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

Alkenes form a homologous series, represented by a general formula : C_nH_{2n}. These have one C=C bond or one can say that two carbon atoms (adjacent) in alkenes show sp^2 type of hybridisation. The important members of alkenes are: Ethene ($CH_2=CH_2$), Propene ($CH_3\,CH=CH_2$), 1-Butene ($CH_3CH_2CH=CH_2$) and its isomers, 2-Butene ($CH_3CH=CHCH_3$) and Iso-butene $(CH_3)_2C=CH_2$.

Generally, alkenes are also represented as : (R : alkyl radical)

1. Terminal alkenes $RCH=CH_2, R_2C=CH_2$
2. Non-terminal alkenes $RCH=CHR, R_2C=CHR, R_2C=CR_2$

Preparation of Alkenes :

1. Dehydration of Alcohols :

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

(a) Heating the alcohol with conc. H_2SO_4 or H_3PO_4 to temperature as high as 170°C.

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

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

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

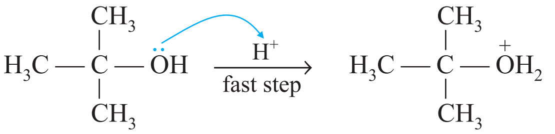
Dehydration is governed by Saytzeff or Zaitsev rule i.e., the greater is number of alkyl groups attached to doubly bonded 'C' atoms, the more stable is the alkene.

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.

Consider Dehydration in tertiary butyl alcohol

Step 1 : *Formation of Oxonium* :

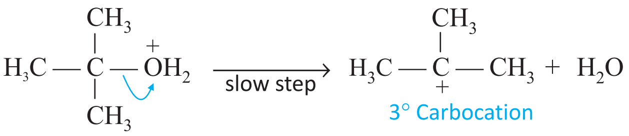
In this reaction, first conc. H_2SO_4 gives a proton (H^+). The electrophile (H^+) attacks oxygen atom (–OH) containing lone pairs of electrons to form an unstable intermediate called as Oxonium (protonated alcohol).



$$(CH_3)_3C-\ddot{O}H \xrightarrow[\text{fast step}]{H^+} (CH_3)_3C-\overset{+}{O}H_2$$

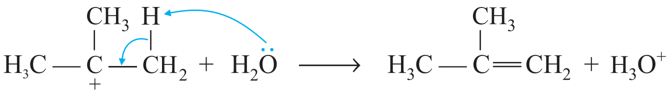
Oxonium
(Protonated alcohol)

Step 2 : *Formation of Carbocation* : The oxonium ion (being unstable) loses a water molecule to give a carbocation.



$$(CH_3)_3C-\overset{+}{O}H_2 \xrightarrow{\text{slow step}} H_3C-\underset{+}{C}(CH_3)-CH_3 + H_2O$$

Step 3 : *Elimination of Proton* : This carbocation loses a proton to give an alkene at 170°C.

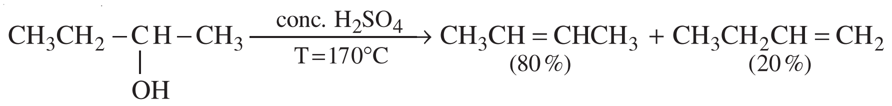


$$H_3C-\underset{+}{C}(CH_3)-CH_2H + H_2\ddot{O} \longrightarrow H_3C-C(CH_3)=CH_2 + H_3O^+$$

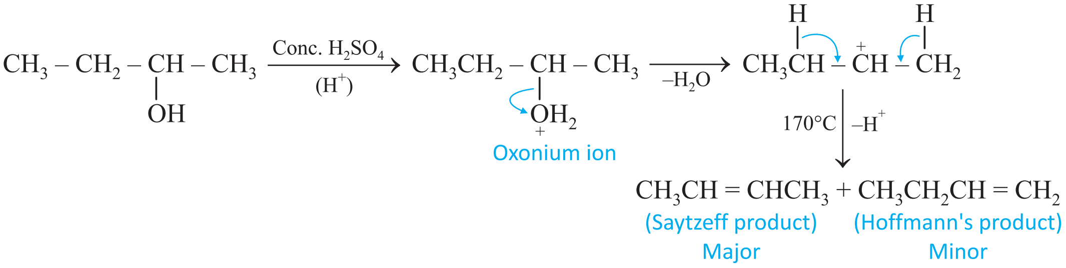
An alkene is formed and water accepts a proton (H^+) to give H_3O^+.

- The important intermediate in this reaction is carbocation ion. So you have to check its stability, while proposing the mechanism. In the above case, the carbocation ion formed is tertiary butyl carbocation, which being a tertiary ion is highly stable (Recall the stability of carbocation). In other case, you have to make *proper rearrangements* for the stability of carbocation.

  Visualise dehydration of 2-Butanol using conc. H_2SO_4 at 170°C involving formation of carbocation shown below :



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



$$CH_3-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 \xrightarrow[(H^+)]{Conc.\ H_2SO_4} CH_3CH_2-\underset{\displaystyle \overset{+}{O}H_2}{\underset{|}{CH}}-CH_3 \xrightarrow[-H_2O]{} CH_3\overset{H}{\overset{|}{C}}H-\overset{+}{C}H-\overset{H}{\overset{|}{C}}H_2$$

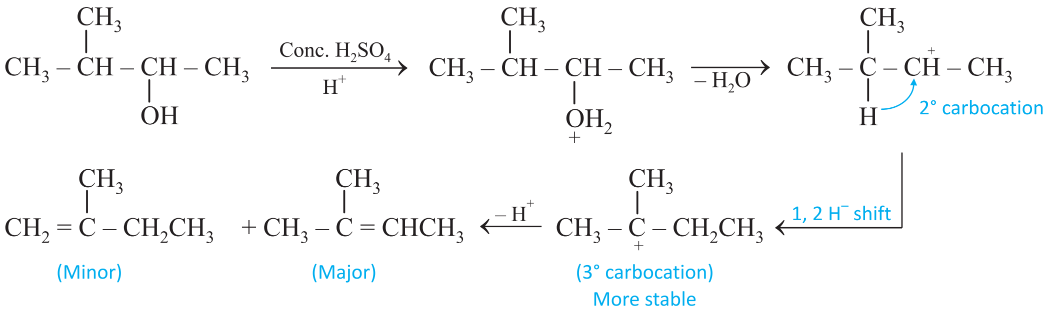
$$\xrightarrow[170°C]{-H^+} \underset{\text{Major}}{\underset{\text{(Saytzeff product)}}{CH_3CH=CHCH_3}} + \underset{\text{Minor}}{\underset{\text{(Hoffmann's product)}}{CH_3CH_2CH=CH_2}}$$

The final product formed follows Saytzeff rule to give 2-Butene (Major).

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

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

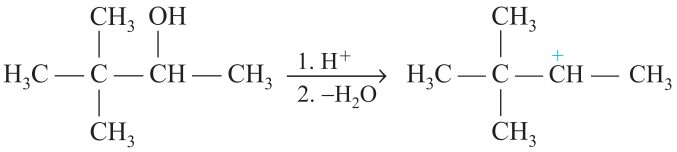
- Note that the alkene will be formed from the most stable carbocation, so wherever applicable visualise the formation of most stable carbocation via rearrangement as shown below:



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 \xrightarrow[H^+]{Conc.\ H_2SO_4} CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-\underset{\displaystyle \overset{+}{O}H_2}{\underset{|}{CH}}-CH_3 \xrightarrow[-H_2O]{} CH_3-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-\overset{+}{C}H-CH_3$$

$$\underset{\text{(Minor)}}{CH_2=\overset{\displaystyle CH_3}{\overset{|}{C}}-CH_2CH_3} + \underset{\text{(Major)}}{CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CHCH_3} \xleftarrow{-H^+} \underset{\text{More stable}}{\underset{\text{(3° carbocation)}}{CH_3-\overset{\displaystyle CH_3}{\overset{|}{\overset{+}{C}}}-CH_2CH_3}} \xleftarrow{1,\ 2\ H^-\ shift}$$

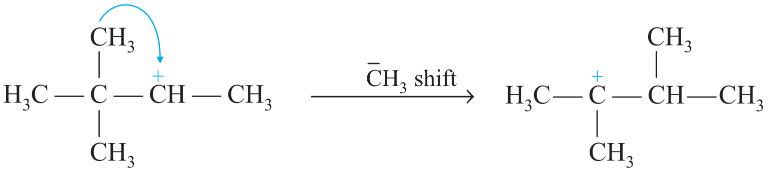
For example consider Dehydration of the following alcohol :



$$H_3C-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-\overset{\displaystyle OH}{\overset{|}{CH}}-CH_3 \xrightarrow[2.\ -H_2O]{1.\ H^+} H_3C-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-\overset{+}{C}H-CH_3$$

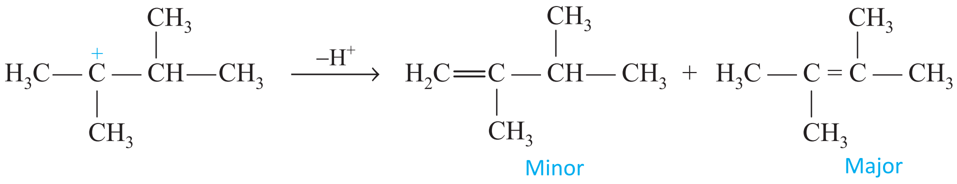
(3, 3 - Dimethyl-2-butanol)

A secondary carbocation (less stable than 3°) is formed. So it will undergo 1, 2 methide (CH_3^-) shift to generate a tertiary carbocation ion.



$$H_3C-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-\overset{+}{C}H-CH_3 \xrightarrow{\bar{C}H_3\ shift} H_3C-\underset{\displaystyle CH_3}{\underset{|}{\overset{+}{C}}}-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_3$$

A tertiary carbocation is more stable than 2°.

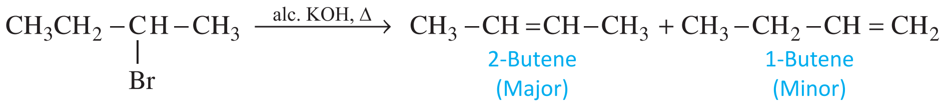


$$H_3C-\overset{+}{\underset{CH_3}{C}}-\overset{CH_3}{CH}-CH_3 \xrightarrow{-H^+} H_2C=\underset{CH_3}{C}-\overset{CH_3}{CH}-CH_3 + H_3C-\underset{CH_3}{C}=\overset{CH_3}{C}-CH_3$$

Minor Major

2. Dehydrohalogenation of Alkyl Halides :

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



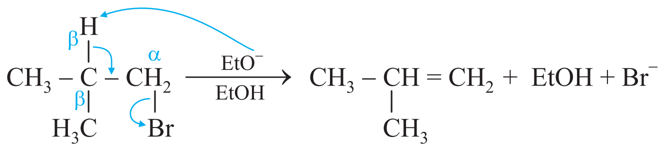
$$CH_3CH_2-\underset{Br}{CH}-CH_3 \xrightarrow{\text{alc. KOH, }\Delta} CH_3-CH=CH-CH_3 + CH_3-CH_2-CH=CH_2$$

2-Butene (Major) Saytzeff product

1-Butene (Minor) Hoffmann product

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 : Alkyl iodide > Alkyl bromide > Alkyl chloride.

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



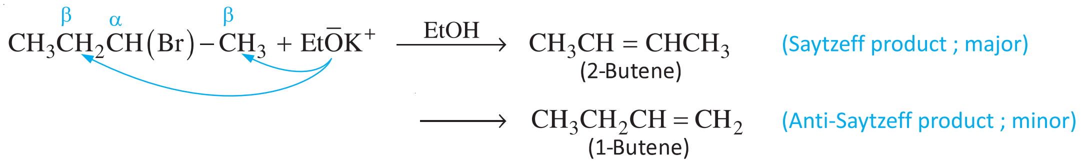
$$CH_3-\overset{\overset{\beta}{H}}{\underset{\underset{\beta}{H_3C}}{C}}-\overset{\alpha}{\underset{Br}{CH_2}} \xrightarrow[EtOH]{EtO^-} CH_3-\underset{CH_3}{CH}=CH_2 + EtOH + Br^-$$

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

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

(iii) You will learn more detail of elimination reaction later in Class 12.

- Two different alkenes may be formed when there are two β-hydrogen atoms. The major is one having more alkylation about the double bond (in accordance with Zaitsev Rule or Saytzeff Rule).



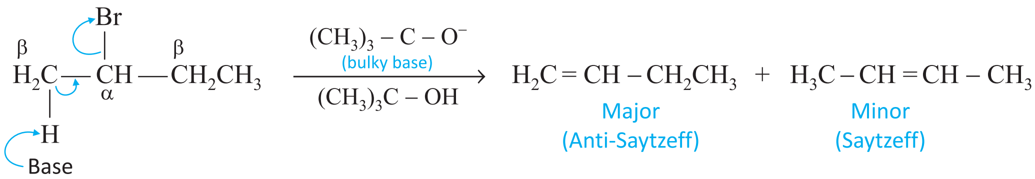
$$CH_3\overset{\beta}{CH_2}\overset{\alpha}{CH}(Br)-\overset{\beta}{CH_3} + Et\bar{O}K^+ \xrightarrow{EtOH} CH_3CH=CHCH_3$$

(2-Butene) (Saytzeff product ; major)

$$\longrightarrow CH_3CH_2CH=CH_2$$

(1-Butene) (Anti-Saytzeff product ; minor)

This is referred to as *Saytzeff Rule*. The exception to Saytzeff rule comes when a large (bulky) and strong bases such as tertiary butoxide are used, then due to steric hindrance (in base) less substituted alkene (Anti-saytzeff product) is formed. It is also known as Hoffmann's product.



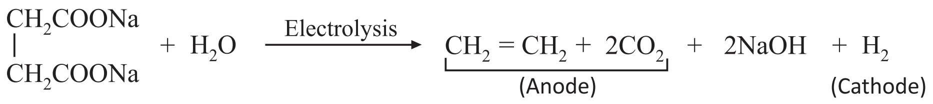
$$\underset{\underset{H}{|}}{\overset{\beta}{H_2C}}-\overset{Br}{\underset{\alpha}{CH}}-\overset{\beta}{CH_2CH_3} \xrightarrow[(CH_3)_3C-OH]{(CH_3)_3-C-O^-} H_2C=CH-CH_2CH_3 + H_3C-CH=CH-CH_3$$

Major (Anti-Saytzeff) Minor (Saytzeff)

3. By dehalogenation of Vicinal Halides :

$$CH_2BrCH_2Br + Zn \longrightarrow CH_2=CH_2 + ZnBr_2$$

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



$$\begin{array}{l} CH_2COONa \\ | \\ CH_2COONa \end{array} + H_2O \xrightarrow{\text{Electrolysis}} \underbrace{CH_2=CH_2 + 2CO_2}_{\text{(Anode)}} + 2NaOH + \underset{\text{(Cathode)}}{H_2}$$

5. Cracking of Alkanes :

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

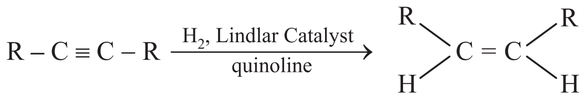
$$CH_3CH_2CH_3 \xrightarrow[Cr_2O_3]{500°C} CH_3CH=CH_2 + H_2$$

6. Partial Hydrogenation of Alkynes :

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

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

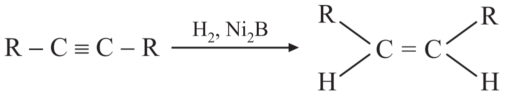
(a) Using Lindlar catalyst ($Pd/CaCO_3$ or $Pd/BaSO_4$) in quinoline to give a *cis* alkene.



cis - alkene

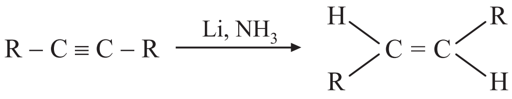
This is called as *syn* addition, as two H-atoms are added to the same side.

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



cis- alkene

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



trans- alkene

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

Stability of Alkenes :

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

$$CH_2=CH_2 > R-CH=CH_2 > R-CH=CH-R > R_2C=CH_2 > R_2C=CHR > R_2C=CR_2$$

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

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

(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 :

$$R_2C=CR_2 > R_2C=CHR > R_2C=CH_2 > \underset{\text{trans} > \text{cis}}{RCH=CHR} > RCH=CH_2 > CH_2=CH_2$$

Physical Properties of Alkenes :

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

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

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

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

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

5. **Density :** The densities of alkenes, like those of alkanes, increase with the increase in molecular mass till they have a limiting value of 0.89 g cm^{-3}. Thus, all alkenes are lighter than water.

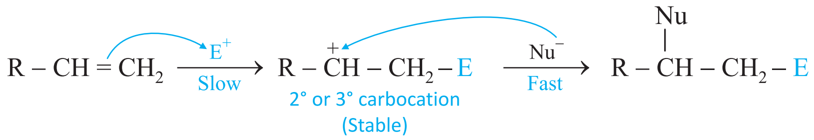
Compound	M.P. (°C)	B.P. (°C)	Density (g/mL)
Ethene	–169	–104	0.384
Propene	–185	–47	0.514
1-Butene	-	–6.3	0.595
cis-2-Butene	–139	3.7	0.621
trans-2-Butene	–106	0.9	0.604
1-Pentene	–165	30	0.641
2-Methyl-1-butene	–138	31	0.650

Reaction of Alkenes :

Electrophilic Addition Reactions :

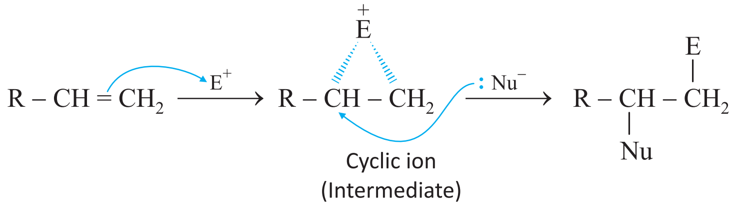
Alkenes are nucleophilic substrate due to localised π-electrons. Hence electrophiles approach alkenes resulting in the formation of saturated products (electrophilic addition reactions). Electrophilic addition on alkenes proceed through following two types of mechanisms :

Mechanism I :



- ➤ Electrophile causes shifting of π-bond (i.e. electromeric effect) in a manner so as to form a stable carbocation. The nucleophile then adds to more stable carbocation. This is referred to as **Markovnikov's addition**.

Mechanism II :

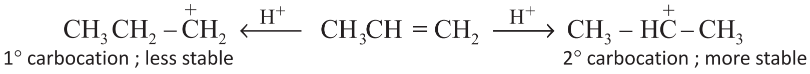


- ➤ **(i)** Electrophile causes polarisation of π bond e^- density to form a cyclic ion.
  (ii) No rearrangement, as carbocation is not involved.

1. Addition of hydrogen halides (HX) :

The addition of HX to alkene is an electrophilic addition reaction. The reactivity order follows : $HI > HBr > HCl$. The addition follows Markovnikov'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 Markovnikov's addition.

(a) Visualise addition of HBr in an unsymmetric alkene, propene :
A positive electromeric shift (+E effect) occurs in alkene in presence of HBr to form two possible carbocations as illustrated below.

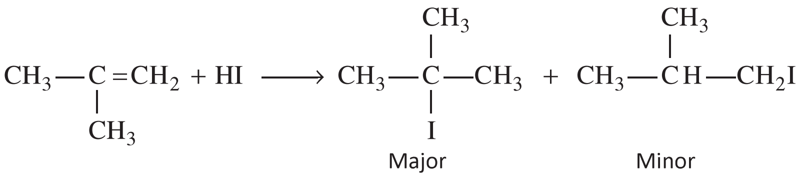


$$CH_3CH_2-\overset{+}{C}H_2 \xleftarrow{H^+} CH_3CH=CH_2 \xrightarrow{H^+} CH_3-H\overset{+}{C}-CH_3$$

1° carbocation ; less stable 2° carbocation ; more stable

Hence the major product formed is $CH_3-HC(Br)-CH_3$. This is in accordance with Markovnikov's addition.

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



$$CH_3-\underset{CH_3}{C}=CH_2 + HI \longrightarrow CH_3-\overset{CH_3}{\underset{I}{C}}-CH_3 + CH_3-\overset{CH_3}{C}H-CH_2I$$

Major Minor

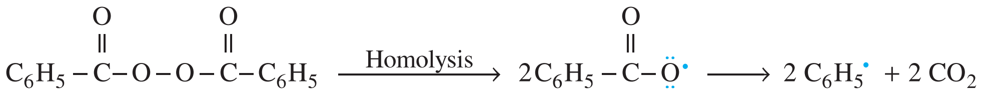
Note : Visualise formation of tert-butyl carbocation via +E effect.

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

$$CH_3CH = CH_2 + HBr \xrightarrow{ROOR} CH_3CH_2CH_2Br$$

In presence of peroxides, free radical addition occurs in an anti-Markovnikov's fashion unlike the electrophillic addition in above case (i.e., Markovnikov's addition). The mechanism of the reaction is given below :

Chain initiation :

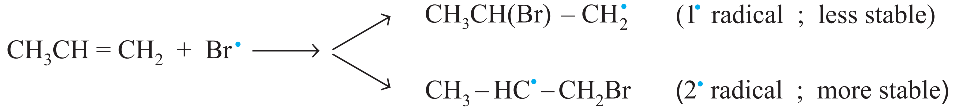
(i) 

$$C_6H_5-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-C_6H_5 \xrightarrow{\text{Homolysis}} 2C_6H_5-\overset{\overset{O}{\|}}{C}-\ddot{\underset{\cdot\cdot}{O}}^{\bullet} \longrightarrow 2\,C_6H_5^{\bullet} + 2\,CO_2$$

Benzoyl peroxide

(ii) $C_6H_5^{\bullet} + H-Br \xrightarrow{\text{Homolysis}} C_6H_6 + Br^{\bullet}$

Chain Propagation Step :

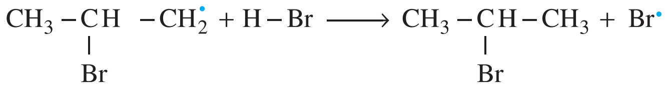
(i) 

$$CH_3CH=CH_2 + Br^{\bullet} \longrightarrow \begin{cases} CH_3CH(Br)-\dot{C}H_2 & (1^{\bullet} \text{ radical ; less stable}) \\ CH_3-HC^{\bullet}-CH_2Br & (2^{\bullet} \text{ radical ; more stable}) \end{cases}$$

Recall stability of free radicals via Hyperconjugation effect.

(ii) $CH_3-CH^{\bullet}-CH_2-Br + H-Br \xrightarrow{\text{Homolysis}} CH_3-CH_2-CH_2-Br + Br^{\bullet}$

(Major product)

and 

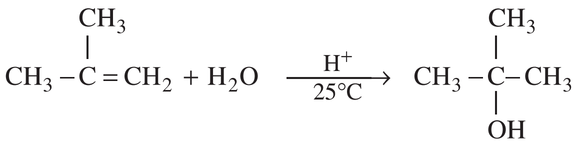
$$CH_3-\underset{\underset{Br}{|}}{C}H-\dot{C}H_2 + H-Br \longrightarrow CH_3-\underset{\underset{Br}{|}}{C}H-CH_3 + Br^{\bullet}$$

(Minor product)

However, the addition of HCl in peroxide follows Markovnikov's additions.

2. Addition of H_2O :

The acid catalysed addition of H_2O produces alcohols and follows Markovnikov's addition. The acids used to catalyse the reaction are H_2SO_4 or H_3PO_4 (phosphoric acid).

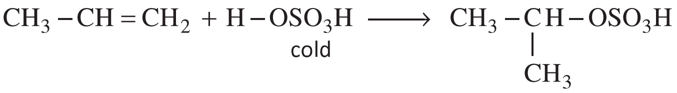


$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 + H_2O \xrightarrow[25°C]{H^+} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

Isobutene tert. butyl alcohol

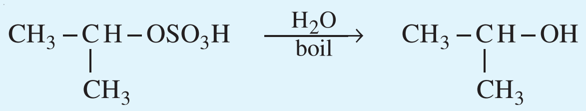
3. Addition of H_2SO_4 (cold and concentrated) :

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



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

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

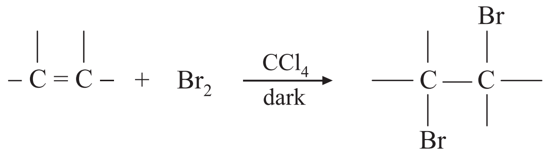


$$\underset{\underset{\text{CH}_3}{|}}{\text{CH}_3-\text{CH}}-\text{OSO}_3\text{H} \xrightarrow[\text{boil}]{\text{H}_2\text{O}} \underset{\underset{\text{CH}_3}{|}}{\text{CH}_3-\text{CH}}-\text{OH}$$

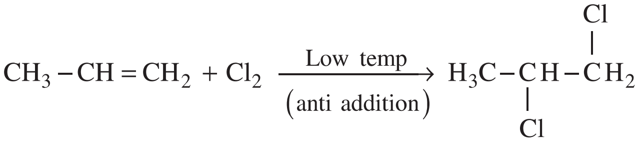
Isopropyl hydrogen sulphate Isopropyl alcohol

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

Alkenes decolourises Bromine water (Br_2 in CCl_4) following addition of Br_2 across double bond. This serves as a test of unsaturation. It follows *anti-addition*.



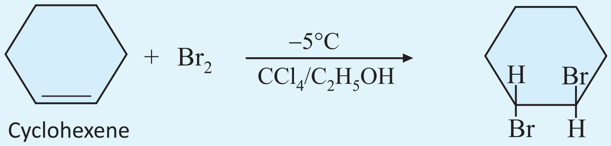
$$-\overset{|}{\text{C}}=\overset{|}{\text{C}}- + \text{Br}_2 \xrightarrow[\text{dark}]{\text{CCl}_4} -\underset{\underset{\text{Br}}{|}}{\overset{|}{\text{C}}}-\overset{\overset{\text{Br}}{|}}{\underset{|}{\text{C}}}-$$



$$\text{CH}_3-\text{CH}=\text{CH}_2 + \text{Cl}_2 \xrightarrow[\text{(anti addition)}]{\text{Low temp}} \text{H}_3\text{C}-\underset{\underset{\text{Cl}}{|}}{\text{CH}}-\overset{\overset{\text{Cl}}{|}}{\text{CH}_2}$$

Vicinal dichloride

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

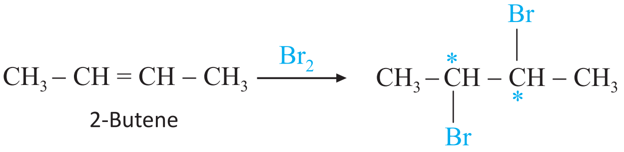


Cyclohexene

trans-1, 2-dibromocyclohexane

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

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

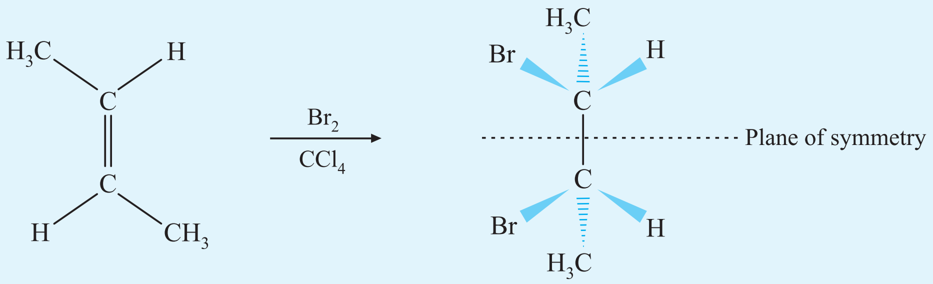


$$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3 \xrightarrow{\text{Br}_2} \text{CH}_3-\underset{\underset{\text{Br}}{|}}{\overset{*}{\text{CH}}}-\overset{\overset{\text{Br}}{|}}{\underset{*}{\text{CH}}}-\text{CH}_3$$

2-Butene

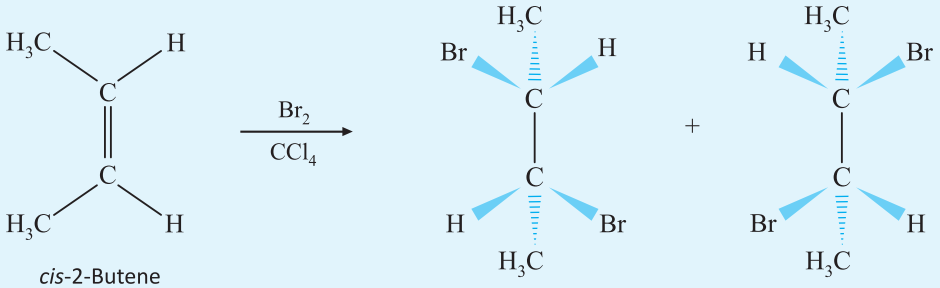
Observe that the product has two chiral centres.

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



trans-2-Butene

A meso compound is formed

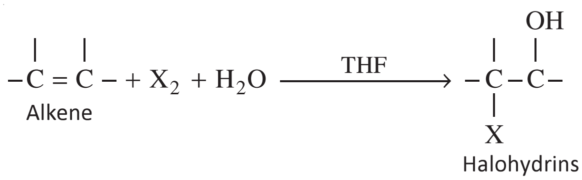


cis-2-Butene

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

5. Addition of halogen in aqueous solution :

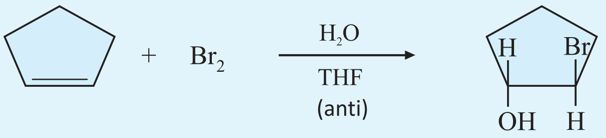
When halogens are added in presence of H_2O / THF (tetrahydrofuran) or NBS (N-bromo succinimide), halohydrins are formed.



$$\underset{\text{Alkene}}{-\overset{|}{C}=\overset{|}{C}-} + X_2 + H_2O \xrightarrow{\text{THF}} \underset{\text{Halohydrins}}{-\underset{X}{\underset{|}{\overset{|}{C}}}-\overset{OH}{\overset{|}{C}}-}$$

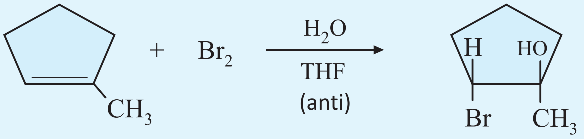
The above reaction follows Markovnikov's rule. It is an *anti-addition* reaction.

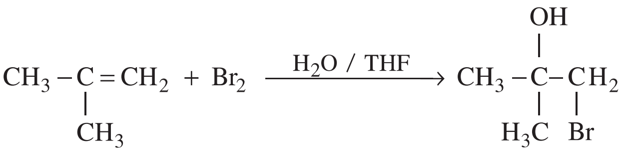
Note : **(i)** The cycloalkenes also reacts with aqueous Br_2 to give anti-addition products.



(Bromohydrin)

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



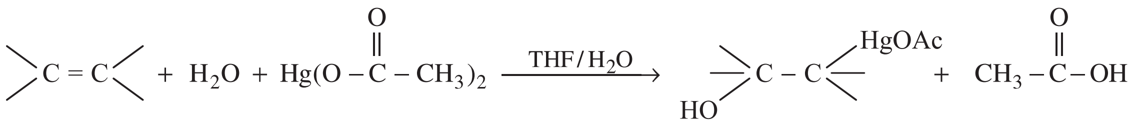


$$CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2 + Br_2 \xrightarrow{H_2O\ /\ THF} CH_3-\overset{OH}{\overset{|}{\underset{H_3C}{\underset{|}{C}}}}-\underset{Br}{\underset{|}{CH_2}}$$

6. Oxymercuration - Demercuration :

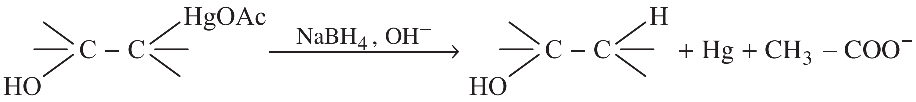
An important method of formation of alcohols from alkenes. It occurs in two steps.

(i) Alkenes react with mercuric acetate Hg $(CH_3COO)_2$ or represented as, Hg $(OAc)_2$ in a mixture of THF and water to give a mercury compound. It is also an *anti-addition*.

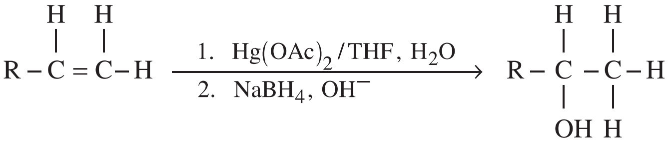


This step is known as Oxymercuration.

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

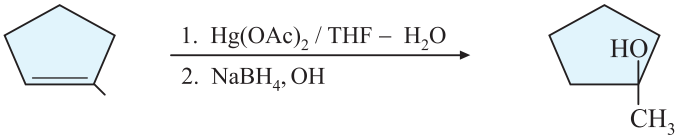


The above reaction occurs in accordance with Markovnikov's addition. The 'H' becomes attached to the carbon atom of the double bond with greater number of hydrogen atom.



$$R-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H \xrightarrow[\text{2. NaBH}_4,\ OH^-]{\text{1. Hg(OAc)}_2/THF,\ H_2O} R-\overset{H}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-H$$

2° alcohol

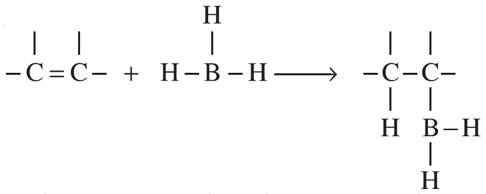


(Markonikov's addition) 1 - Methyl cyclopentanol

Note : Observe that in the final product, OH comes from H_2O and H comes from $NaBH_4/OH^-$.

7. Hydroboration - Oxidation :

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



$$-\overset{|}{C}=\overset{|}{C}- + H-\overset{H}{\overset{|}{B}}-H \longrightarrow -\underset{H}{\underset{|}{\overset{|}{C}}}-\underset{\underset{H}{|}}{\underset{B-H}{\underset{|}{\overset{|}{C}}}}-$$

Alkene Boron hydride Organoborane

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

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

$$3CH_2=CH_2 \xrightarrow{BH_3/THF} \underset{\text{Triethyl borane}}{(C_2H_5)_3B}$$

$$CH_3CH=CH_2 \xrightarrow{BH_3/THF} (n-Pr)BH_2 \xrightarrow{CH_3CH=CH_2} (n-Pr)_2BH \xrightarrow{CH_3CH=CH_2} (n-Pr)_3B$$

(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-Markovnikov's addition.

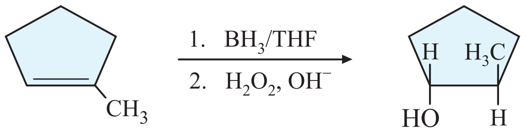
The organoboranes formed are oxidised and hydrolysed to alcohols by the addition of hydrogen peroxides in an aqueous base.

$$R_3B \xrightarrow[\text{NaOH, }25^\circ C]{H_2O_2} 3ROH + Na_3BO_3 \qquad (n-Pr)_3B \xrightarrow[\text{NaOH, }25^\circ C]{H_2O_2} 3PrOH + Na_3BO_3$$

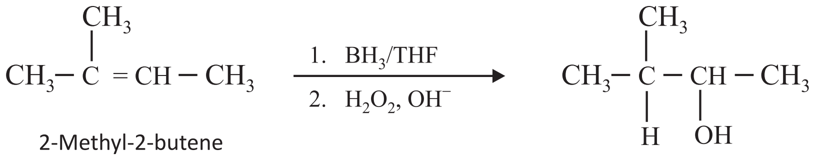
Note that alcohol formed is a primary alcohol (unlike that in Markovnikov's addition)

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

Note : Observe that in the final product, OH comes from H_2O_2/OH^- and H comes from BH_3.



trans - 2 - Methyl cyclopentanol



$$\underset{\text{2-Methyl-2-butene}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_3} \xrightarrow[\text{2. } H_2O_2,\ OH^-]{\text{1. } BH_3/THF} \underset{\text{Anti-Markonikov's addition of } H_2O}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_3}$$

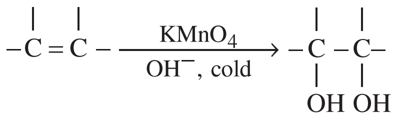
2-Methyl-2-butene

Anti-Markonikov's addition of H_2O

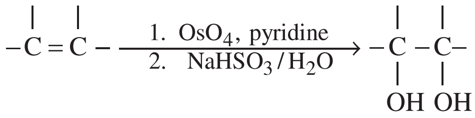
Note : Compare the alcohols formed above with those formed by Oxymercuration-Demercuration.

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

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

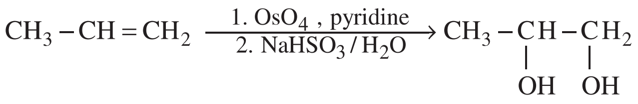


$$-\overset{|}{C}=\overset{|}{C}- \xrightarrow[OH^-,\text{ cold}]{KMnO_4} -\overset{|}{\underset{\underset{\displaystyle OH}{|}}{C}}-\overset{|}{\underset{\underset{\displaystyle OH}{|}}{C}}- \qquad \text{(Vicinal alcohols or glycols)}$$



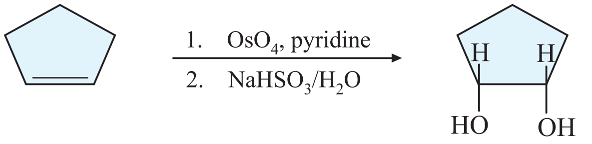
$$-\overset{|}{C}=\overset{|}{C}- \xrightarrow[\text{2. } NaHSO_3/H_2O]{\text{1. } OsO_4,\text{ pyridine}} -\overset{|}{\underset{\underset{\displaystyle OH}{|}}{C}}-\overset{|}{\underset{\underset{\displaystyle OH}{|}}{C}}- \qquad \text{(Vicinal alcohols or glycols)}$$

It represents *syn-addition*.



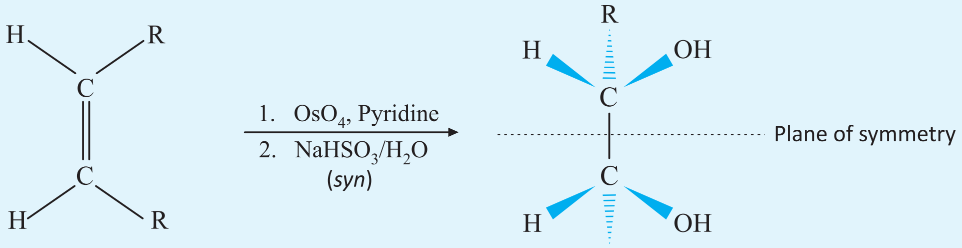
$$CH_3-CH=CH_2 \xrightarrow[\text{2. } NaHSO_3/H_2O]{\text{1. } OsO_4\text{ , pyridine}} CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-\underset{\underset{\displaystyle OH}{|}}{CH_2}$$

1, 2 - Propanediol



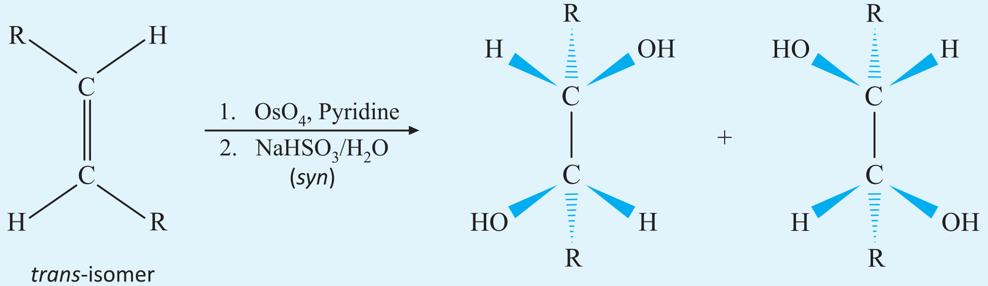
cis-1, 2-cyclopentanediol

Note : Osmium tetra oxide, OsO_4 gives a better yield than $KMnO_4$. The hydroxylation like addition of Br_2 is also stereospecific. Consider hydroxylation in *cis* and *trans* isomeric alkenes.



cis-isomer

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



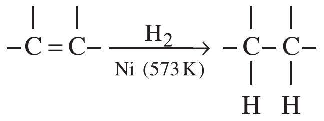
trans-isomer

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

9. Hydrogenation :

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

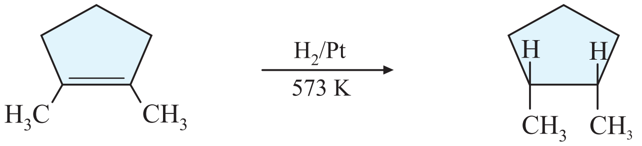
Na in liquid NH_3 and alcohol ; H_2, PtO_2/CH_3COOH ; H_2/Ni at 573 K ; H_2/Pd-Carbon in ethanol.



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

This reaction also follows *syn*-addition rule.

Consider hydrogenation in 1, 2-Dimethyl cyclohexene.



cis-1, 2-Dimethyl cyclopentane

10. Oxidation of Alkenes :

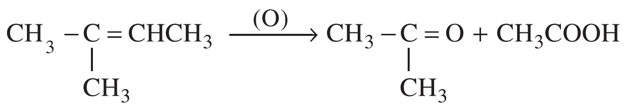
(a) Oxidation by hot. conc. $KMnO_4$:

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

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

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

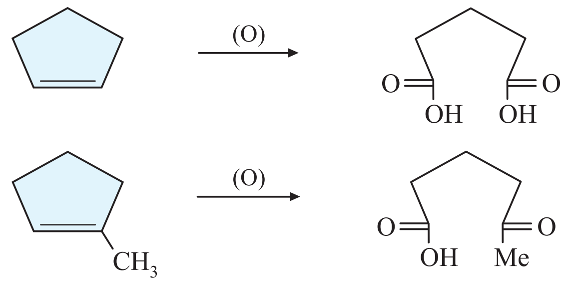
$$R-CH=CH-R' \xrightarrow{(O)} RCOOH+R'COOH$$



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CHCH_3 \xrightarrow{(O)} CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=O+CH_3COOH$$

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

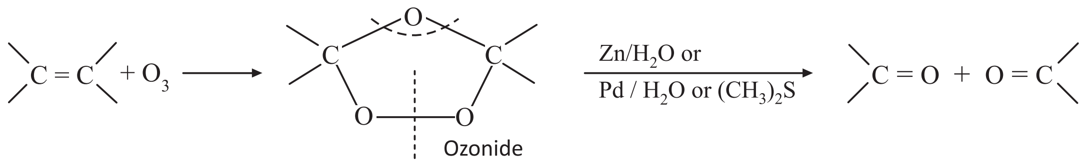
Oxidation of cycloalkenes leads to the ring opening and gives dicarboxylic acids or keto acids.

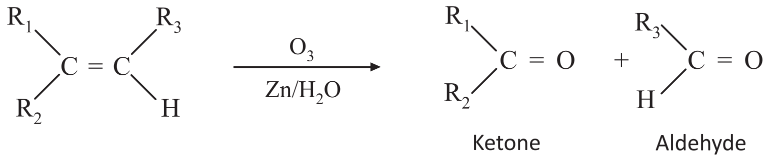


Dicarboxylic acids

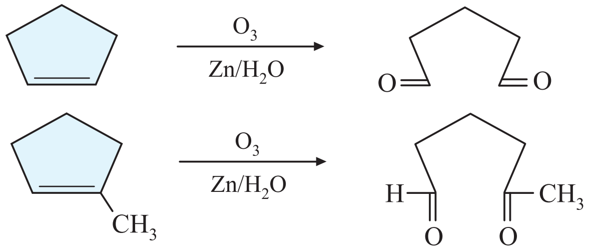
Both acid and keto group are formed

(b) By Ozone (ozonolysis) :



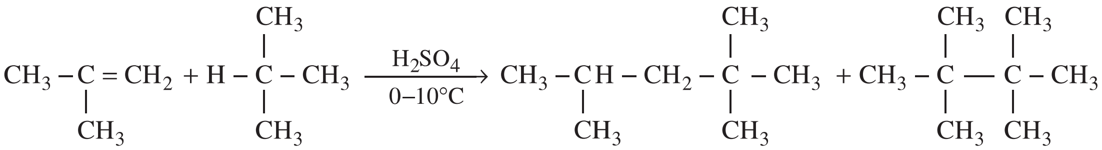


Consider the ozonolysis of cycloalkenes :



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

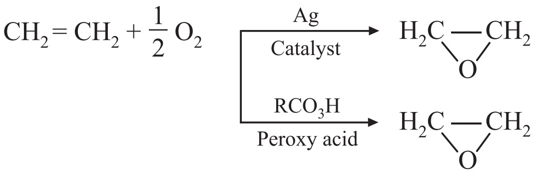
11. Alkylation :



$$CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2 + H-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3 \xrightarrow[0-10^\circ C]{H_2SO_4} CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3 + CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$$

(mixture of higher alkanes is formed)

12. Addition of oxygen :



Ethylene oxide (epoxide) or Oxirane

13. Substitution in alkenes (Partial Oxidation) :

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

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

$$CH_2=CH-CH_3+Cl_2 \xrightarrow[\text{gas phase}]{400^\circ C-500^\circ C} CH_2=CH-CH_2Cl+HCl$$

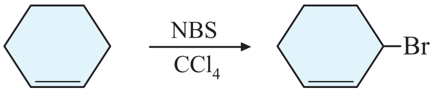
Allyl Chloride

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

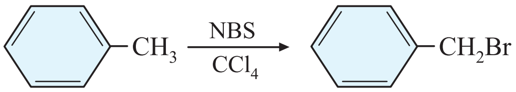
$$CH_2=CH-CH_3 \xrightarrow[\text{in ROOR or light}]{NBS/CCl_4} CH_2=CH-CH_2Br$$

Allyl bromide

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



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



Benzyl bromide

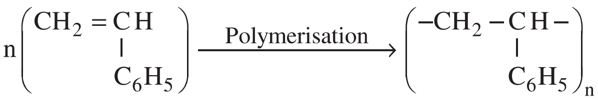
14. Polymerisation

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

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

$$n\left(CH_2=\underset{\underset{Cl}{|}}{CH}\right)\xrightarrow{\text{Polymerisation}}\left(-CH_2-\underset{\underset{Cl}{|}}{CH}-\right)_n$$

Vinyl chloride Polyvinyl chloride (PVC)



$$n\left(CH_2=\underset{\underset{C_6H_5}{|}}{CH}\right)\xrightarrow{\text{Polymerisation}}\left(-CH_2-\underset{\underset{C_6H_5}{|}}{CH}-\right)_n$$

Styrene Polystyrene

$$n\left(CH_2=\underset{\underset{CN}{|}}{CH}\right)\xrightarrow{\text{Polymerisation}}\left(-CH_2-\underset{\underset{CN}{|}}{CH}-\right)_n$$

Acrylonitrile or Polyacrylonitrile (PAN)

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

Tetrafluoroethene Polytetrafluoroethene (PTFE Teflon)

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 :*

(i) CH_3CHO **(ii)** C_2H_5CHO **(iii)** CH_3COCH_3 **(iv)** $(CH_3)_2CHCHO$

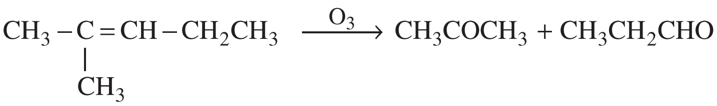
What are the structures of A, B and C ?

SOLUTION :

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

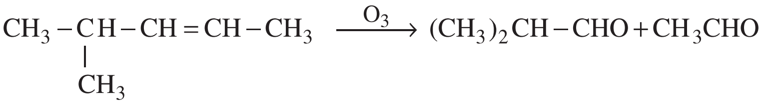
Try to draw the structures of alkenes (working backwards in ozonolysis reaction). Note that while joining the products, keep in mind that on combining two products the sum of carbon atom must be six.

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



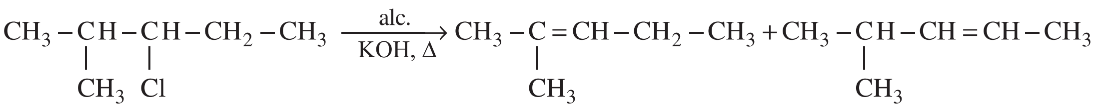
$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_2CH_3\xrightarrow{O_3}CH_3COCH_3+CH_3CH_2CHO$$

and



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

The structure of A must be :



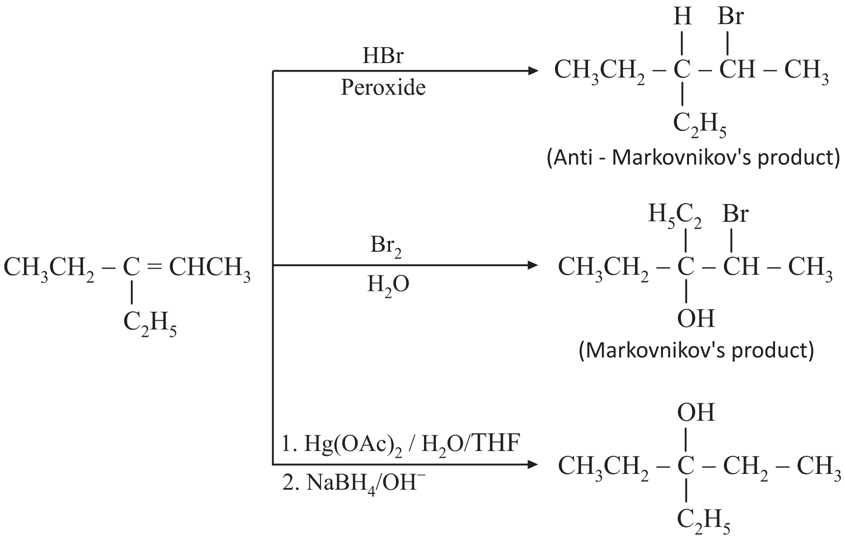
$$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_3\xrightarrow[\text{KOH, }\Delta]{\text{alc.}}CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CH_3+CH_3-\underset{\underset{CH_3}{|}}{CH}-CH=CH-CH_3$$

(Major) (B) (Minor) (C)

Illustration - 3 *Give the structure of the major organic products formed from 3-Ethyl-2-pentene under each of the following reaction conditions :*

(A) *HBr in the presence of peroxide* **(B)** *Br_2/H_2O* **(C)** *$Hg(OAc)_2/THF/H_2O$, $NaBH_4/OH^-$*

SOLUTION :



(Anti - Markovnikov's product)

(Markovnikov's product)

(Markovnikov's product)

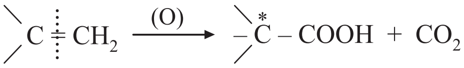
Illustration - 4 *A hydrocarbon X, C_6H_{12} decolourizes bromine water and is oxidized to an acid Y by hot acidic potassium permanganate solution. The acid Y can be resolved into two forms. Identify X and Y.*

SOLUTION :

$$\underset{(X)}{C_6H_{12}} \xrightarrow{Br_2} \text{decolourises} \Rightarrow \text{X has } \left(\rangle C=C\langle\right)$$

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

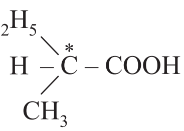
X is terminal alkene as it gives only Y.



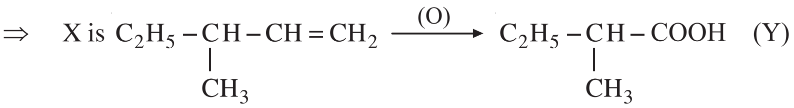
$$\rangle C \vdots\!= CH_2 \xrightarrow{(O)} -\overset{*}{C}\langle-COOH + CO_2$$

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

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

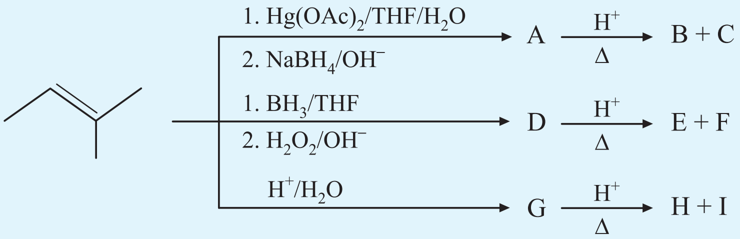
Y is clearly  (5 – C atoms, * : chiral centre).

$$H-\overset{*}{C}(C_2H_5)(CH_3)-COOH$$

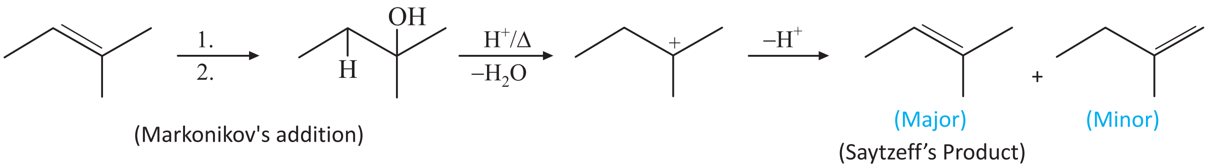


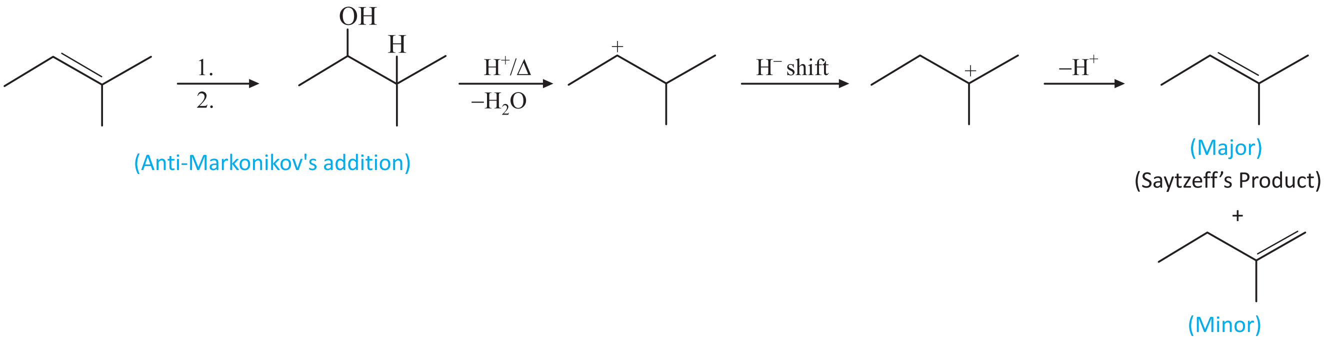
$$\Rightarrow \text{X is } C_2H_5-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2 \xrightarrow{(O)} C_2H_5-\underset{\underset{CH_3}{|}}{CH}-COOH \quad (Y)$$

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



SOLUTION :





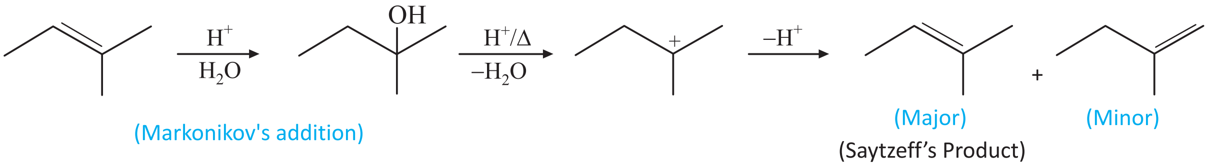
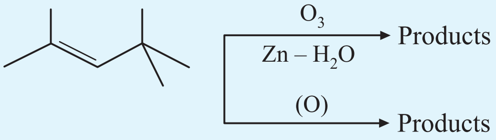
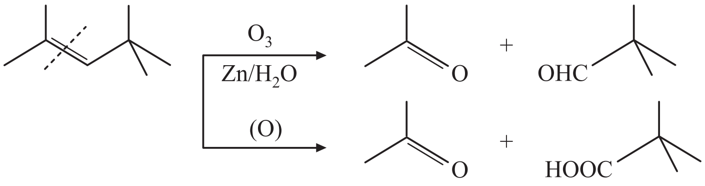


Illustration - 6 *Identify the products.*



SOLUTION :



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

IN-CHAPTER EXERCISE-B

1. *Give the product when ICl reacts with :*

(i) *Isobutene* **(ii)** *2-Methyl-1-butene*

2. *What is the product formed when :*

(i) *1-Pentene* **(ii)** *3, 3-Dimethyl-1-butene*

undergoes oxymercuration - demercuration.

3. *Name the alkene that gives :*

(i) *2-Methyl-1-pentanol* **(ii)** *trans-2-Methyl cyclobutanol*

by hydroboration - oxidation method.

4. *Give the structure of alkenes that would give following products when treated with ozone and then with* Zn/H_2O.

(i) *Acetone and Isobutyraldehyde* **(ii)** *2 mole of* CH_3CH_2CHO

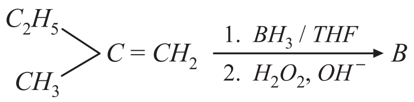
(iii) *Formaldehyde and Cyclopentanone* **(iv)** CO_2, *2 moles of Formaldehyde*

(v) *2 mole of* CH_2O *and α-keto propionaldehyde.*

5. *Identify the products A, B, C, ...*

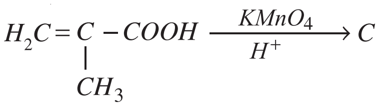
(i) $CH_3CH=CHCH_3 + Cl_2 \xrightarrow{400°C} A$

(ii)



$(C_2H_5)(CH_3)C=CH_2 \xrightarrow[2.\ H_2O_2,\ OH^-]{1.\ BH_3\ /\ THF} B$

(iii)



$H_2C=\underset{\displaystyle CH_3}{\underset{|}{C}}-COOH \xrightarrow[H^+]{KMnO_4} C$

(iv) $CH_3CH=CHC_6H_5 \xrightarrow[H^+]{hot\ KMnO_4} D + E$

Choose the correct alternative. Only one choice is correct.

***6.** *In which of the following, addition of HBr in peroxide take place against Markovnikov's rule ?*

(A) *Propene* **(B)** *But-1-ene* **(C)** *But-2-ene* **(D)** *Pent-1-ene*

7. *When alcoholic solution of Ethylene dibromide is heated with granulated Zinc, the compound formed is :*

(A) *Ethylene* **(B)** *Ethyne* **(C)** *Cyclobutane* **(D)** *Butane*

8. *Electrolysis of cold concentrated aqueous solution of Potassium succinate yields :*

(A) *Ethane* **(B)** *Ethyne* **(C)** *Ethene* **(D)** *Ethane-1, 2-diol*

9. *A hydrocarbon reacts with Hypochlorous (HOCl) acid to give 1-Chloroethan-2-ol. The hydrocarbon is :*

(A) *Ethylene* **(B)** *Propylene* **(C)** *Ethane* **(D)** *Acetylene*

10. $CH_3CH=CHCHO$ *is oxidized to oxalic acid and acetic acid using :*

(A) $KMnO_4/OH^-$ **(B)** $KMnO_4/H^+$ **(C)** SeO_2 **(D)** O_3-Zn/H_2O

11. *Propene can be converted into 1-Propanol. Indicate which set of reagents amongst the following is ideal to effect the above conversion :*

(A) $KMnO_4$ *(alkaline)* **(B)** *Oxymercuration - Demercuration*

(C) B_2H_6 *and alkaline* H_2O_2 **(D)** H_2O/H^+

12. *Isobutylene on hydroboration-oxidation gives :*

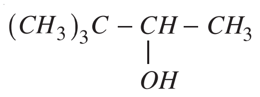
(A)	*Primary alcohol*	**(B)**	*Secondary alcohol*
(C)	*Tertiary alcohol*	**(D)**	*Dihydric alcohol*

13. *Of the following, the least stable compound is :*

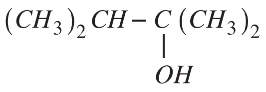
(A)	$(CH_3)_2C=C(CH_3)_2$	**(B)**	$CH_2=CH-CH_3$
(C)	$CH_2=CH_2$	**(D)**	*None of these*

14. *The product of following reaction is :*

$$(CH_3)_3C-CH=CH_2 \xrightarrow[\text{2. } NaBH_4/OH^-]{\text{1. } Hg(OAc)_2/THF}$$

(A) 
$(CH_3)_3C-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$

(B) $(CH_3)_3C-CH_2-CH_2OH$

(C) 
$(CH_3)_2CH-\underset{\displaystyle OH}{\underset{|}{C}}(CH_3)_2$

(D) $(CH_3)_3C-CH=CH-CH_3$

15. *There are three isomeric Butenes (1-Butene, 2-Butene and 2-Methylpropene). These can be distinguished from one another by :*

(A)	*Bromine in carbon tetrachloride*	**(B)**	*Cold aqueous alkaline* $KMnO_4$ *solution*
(C)	*Ammonical silver nitrate solution*	**(D)**	*Analysing the products of ozonolysis*

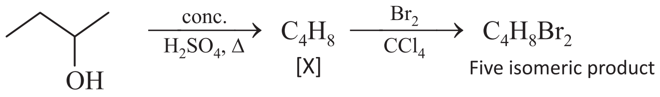
16. *Which of the following alkenes can be used in the reaction with HBr to synthesize only 3-bromohexane ?*

(A) 1-*Hexene* **(B)** 2-*Hexene* **(C)** 3-*Hexene* **(D)** *Both (B) and (C)*

17. *The catalytic hydrogenation is most easy in the case of alkenes of the type :*

(A) $R_2C=CH_2$ **(B)** $RCH=CHR$ **(C)** $R_2C=CHR$ **(D)** $R_2C=CR_2$

18. *Consider the following reaction sequence :*



How many structures are possible for intermediate product [X] ?

(A) 2 **(B)** 3 **(C)** 4 **(D)** 5

19. *Identify the correct statement for the given reaction* $CH_3-CH=CH_2+HCl \xrightarrow{\text{Peroxide}}$

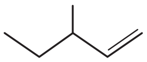
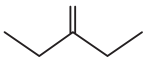
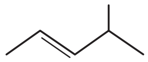
(A) *Product is* $CH_3-CH_2CH_2Cl$ *and formed by free radical addition reaction*

(B) *Product is* $CH_3-CH(Cl)-CH_3$ *and formed by free radical addition reaction*

(C) *Product is* $CH_3-CH_2-CH_2Cl$ *and formed by electrophilic addition reaction*

(D) *Product is* $CH_3CH(Cl)CH_3$ *and formed by electrophilic addition reaction*

20. *An optically active compound (A) having moelcular formula* C_6H_{12} *on hydrogenation in presence of platinum produce optically inactive compound (B) having molecular formula* C_6H_{14}*. The structure of compound (A) is :*

(A) 
(B) 
(C) 
(D)