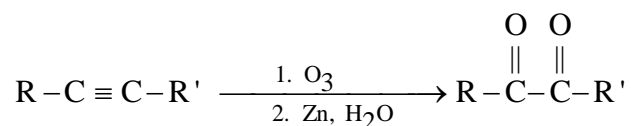
(c) Oxidation by acidic KMnO_4 (hot) :



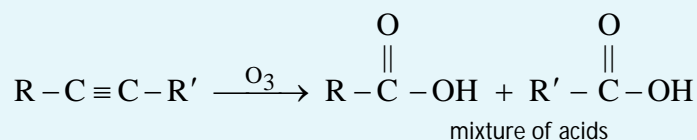
Not that it is similar to the oxidation of alkenes.

6. Ozonolysis :

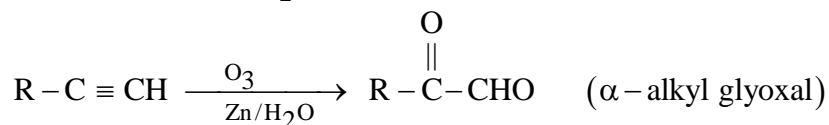
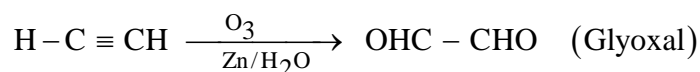
(a) For non-terminal alkynes :



Note: If, Zn or Pb is not used, then the product is mixture of acids.



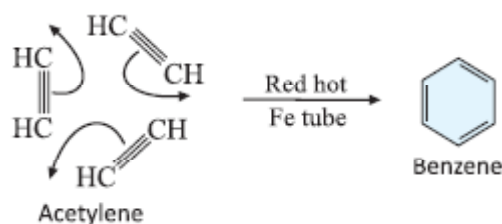
(b) For terminal alkynes :



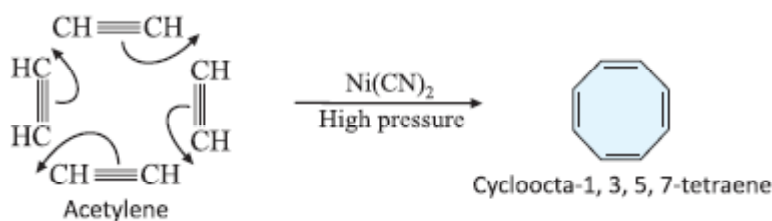
7. Polymerization Reactions of Alkynes :

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

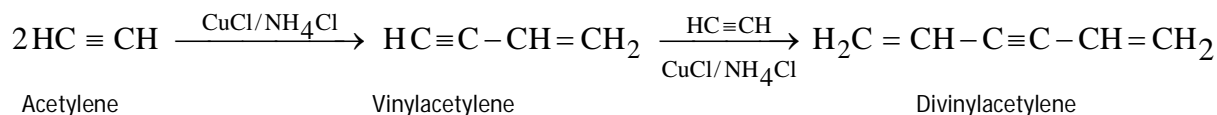
(a) When acetylene is passed through red hot iron tube, it trimerises to give benzene.



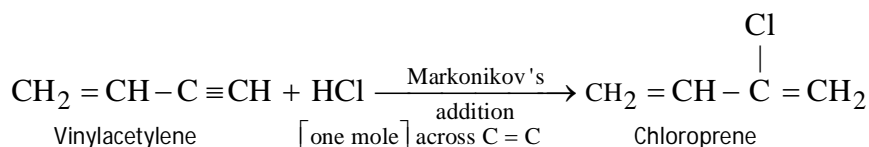
(b) In presence of nickel cyanide as catalyst and under high pressure, four molecules of acetylene combine to form a tetramer called cycloocta-1, 3, 5, 7-tetraene.



(c) However, in presence of $\text{CuCl}/\text{NH}_4\text{Cl}$, acetylene first gives vinylacetylene and then divinylacetylene. Thus,



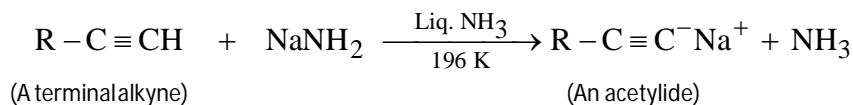
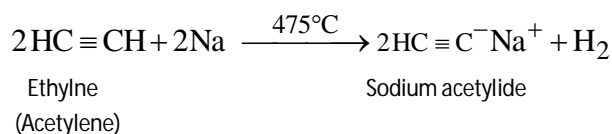
Vinylacetylene is widely used in the manufacture of chloroprene which is the starting material for the synthetic rubber neoprene.



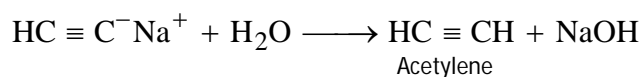
- (d) Under suitable conditions, polymerization of acetylene produces the linear polymer polyacetylene. It is a high molecular weight conjugated polyene containing the repeating unit $(-\text{CH} = \text{CH} - \text{CH} = \text{CH}-)_n$. Under proper conditions, this material conducts electricity. Since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

Acidic character of Alkynes :

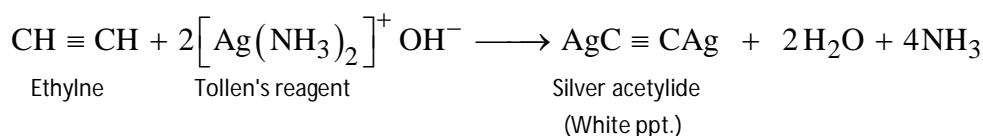
(a) Formation of alkali metal acetylides :

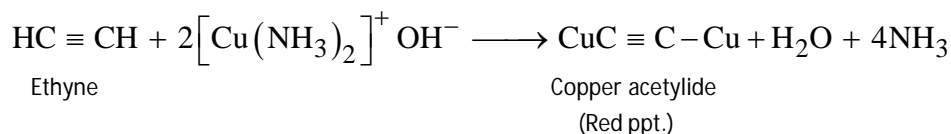
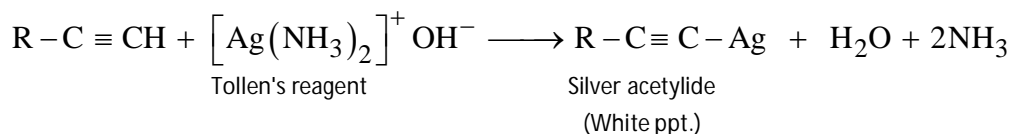


During these reactions, the acetylenic hydrogen is removed as a proton to form stable carbanions (acetylide ions). Sodium acetylide is decomposed by water regenerating acetylene. This shows that water is a stronger acid than acetylene and thus displaces acetylene from sodium acetylide.

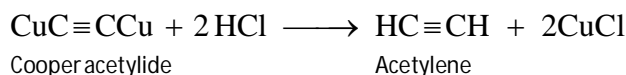
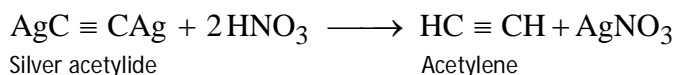


(b) Formation of heavy metal acetylides :





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.



(c) Formation of alkynyl Grignard reagents :

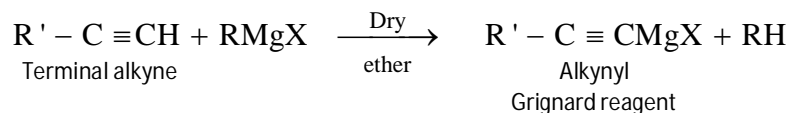
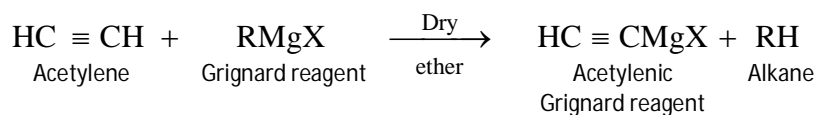
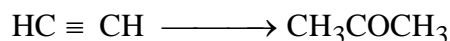


Illustration - 7 How would convert acetylene to acetone ?

SOLUTION :



In such question, try to visualise formation of CH_3COCH_3 . It is formed by hydration of $\text{CH}_3\text{C}\equiv\text{CH}$.

So now convert $\text{HC}\equiv\text{CH}$ to $\text{CH}_3\text{C}\equiv\text{CH}$.

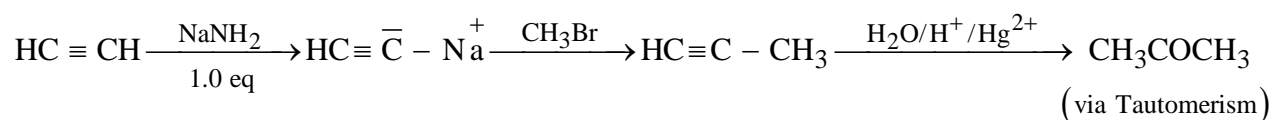
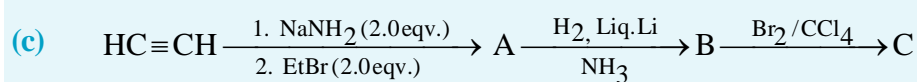
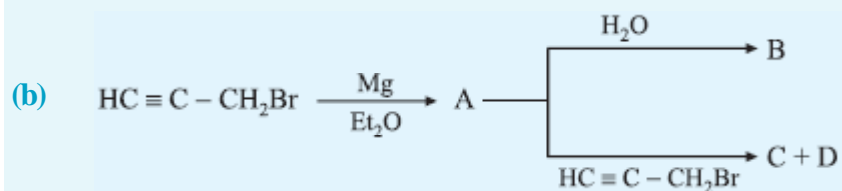
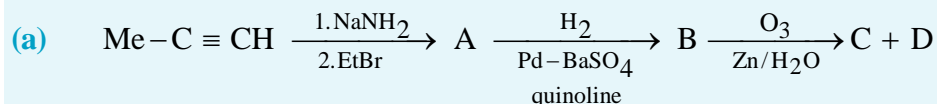
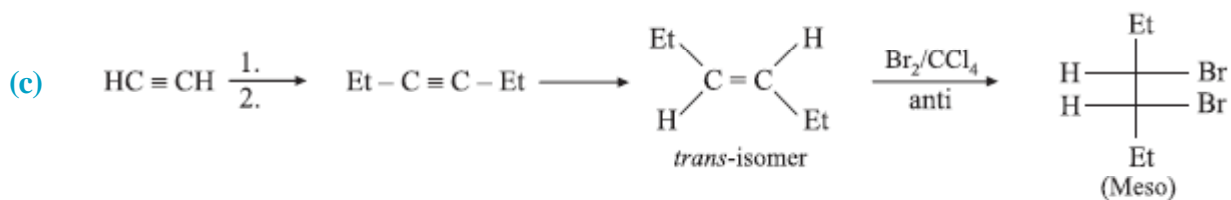
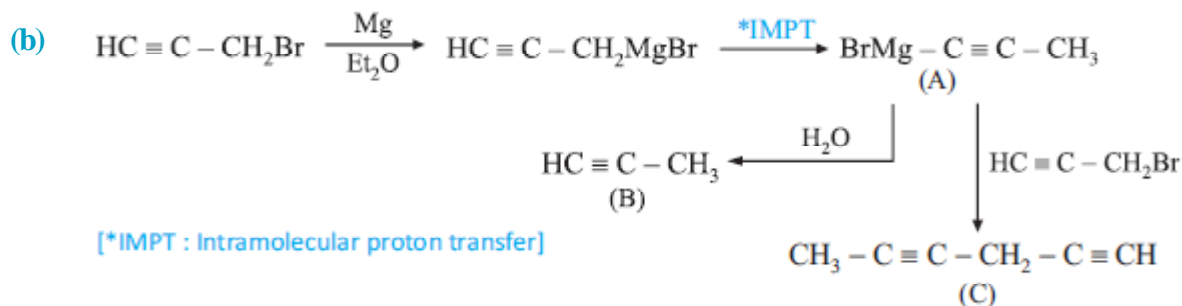
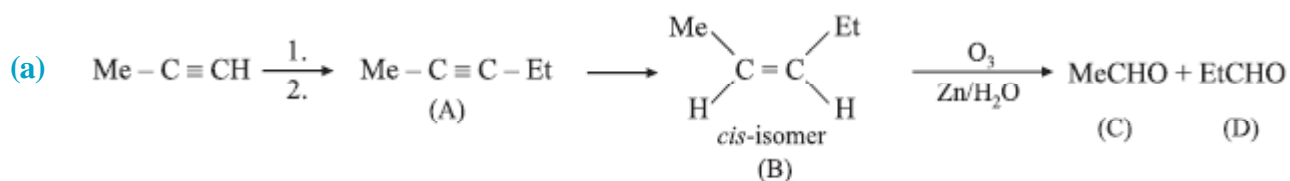


Illustration - 8

Identify A, B, C



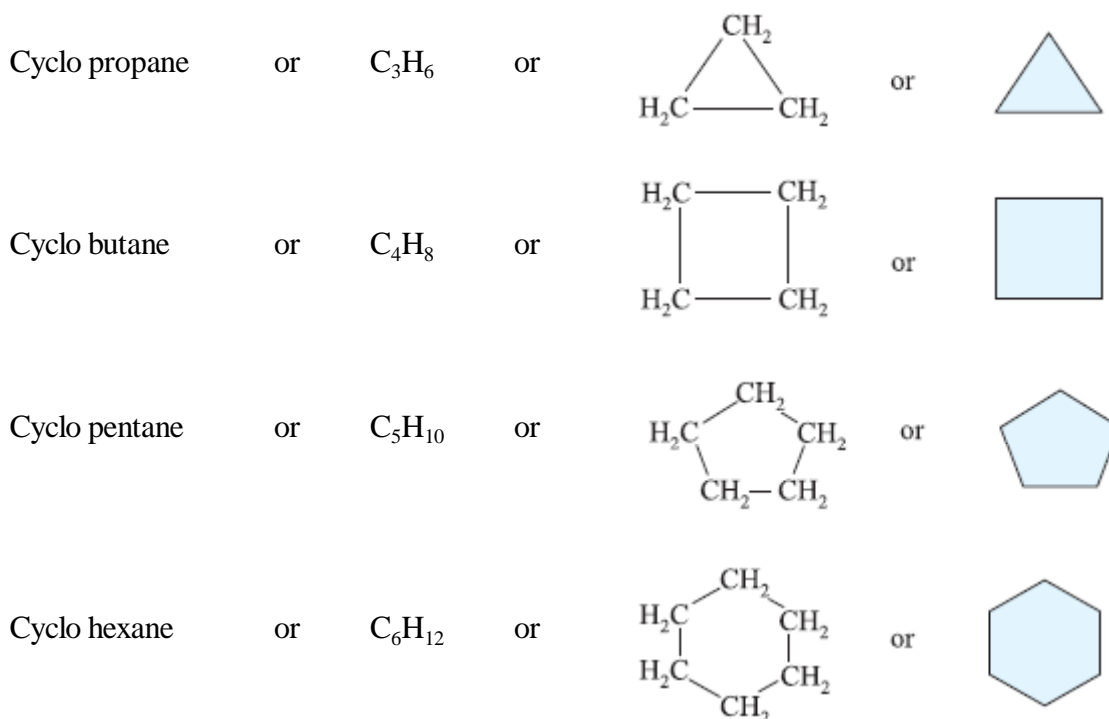
SOLUTION :



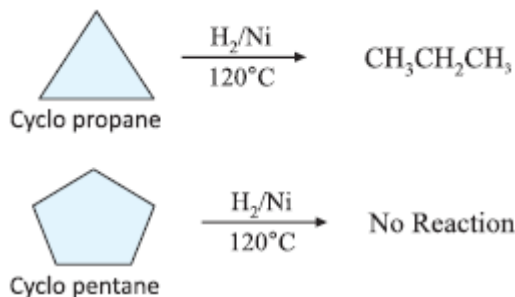
CYCLOALKANES AND CYCLOALKENES

Section - 4

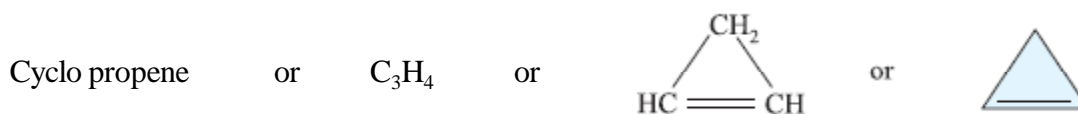
These are closed chain hydrocarbons having C_nH_{2n} as general formula. These are isomeric to alkenes.

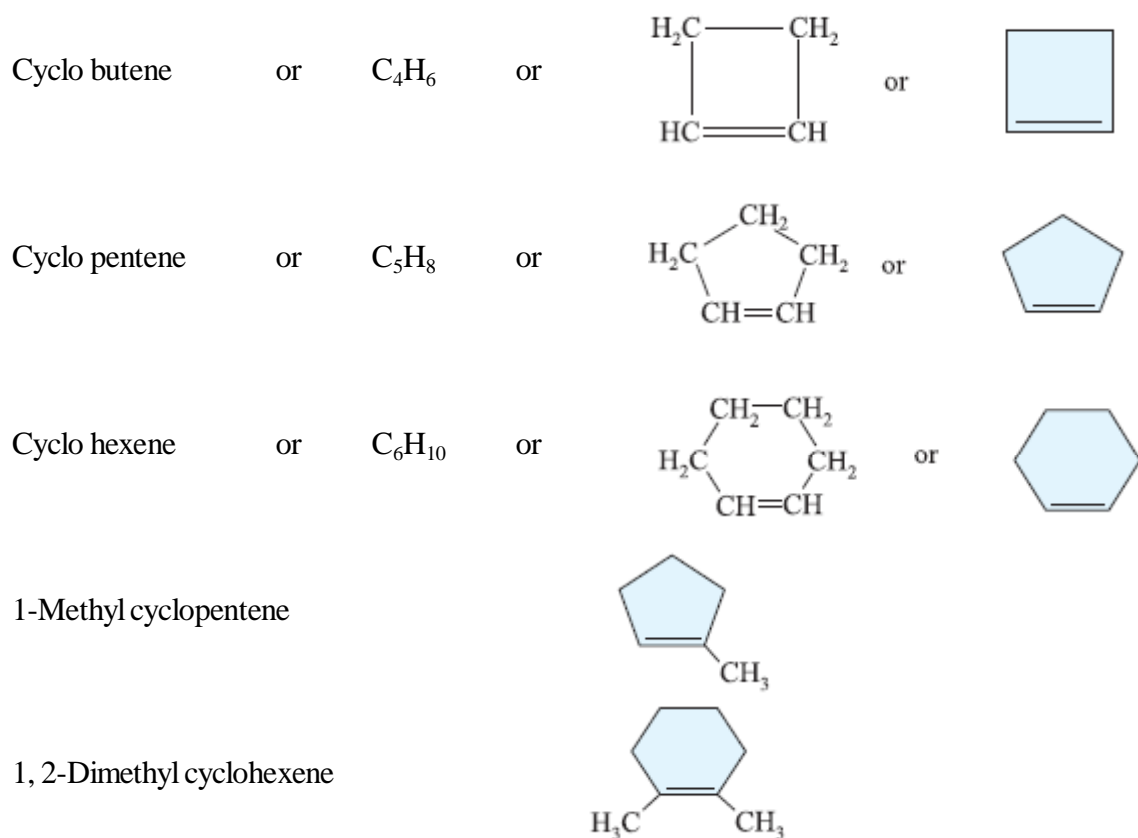


The bond angles in lower members, i.e., in cyclopropane and cyclobutane are quite different from normal tetrahedral bond angle of 109.5° . Hence these are unstable as compared to higher member such as cyclopentane and cyclohexane which have bond angles nearer to tetrahedral bond angles. The two small 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.



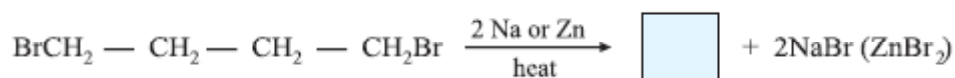
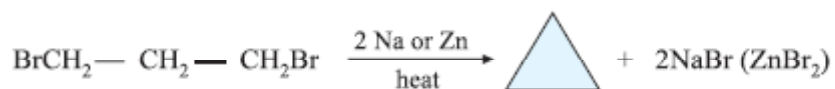
Cycloalkenes : These are isomeric to alkynes and alkadienes. Some important cycloalkenes are :





Preparation of cycloalkanes and cycloalkenes :

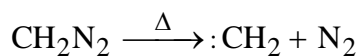
1. Dehalogenation of isolated dibromides :

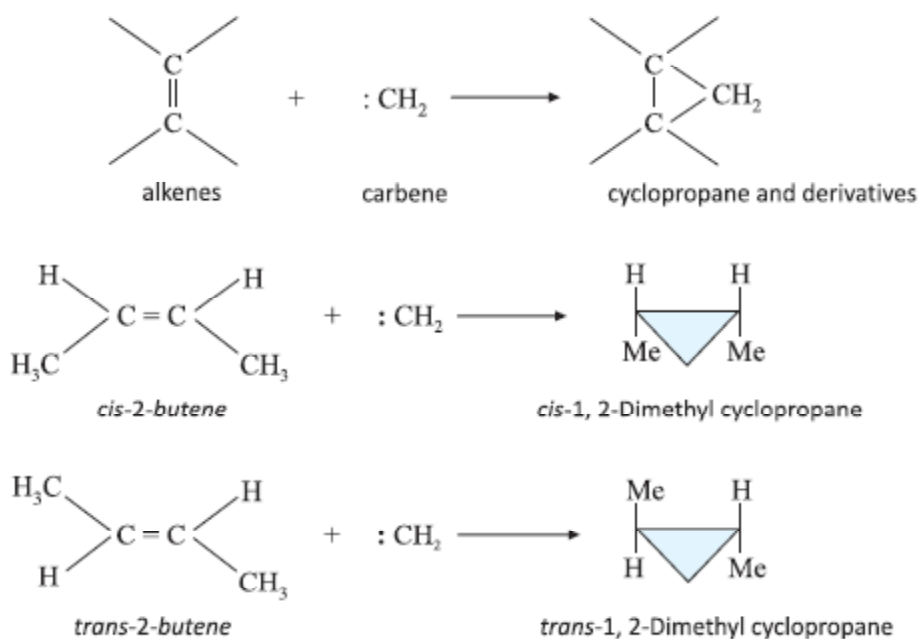


It is not a good method because of poor yield.

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.

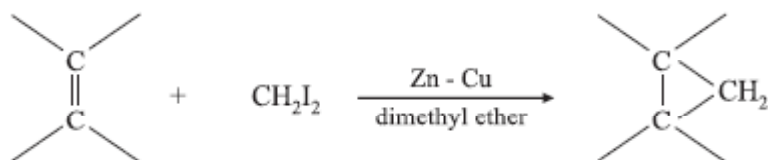




Note that the addition of :CH_2 (carbene) is **stereospecific** as 2-butene exist in *cis* and *trans* forms.

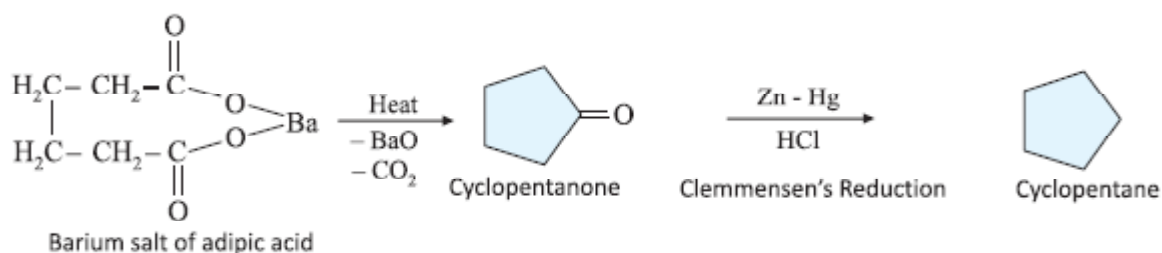
3. Simmon - Smith Reaction :

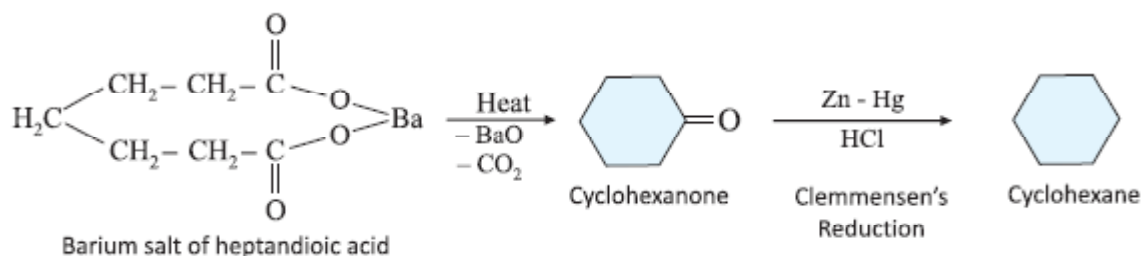
It is another method to form cyclopropane and its derivatives. Instead of diazomethane, di-iodomethane, CH_2I_2 with Zn-Cu alloy in diethyl ether is used. The rest of the reaction is same as above.



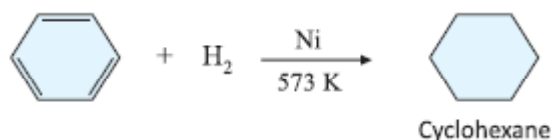
4. Heating calcium/barium salts of dicarboxylic acids :

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



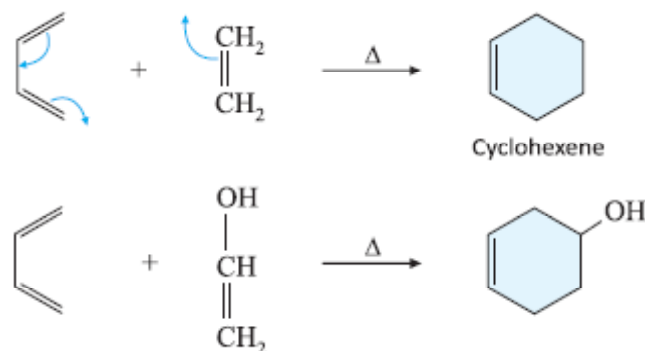


5. Hydrogenation of benzene :

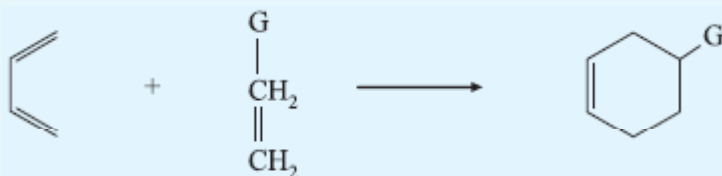


6. Diel - Alder Reaction :

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 because of formation of six membered cyclic transition state.



Note : (i)



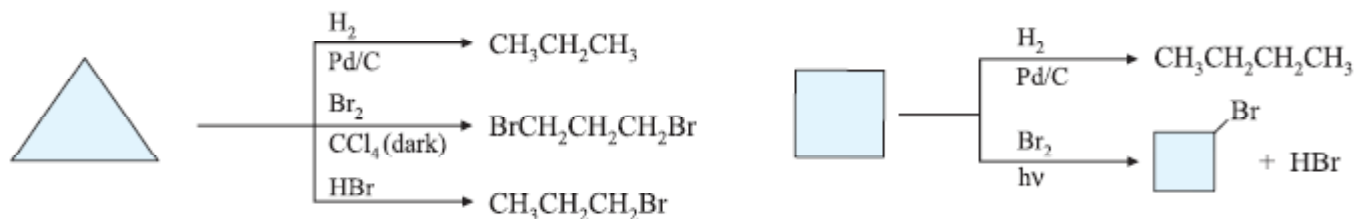
'G' is preferably an electron withdrawing group (electronegative in nature) such as -OH, -NH₂, -CN, -NO₂, etc.

(ii)

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

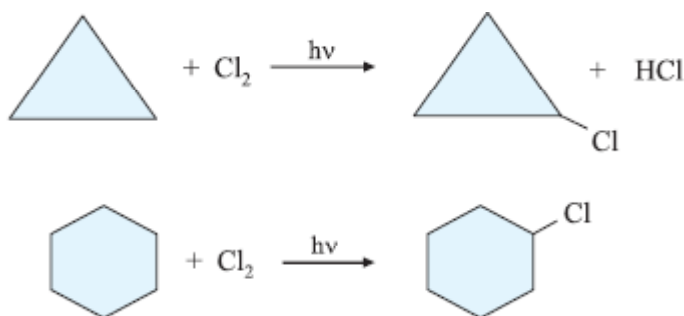
Reaction of cycloalkanes :

1. Ring opening :

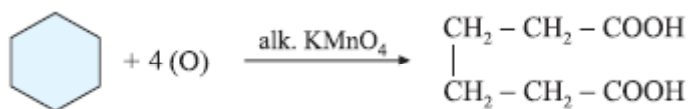


The ring of 5 carbons being stable does not open after reaction with hydrogen.

2. Chlorination :



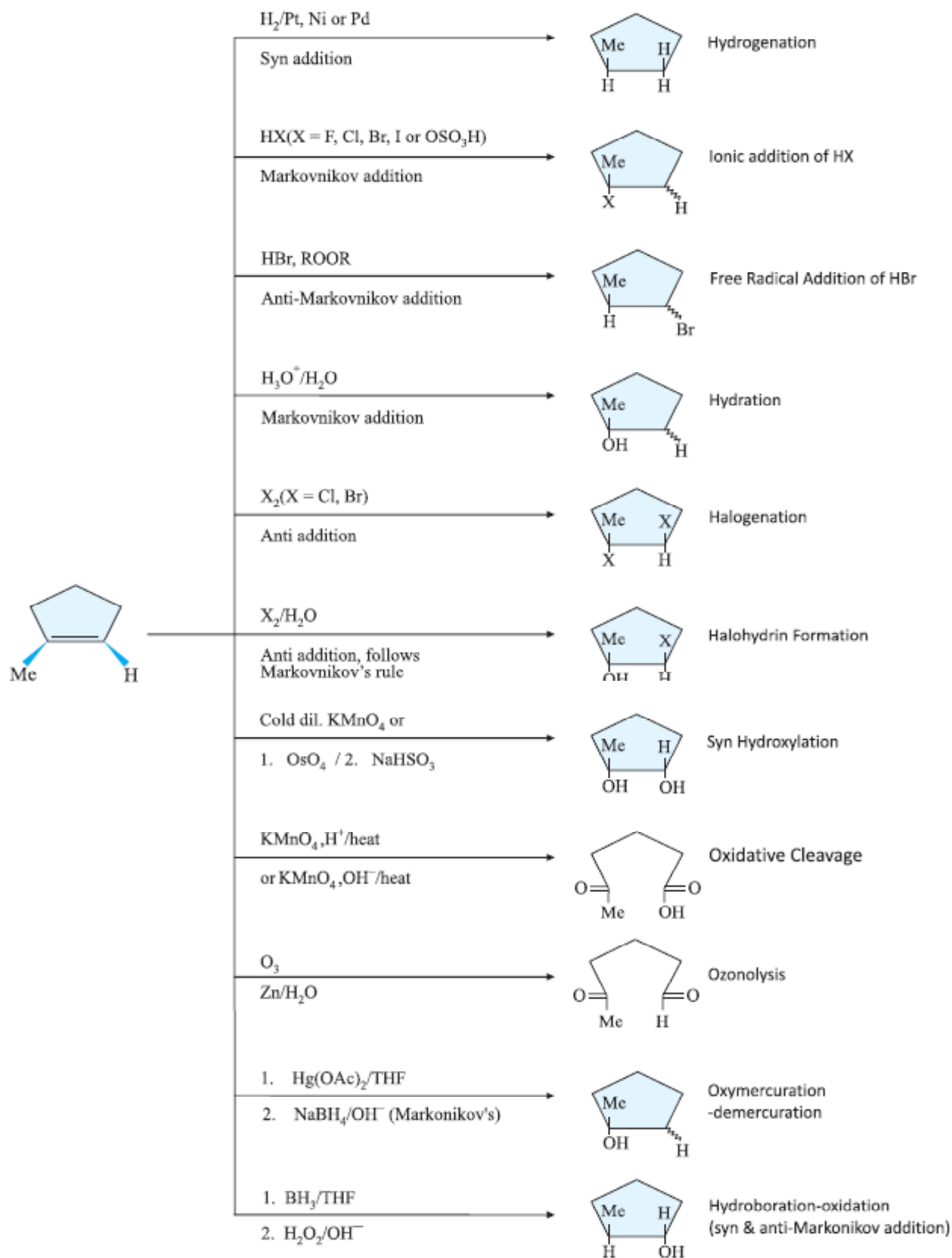
3. Oxidation :



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.



ALKADIENES

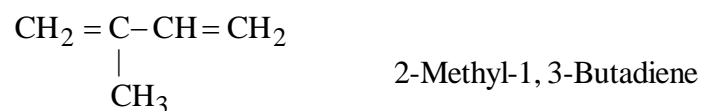
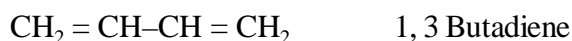
Section - 5

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.

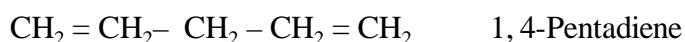


- (b) Those dienes which have an alternate system of double and single bonds are called conjugated dienes.



1, 3-Cyclohexadiene

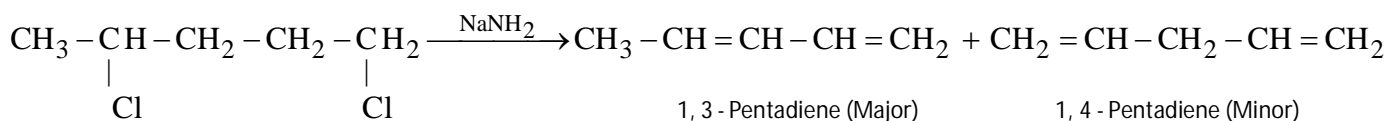
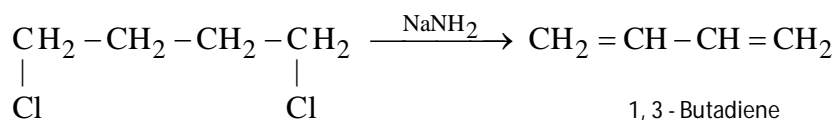
- (c) In case, when two or more sp^3 hybridised carbon atoms come in between the double bonds in dienes, then they are called isolated dienes.



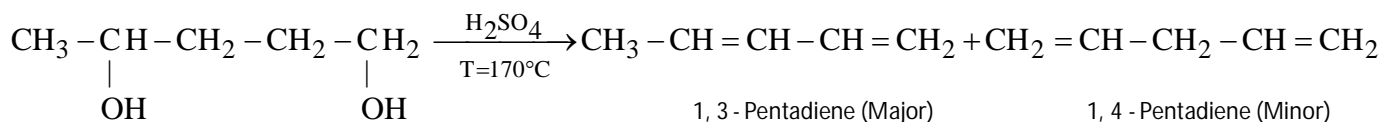
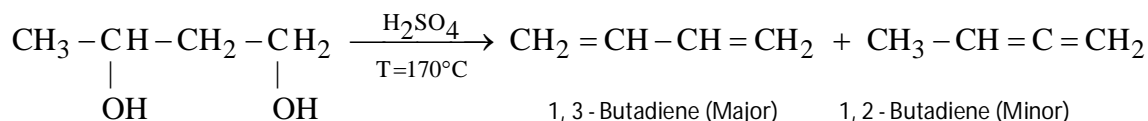
Note: Conjugated dienes are most stable among dienes. They are stabilised due to resonance.

Preparation of Conjugate dienes :

1. From isolated dihalides



2. From isolated diols :



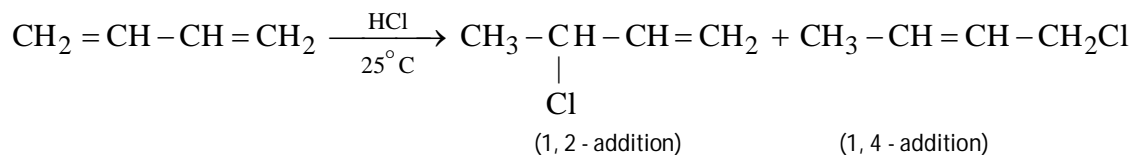
Reactions of Conjugate Dienes :

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

1. Electrophillic Addition :

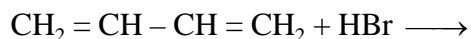
1, 3-Butadiene when reacts with HCl show unusual behaviour to give mixture of two products :
3-Chloro-1-butene (1, 2-addition product) and 1-Chloro-2-butene (1, 4-addition product)

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

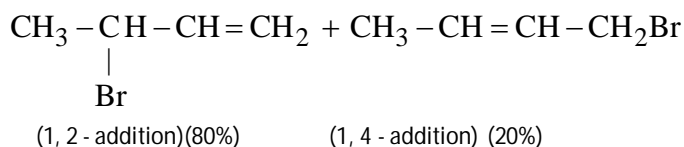


Note : Usually 1, 4-addition product is major.

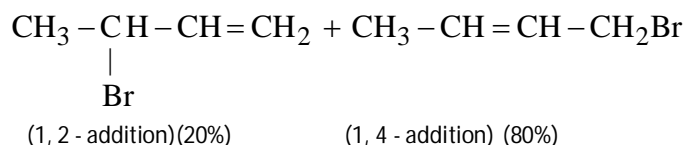
(b) Addition of HBr to 1, 3-Butadiene takes place differently at different temperatures to give 1, 2-addition and 1, 4-addition products as follows :



(i) At -80°C (Low temperature) :

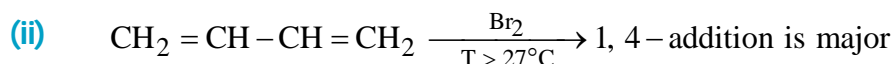
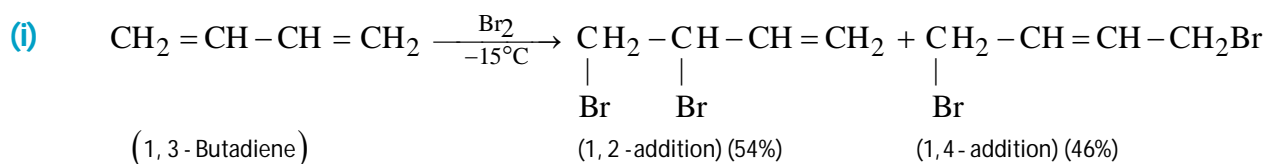


(ii) A 40°C (Near room temperature and above) :



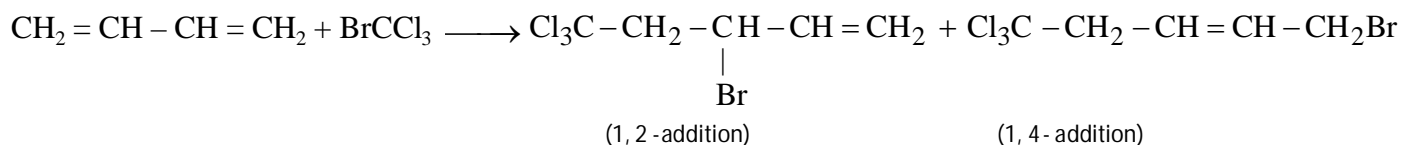
Note : At high temperatures, in case of HBr, 1, 2-addition product rearranges to give 1, 4-addition product.

(c) Addition of Br₂ to 1, 3-Butadiene also gives a mixture of 1, 2-addition and 1, 4-addition products.



2. Free radical addition :

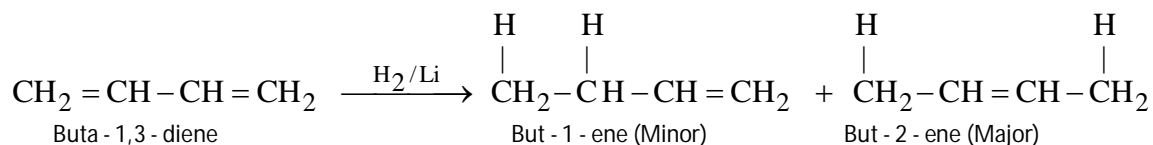
In presence of peroxides, both 1, 2-addition product and 1, 4-addition products are formed. Consider addition of BrCCl₃ in presence of peroxide.



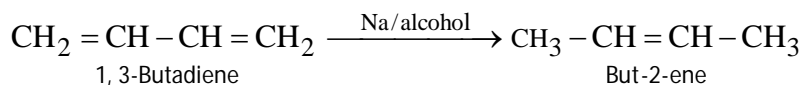
Note : Temperature dependency of products is similar to that HBr addition. Also refer to Diel - Alder reactions (diene with alkenes) in cycloalkenes.

3. Reduction :

Catalytic hydrogenation of conjugated dienes in presence of H₂/Li gives a mixture of 1, 2-addition and 1, 4-addition product with the 1, 4-addition products being major.

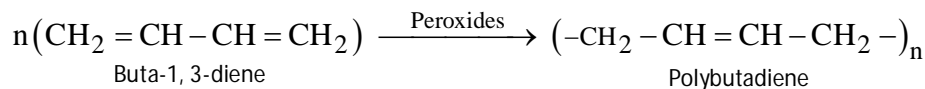


However, the chemical reduction of 1, 3-Butadiene with sodium in alcohol gives mainly the 1, 4-addition product, i.e., But-2-ene.

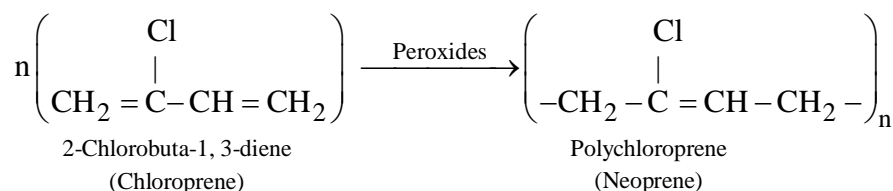
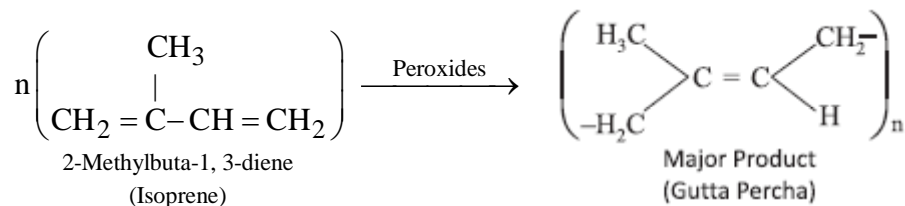


Under these conditions the isolated double bonds are not reduced. This suggests that dienes are much more reactive than simple alkenes.

4. Polymerization :



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.



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

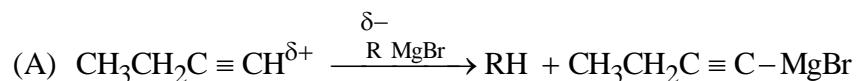
Isomers A, B, C, and E have a common molecular formula C_4H_6 . Identify A, B, C.....as per given instructions.

- (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.

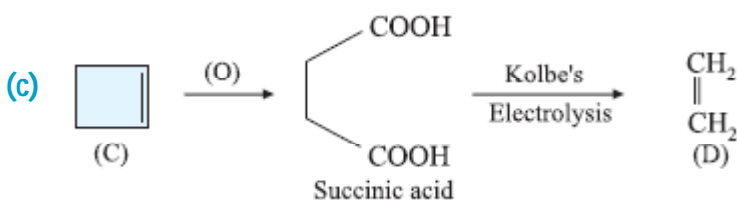
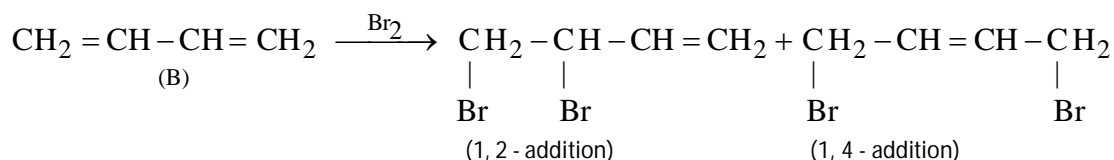
SOLUTION :

C_4H_6 : can be alkyne, or alkadiene, or cycloalkene

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



- (b) B should be a conjugated diene as it gives a mixture of products.



D is clearly ethene as it is the only alkene formed by Kolbe's electrolysis.

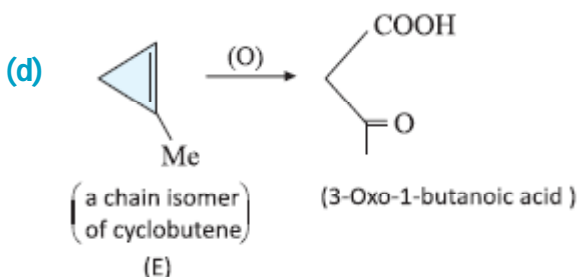
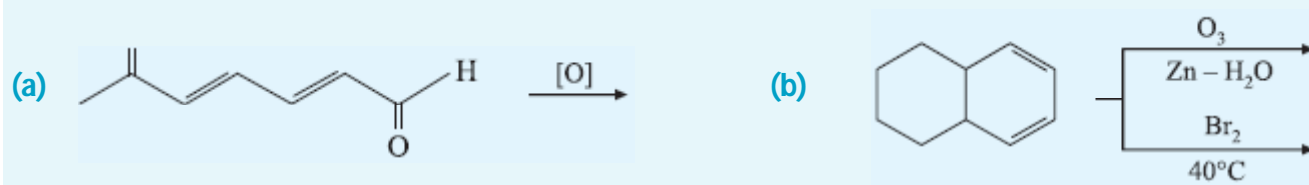
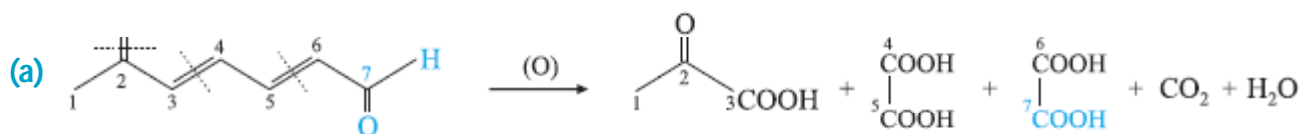


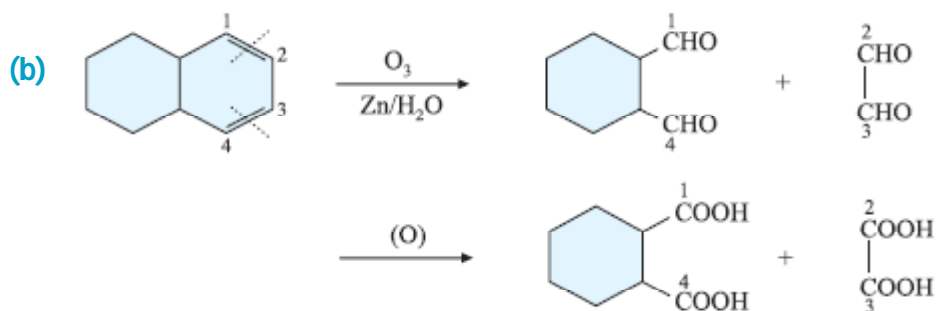
Illustration - 10 Give the products.



SOLUTION :



Note that aldehyde group is oxidised to acidic group



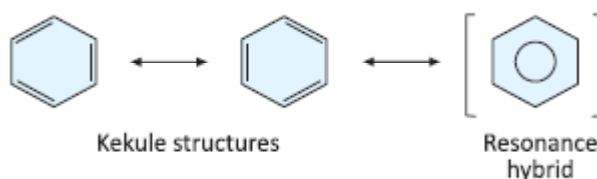
AROMATIC HYDROCARBONS

Section - 6

Benzene : $[C_6H_6]$ **Structure :**

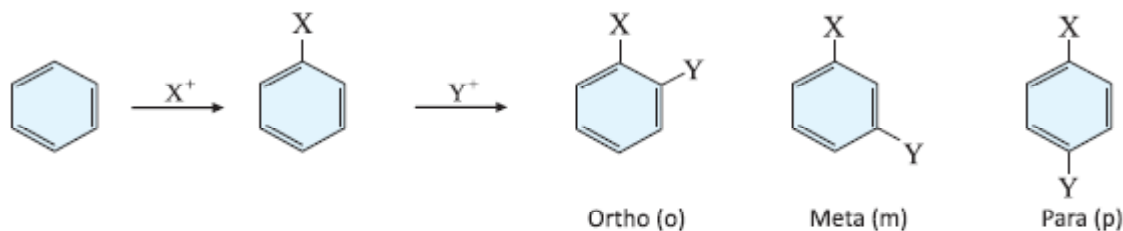
Its molecular formula is C_6H_6 . This implies unsaturation in benzene. It shows addition reactions : addition of 3 molecules of Hydrogen, 3 moles of Cl_2 and 3 moles of Ozone (like alkenes).

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 :



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, addition reaction (electrophilic) are not common in benzene. However, in benzene electrophilic 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 (monosubstituted) is obtained. On the other hand, when a group of electrophilic nature is introduced in a mono-substituted benzene, three different isomers are possible.



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

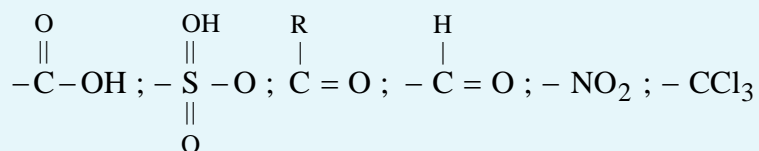
Directive (orienting) influence of groups :

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

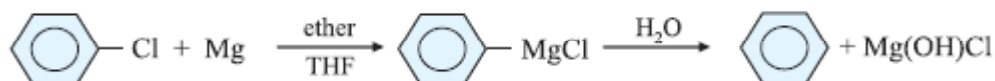
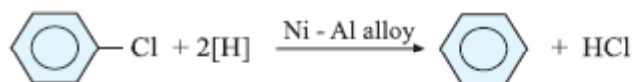


All of these groups exerts +M effect over benzene and tends to increase electron-density over benzene and make benzene strongly nucleophilic towards electrophiles. These groups are called **activating groups**. -I effect (electronegative or electron withdrawing nature) of these groups is weaker as compared 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 electrophilic substitution in halo benzenes. Alkyl group (R) are *o* and *p* directing due to hyperconjugation (to be discussed later).

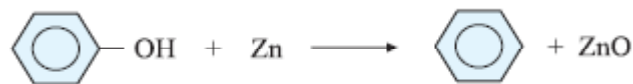
- (b) ***m*-directing groups :** These groups direct the incoming groups predominantly to *m*-positions. Some of the important groups are :



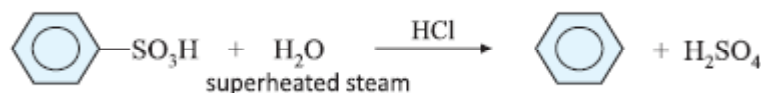
All *m*-directing groups, (except $-\text{CCl}_3$) either possess a positive charge or the key atom of substituents has an electronegative atom linked by a multiple bond. The benzene nucleus containing these groups undergo strong $-\text{M}$, $-\text{I}$, effect such that the displacement of electron takes place away from the benzene ring. These groups tends to deactivate the benzene ring and hence makes it less nucleophilic towards electrophiles. These are called as **de-activating groups**. Benzene having these groups will have greater difficulty in electrophilic substitution reactions.

Preparation of Benzene :**1. Decarboxylation of Sodium Benzoate :****2. From Chlorobenzene :**

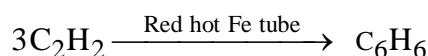
3. From Phenol :



4. From Sulphonic Acid :



5. Synthesis :

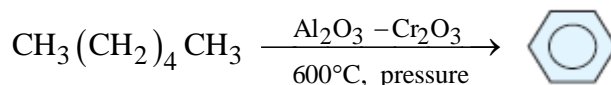


6. From Benzene Diazonium Chloride :



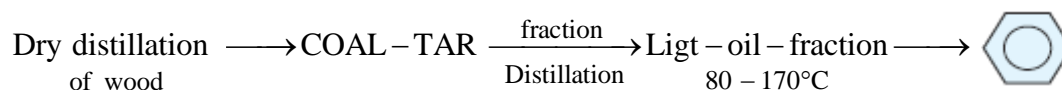
7. Manufacture :

(a) n-hexane :



This is known as Hydroforming or catalytic Reforming or aromatisation

(b) Coal Tar :



Physical properties of Arenes :

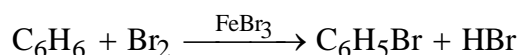
1. Benzene and its homologues containing upto eight carbon atoms are colourless liquids with characteristic smell.
2. Due to large hydrophobic hydrocarbon part, arenes are not soluble in water but are soluble in organic solvents.
3. The melting points and boiling points of arenes increase with increase 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 :



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 $\text{C}_6\text{H}_5\text{Br}$ is found among the products. Similarly, when benzene is chlorinated, only one monochlorobenzene results.

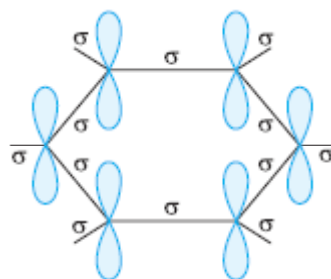
Two possible explanations can be given for these observations. The first is that only one of the six hydrogen atoms in benzene is reactive toward these reagents. The second is that all six hydrogen atoms in benzene are equivalent, and replacing any one of them with a substituent results in the same product. 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

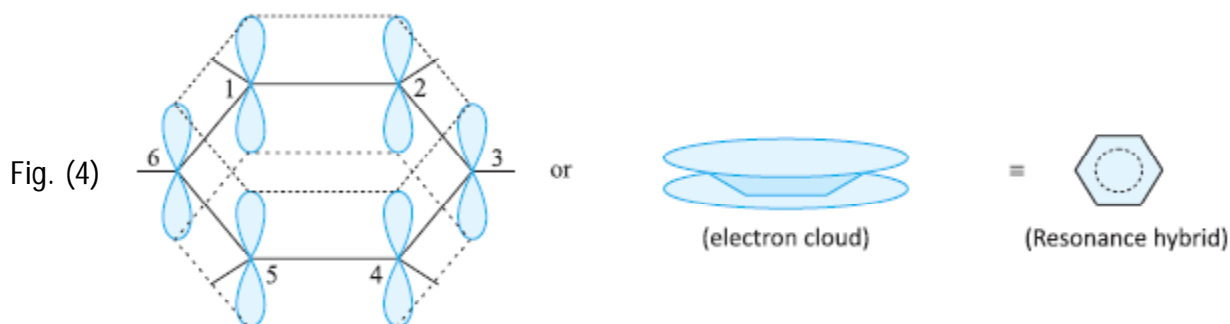
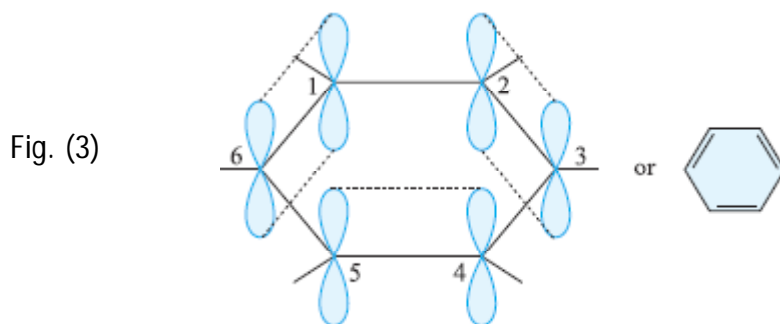
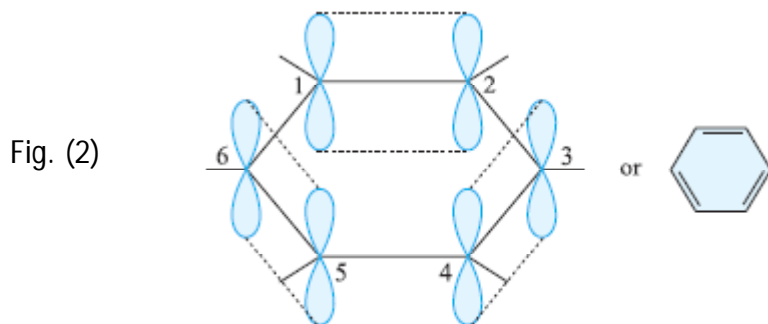
The fact that the bond angles of the carbon atoms in the benzene ring are all 120° strongly suggests that the carbon atoms are sp^2 hybridized. If we accept this suggestion and construct a planar six-membered ring from sp^2 carbon atoms, a representation like and shown in figure emerges. In this model,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

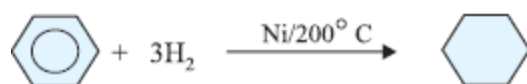


- (b) Overlap of the p-orbitals forming $\pi(\pi)$ bonds around the ring results in the delocalisation of $\pi(\pi)$ electrons on the ring. [Refer to Fig.(2), (3), (4)]

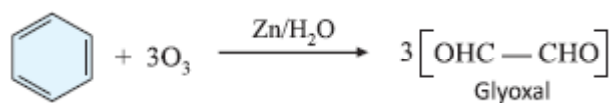


The six π electrons are thus delocalised and can move freely about the six carbon nuclei, instead of any two as shown in figure (4). The delocalised π electron cloud is attracted more strongly by the nuclei of the carbon atoms than the electron cloud localised between two carbon atoms. Therefore, presence 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 :

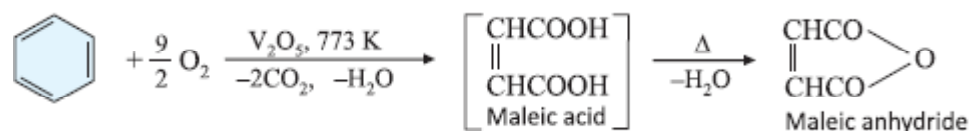


3. Oxidation :

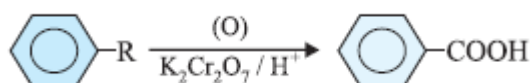
Benzene is unreactive towards even strong oxidising agents such as : $\text{KMnO}_4/\text{K}_2\text{Cr}_2\text{O}_7$. However in drastic conditions, it can be oxidised slowly to CO_2 and H_2O . It can be burned (i.e., combustion) to give luminous and smoky flame.

(a) **Controlled oxidation with air :**

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



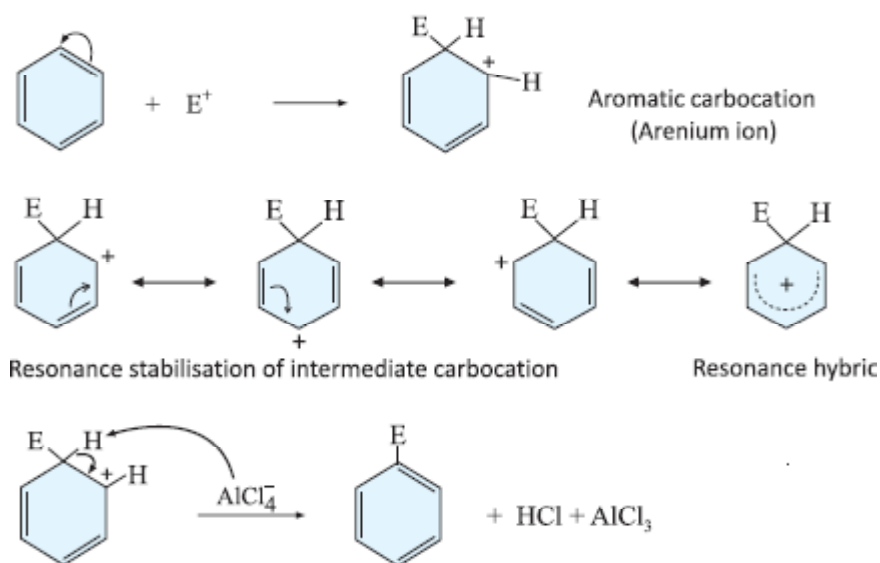
(b) Oxidation of alkyl benzene :



Note: If R is a 3° alkyl group, then it resists oxidation the benzene ring is destroyed.

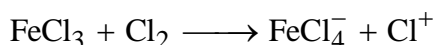
3. Substitution Reactions :

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

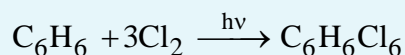


Electrophiles :

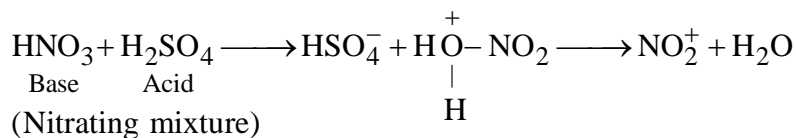
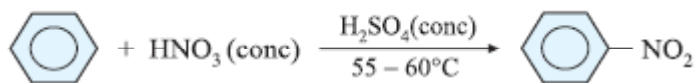
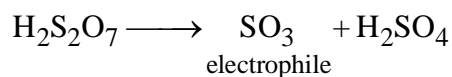
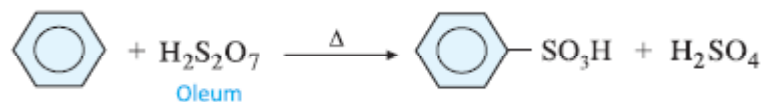
Cl^+ (Chloronium ion), N^+O_2 (Nitronium ion), SO_3 (Sulphur trioxide), R^+ (Carbonium ion), $\text{R}-\text{C}\equiv\text{O}^+$ (Acylium ion).

(a) Halogenation :

- 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.

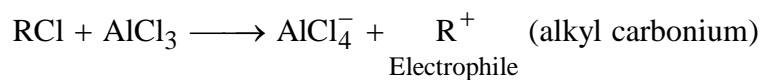
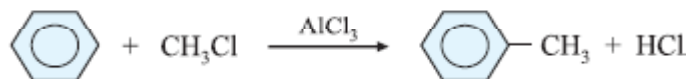
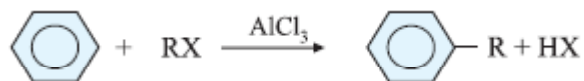


It may be noted that this is an addition reaction, not a substitution reaction.

(b) Nitration :**(c) Sulphonation :**

- (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 **Friedel Craft** reactions.

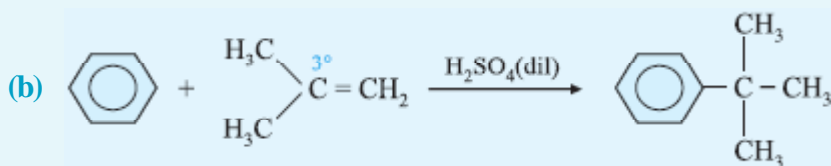
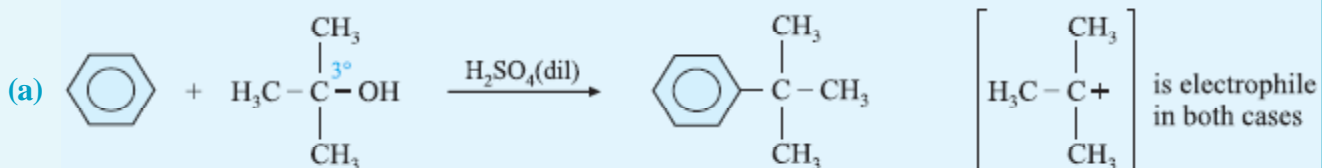
(i) Alkylation :



Note: The above reaction can be achieved with :

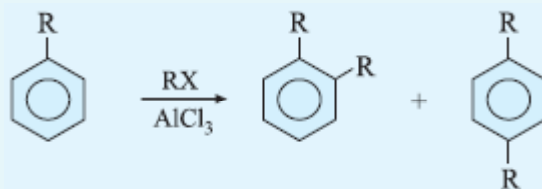
(a) An alcohol in HF or dil H_2SO_4

(b) An alkene in HF or dil. H_2SO_4 (at low temperature)

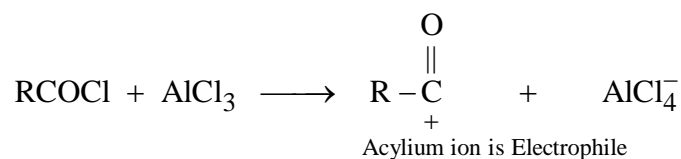


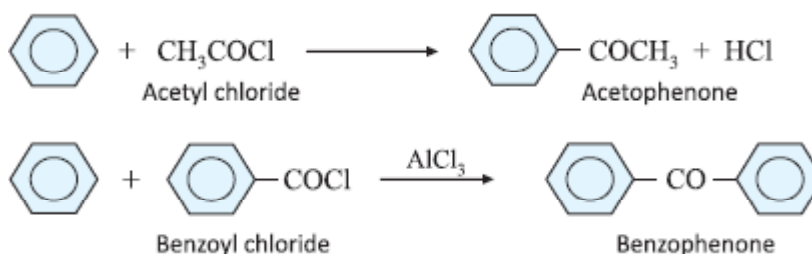
Observe that 3° carbon is attached to the ring.

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



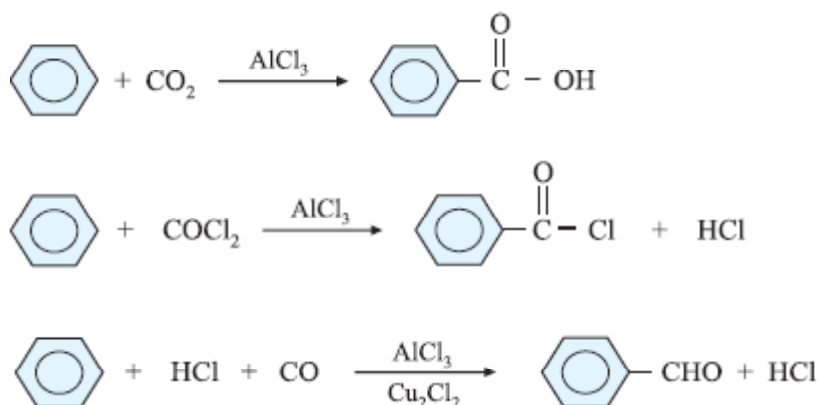
(ii) Acylation :





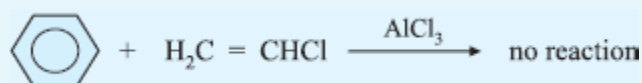
The above two reactions are called as Acetylation and Benzoylation respectively.

Some Friedel-Craft acylation reactions are shown below :

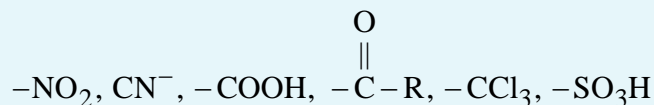


The above reaction is also known as Gatterman-Koch reaction.

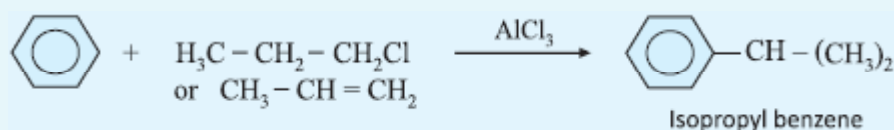
Note: (i) Aryl and vinylic halides cannot be used in Friedel-Craft reactions as they do not form carbocations easily.



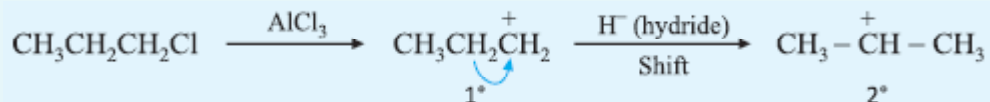
(ii) In substituted benzenes, Friedel-Craft reactions give poor yield when electron withdrawing (deactivating) groups are present on the ring. These include :



(iii) In Friedel-Craft alkylation, the most stable carbocation (from alkyl halide or alkene) determines the final substitution product.

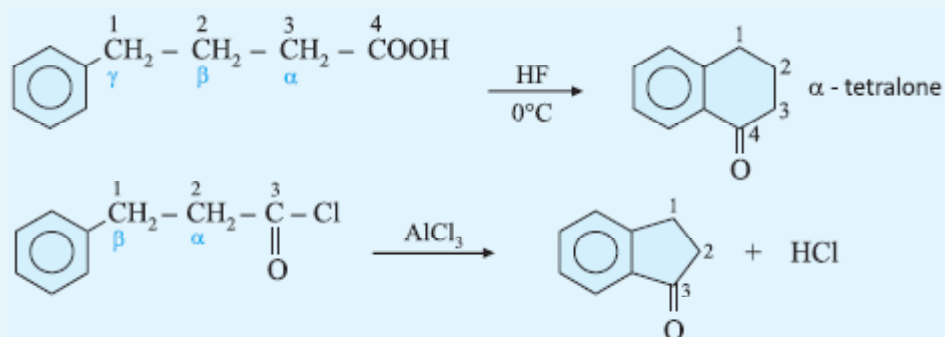


It does not give n-propyl benzene since $\text{CH}_3 - \overset{+}{\text{C}}\text{HCH}_3$, being a 2° carbocation is more stable than $\text{CH}_3\text{CH}_2\text{CH}_2$ (1°).

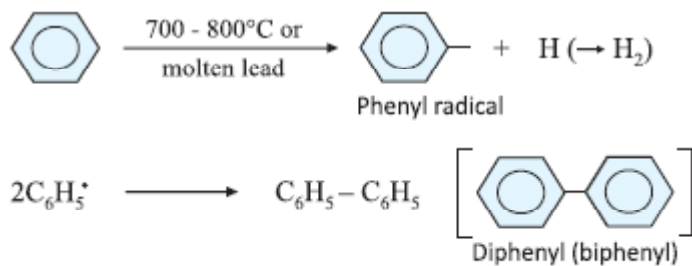


* The detailed mechanism of SE reaction will be discussed later in the chapter “Organic Concepts”.

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



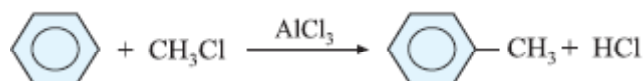
4. Dehydrogenation :



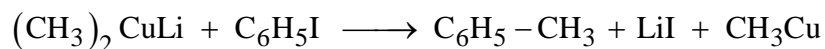
Toluene : 

Preparation of Toluene :

1. Friedel craft alkylation :

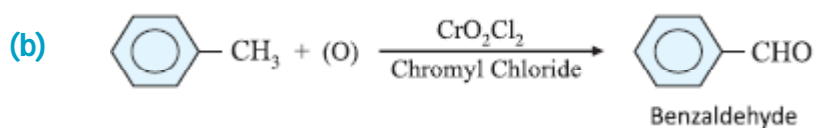
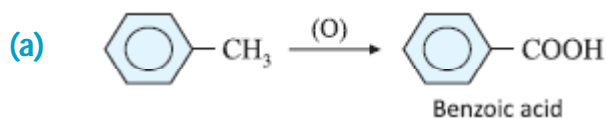


2. From dialkyl cuprates :



Reactions :

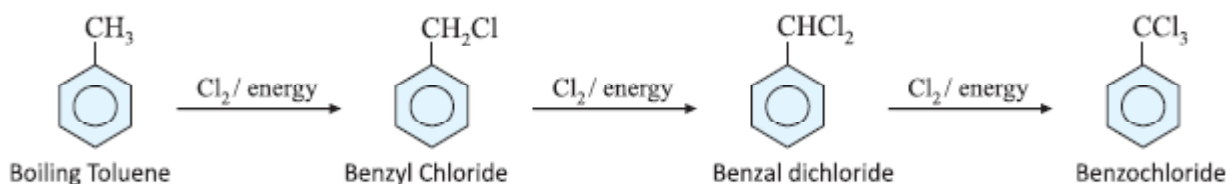
1. Oxidation :



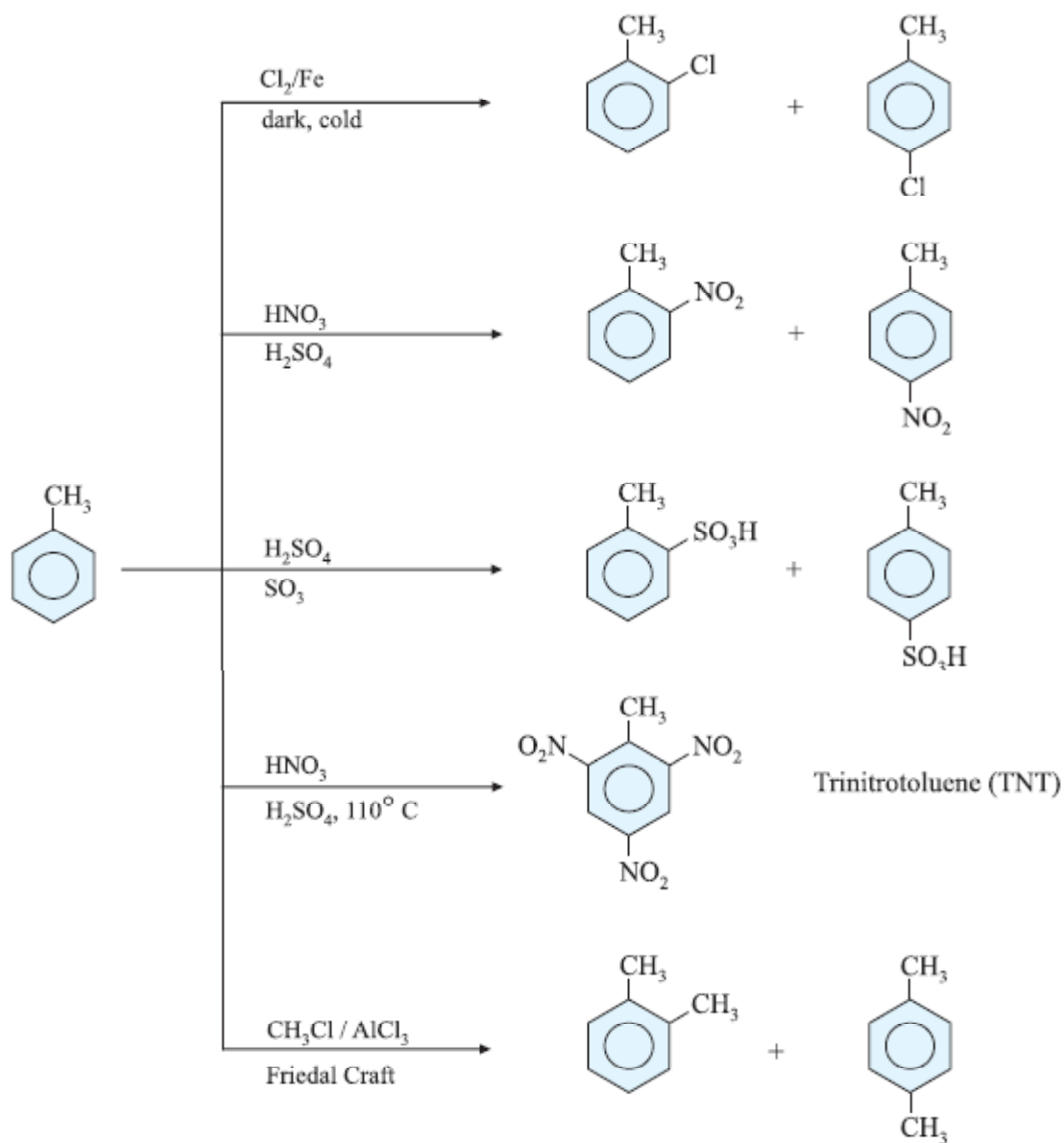
This is also known as [Etard reaction](#).

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 :

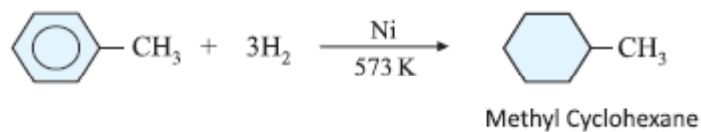
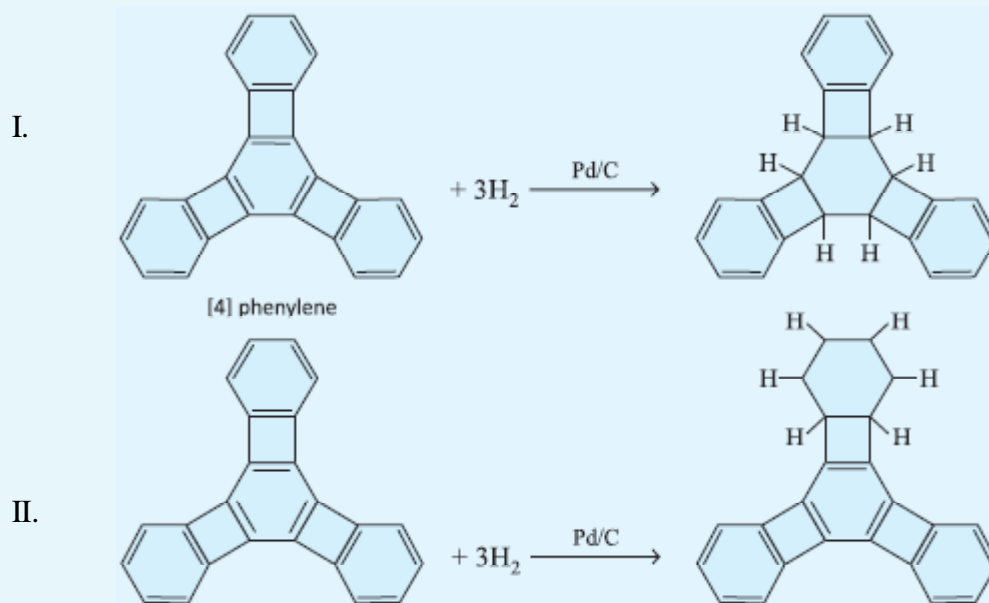


Illustration - 11 One of the benzene ring of [4] phenylene undergoes catalytic hydrogenation readily under conditions usually used for ordinary alkenes, but the other benzene ring do not. Identify which of these two reaction correctly represent product of hydrogenation of [4] phenylene ?

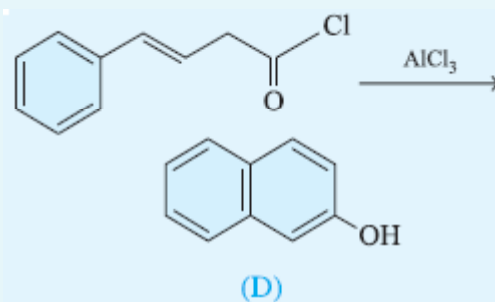
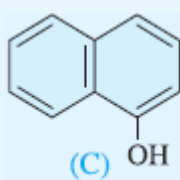
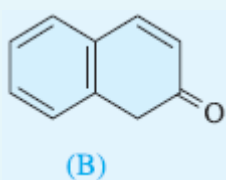
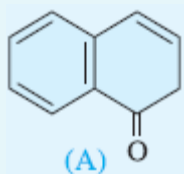


- (A) Only I (B) Only II (C) Both I and II (D) None

SOLUTION

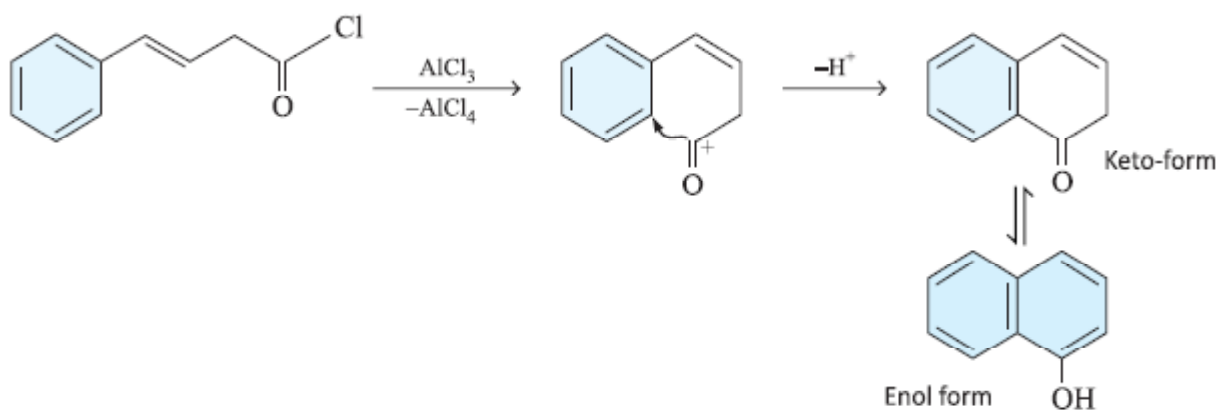
Reaction I correctly represent product of hydrogenation of [4]-phenylene because of loss in anti-aromatic characters of all four membered rings.

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



SOLUTION

Enolic form is more stable than keto form due to more aromatic characters in enolic form.



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

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

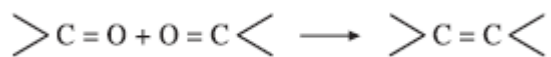
(* : Chiral centre)

optically inactive (No chiral centre)

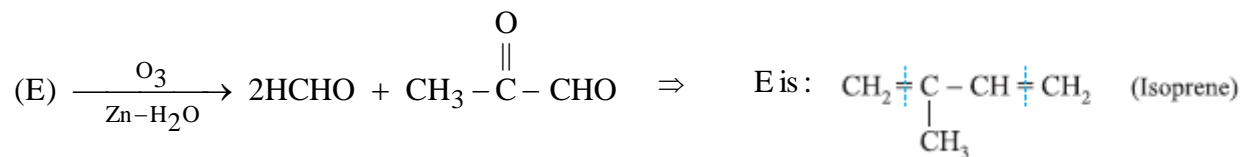
Example - 2

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 :



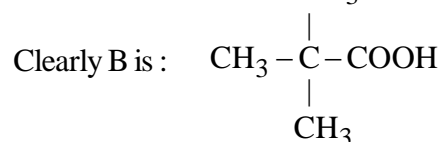
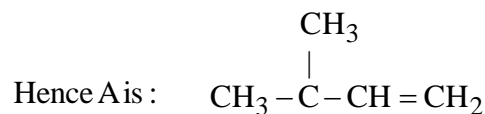
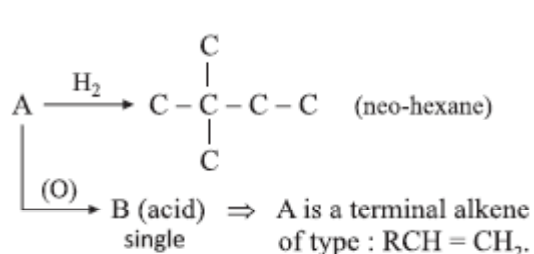
Note: Since 2-ketopropanal has two keto groups, hence there must be 2 moles of HCHO.



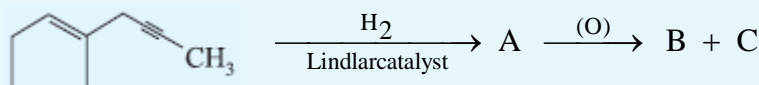
Hydrocarbons

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.

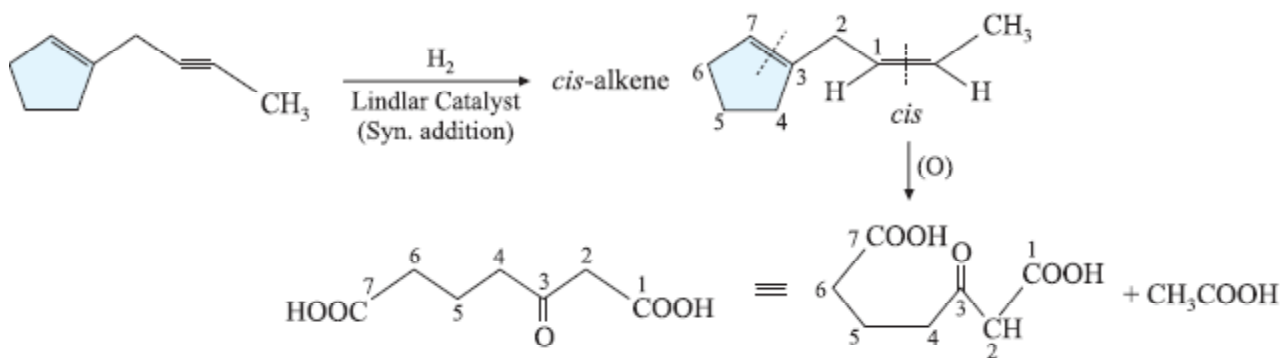
SOLUTION :



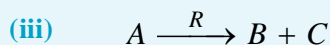
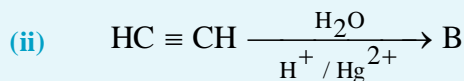
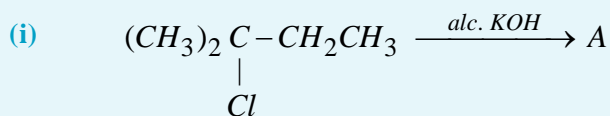
Example - 4 What are product A, B and C in the following reaction ?



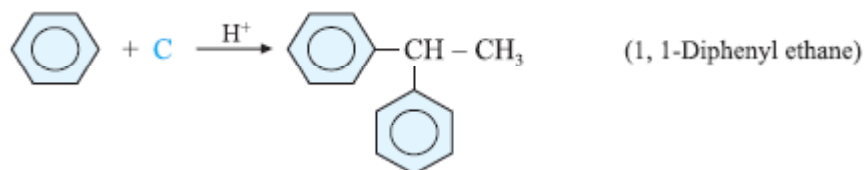
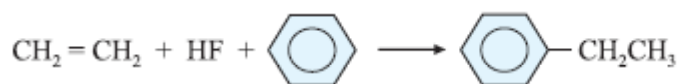
SOLUTION : Visualise the structure of given compound as follows :

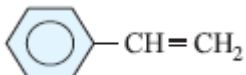


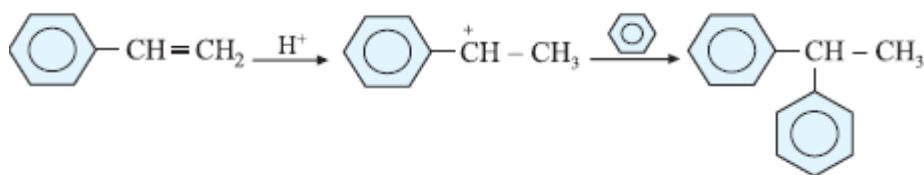
Example - 5 Identify the products A, B and C and the reagent R in the following reactions :



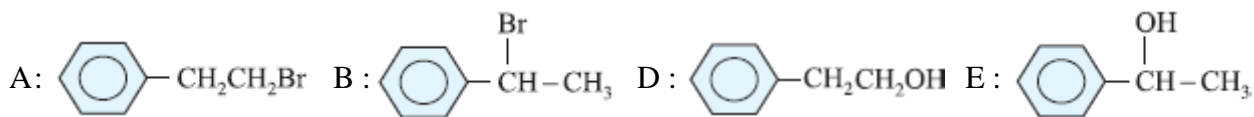
Recall Friedal Craft alkylation



\Rightarrow C is an alkene containing a $\text{C}=\text{C}$ bond, hence C is vinyl benzene. C : 



As per given reactions in question :

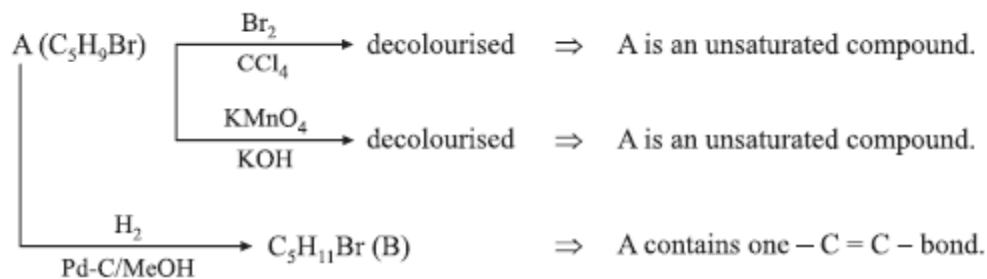


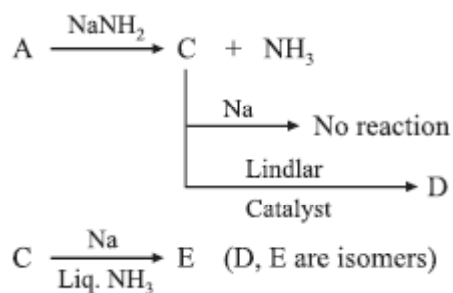
Example - 7

An organic compound A, $\text{C}_5\text{H}_9\text{Br}$ de-colourises bromine water and alk. KMnO_4 . It gives B, $\text{C}_5\text{H}_{11}\text{Br}$ 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 $\text{Na}/\text{liquid NH}_3$ to give E. Both D and E are isomers. Identify the compounds A to E with proper reasoning.

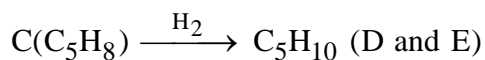
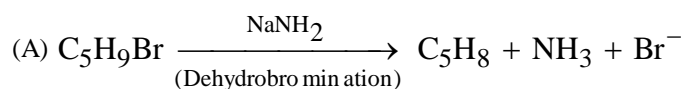
SOLUTION :

Visualizing the flow chart of the question as follows :

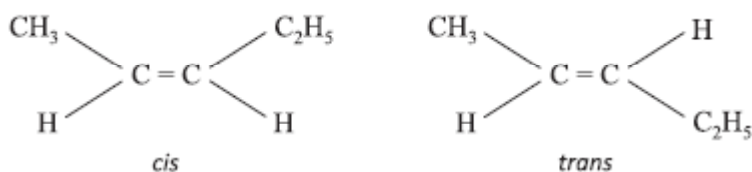
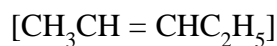




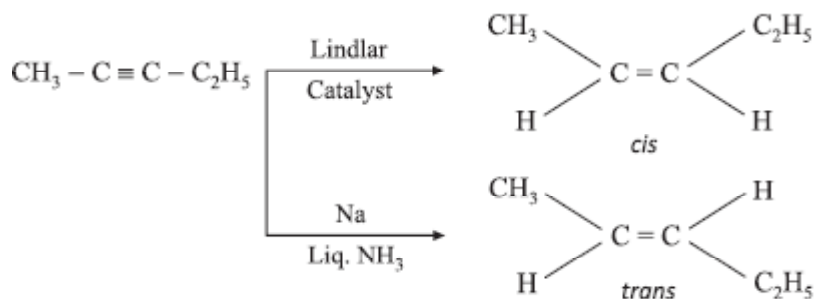
Since D and E are isomers obtained by partial hydrogenation of 'C' (C : an alkyne) from two different reagents, D and E must be geometric isomers with molecular formula C_5H_{10} . "Check this as follows"



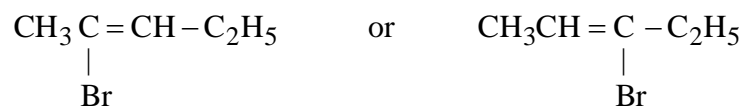
The alkene with molecular formula, C_5H_{10} showing geometric isomerism is only 2-Pentene



Hence the compound (C) is 2-Pentyne (Non-terminal alkynes do not react with Na).



A can be :



Both will give 2-Pentyne with NaNH_2 .

Accordingly B can be :

