

1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 01 (Class XI, Semester - 2)
Module Name/Title	Hydrocarbons: Part 2
Module Id	kech_21302
Pre-requisites	Knowledge about hybridization and orbital overlap, sigma and pi bonds, Rules of IUPAC nomenclature, Substitution reactions, Addition reactions, Free radicals and carbocations
Objectives	After going through this lesson, the learners will be able to: 1. Name alkenes according to IUPAC system of nomenclature. 2. Understand the structure of double bond in alkenes. 3. Recognize and write structures of both structural and geometrical isomers of alkenes. 4. Identify the various methods of preparation of alkenes. 5. Learn the physical and chemical properties of alkenes. 6. Understand the addition reactions to unsymmetrical alkenes according to Markovnikov rule on the basis of mechanism.
keywords	Covalent bond, sigma bond, Pi bond, , chain isomerism , position isomerism, geometrical isomerism, vicinal dihalides, β -elimination, peroxide effect, ozonolysis, polymerization

2. Development Team

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1. Introduction

Alkenes are unsaturated hydrocarbons containing at least one double bond and the general formula for alkenes is C_nH_{2n} . Alkenes are also known as olefins (oil forming) since the first member, ethylene or ethene (C_2H_4) was found to form an oily liquid on reaction with chlorine.

2. Structure Of Double Bond

Carbon-carbon double bond in alkenes consists of one strong sigma (σ) bond (bond enthalpy about 397 kJ mol^{-1}) due to head-on overlapping of sp^2 hybridised orbitals and one weak pi (π) bond (bond enthalpy about

284 kJ mol^{-1}) obtained by lateral or sideways overlapping of the two $2p$ orbitals of the two carbon atoms. The double bond is shorter in bond length (134 pm) than the C–C single bond (154 pm). The pi (π) bond is a weaker bond due to poor sideways overlapping between the two $2p$ orbitals. Thus, the presence of the pi (π) bond makes alkenes behave as sources of loosely held mobile electrons. Therefore, alkenes are easily attacked by reagents or compounds which are in search of electrons. Such reagents are called **electrophilic reagents**. The presence of weaker π -bond makes alkenes unstable molecules in comparison to alkanes and thus, alkenes can be changed into single bond compounds by combining with the electrophilic reagents. Strength of the double bond (bond enthalpy, 681 kJ mol^{-1}) is greater than that of a carbon-carbon single bond in ethane (bond enthalpy, 348 kJ mol^{-1}). Orbital diagrams of ethene molecule are shown in Figs. 1 and 2.

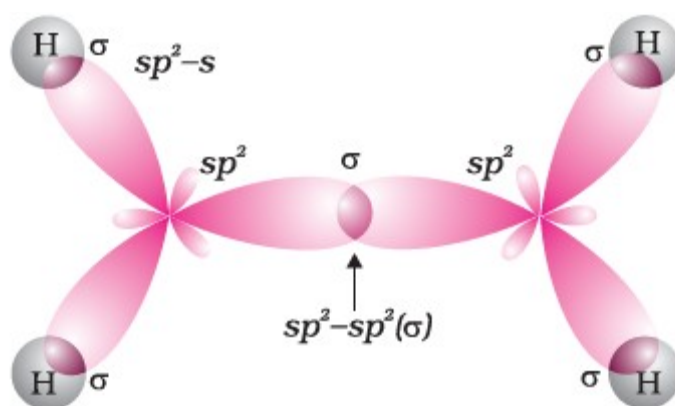


Fig. 1 Orbital picture of ethene depicting σ bonds only

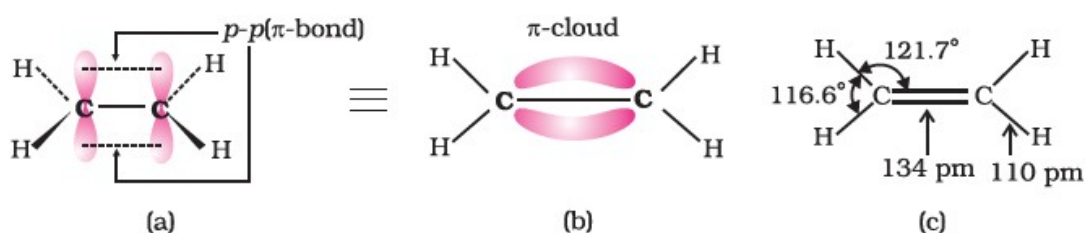


Fig. 2 Orbital picture of ethene showing formation of (a) π -bond, (b) π -cloud and (c) bond angles and bond lengths

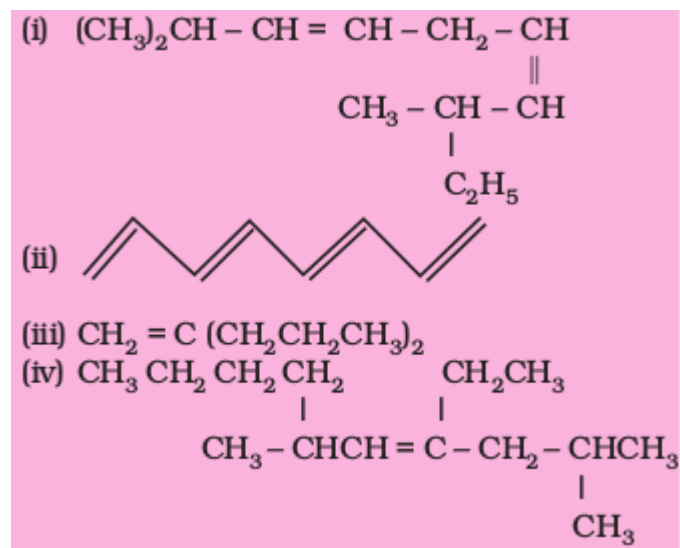
3. Nomenclature of Alkenes

For nomenclature of alkenes in IUPAC system, the longest chain of carbon atoms containing the double bond is selected. Numbering of the chain is done from the end which is nearer to the double bond. The suffix 'ene' replaces 'ane' of alkanes. It may be remembered that first member of alkene series is: CH_2 (replacing n by 1 in C_nH_{2n}) known as methene but has a very short life. As already mentioned, first stable member of alkene series is C_2H_4 known as ethylene (common) or ethene (IUPAC). IUPAC names of a few members of alkenes are given below :

Structure	IUPAC name
$\text{CH}_3 - \text{CH} = \text{CH}_2$	Propene
$\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH}_2$	But - 1 - ene
$\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$	But-2-ene
$\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$	Buta - 1,3 - diene
$\text{CH}_2 = \text{C} - \text{CH}_3$	2-Methylprop-1-ene
$\begin{array}{c} \\ \text{CH}_3 \\ \text{CH}_2 = \text{CH} - \text{CH} - \text{CH}_3 \end{array}$	3-Methylbut-1-ene
$\begin{array}{c} \\ \text{CH}_3 \end{array}$	

Problem 1

Write IUPAC names of the following compounds:



Solution

- (i) 2,8-Dimethyl-3, 6-decadiene;
(ii) 1,3,5,7- Octatetraene;
(iii) 2-*n*-Propylpent-1-ene;
(iv) 4-Ethyl-2,6-dimethyldec-4-ene;

Problem 2.

Calculate number of sigma (σ) and pi (π) bonds in the above structures (i-iv).

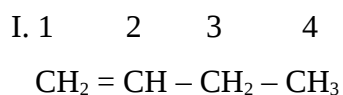
Solution

- (i) σ bonds : 33, π bonds : 2
(ii) σ bonds : 17, π bonds : 4
(iii) σ bonds : 23, π bond : 1
(iv) σ bonds : 41, π bond : 1

4. Isomerism in Alkenes

Alkenes show both structural isomerism and geometrical isomerism.

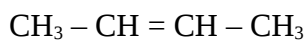
Structural isomerism : As in alkanes, ethene (C_2H_4) and propene (C_3H_6) can have only one structure but alkenes higher than propene have different structures. Alkenes possessing C_4H_8 as molecular formula can be written in the following three ways:



But-1-ene



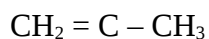
II. 1 2 3 4



But-2-ene



III. 1 2 3



2-Methylprop-1-ene



Structures I and III, and II and III are the examples of **chain isomerism** whereas structures I and II are **position isomers**.

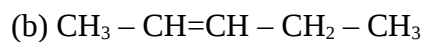
Problem 3.

Write structures and IUPAC names of different structural isomers of alkenes corresponding to C_5H_{10} .

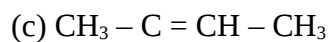
Solution



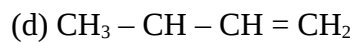
Pent-1-ene



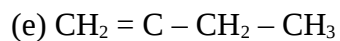
Pent-2-ene

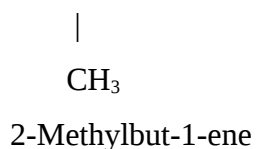


2-Methylbut-2-ene



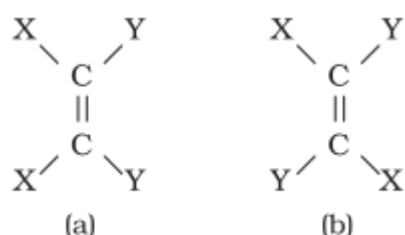
3-Methylbut-1-ene





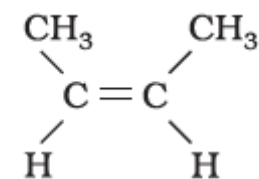
Geometrical isomerism: Doubly bonded carbon atoms have to satisfy the remaining two valences by joining with two atoms or groups. If the two atoms or groups attached to each carbon atom are different, they can be represented by $\text{YX C} = \text{C XY}$ like structure. $\text{YX C} = \text{C XY}$ can be represented in space in the

following two ways:

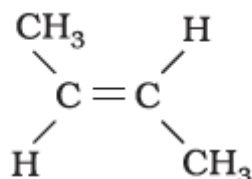


In (a), the two identical atoms *i.e.*, both the X or both the Y lie on the same side of the double bond but in (b) the two X or two Y lie across the double bond or on the opposite sides of the double bond. This results in different geometry of (a) and (b) *i.e.* disposition of atoms or groups in space in the two arrangements is different. Therefore, they are **stereoisomers**. They would have the same geometry if atoms or groups around $\text{C}=\text{C}$ bond can be rotated but rotation around $\text{C}=\text{C}$ bond is not free. It is restricted. For understanding this concept, take two pieces of strong cardboards and join them with the help of two nails. Hold one cardboard in your one hand and try to rotate the other. Can you really rotate the other cardboard ? The answer is no. The rotation is restricted. This illustrates that the restricted rotation of atoms or groups around the doubly bonded carbon atoms gives rise to different geometries of such compounds. The stereoisomers of this type are called **geometrical isomers**. The isomer of the type (a), in which two identical atoms or groups lie on the same side of the double bond is called **cis isomer** and the other isomer of the type (b), in which identical atoms or groups lie on the opposite sides of the double bond is called **trans isomer**. Thus *cis* and *trans* isomers have the same structure but have different configuration (arrangement of atoms or groups in space). Due to different arrangement of atoms or groups in space, these isomers differ in their properties like melting point, boiling point, dipole moment, solubility etc.

Geometrical or *cis-trans* isomers of but-2-ene are represented below :

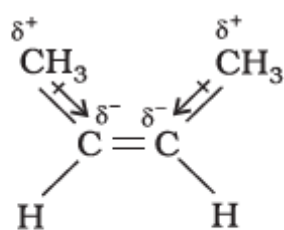


cis-But-2-ene
(b.p. 277 K)

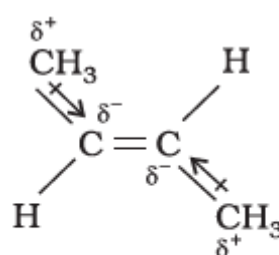


trans-But-2-ene
(b.p. 274 K)

Cis form of alkene is found to be more polar than the *trans* form. For example, dipole moment of *cis*-but-2-ene is 0.33 Debye, whereas, dipole moment of the *trans* form is almost zero or it can be said that *trans*-but-2-ene is non-polar. This can be understood by drawing geometries of the two forms as given below from which it is clear that in *trans*-but-2-ene, the two methyl groups are in opposite directions, Therefore, dipole moments of C-CH₃ bonds cancel, thus making the *trans* form non-polar.



cis-But-2-ene
($\mu = 0.33\text{D}$)



trans-But-2-ene
($\mu = 0$)

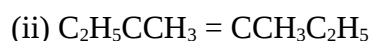
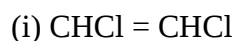
In the case of solids, it is observed that the *trans* isomer has higher melting point than the *cis* form.

Geometrical or *cis-trans* isomerism is also shown by alkenes of the types

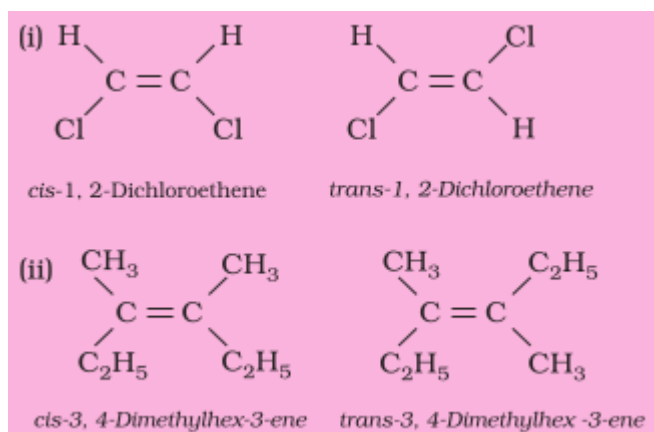


Problem 4.

Draw *cis* and *trans* isomers of the following compounds. Also write their IUPAC names :

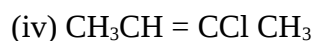
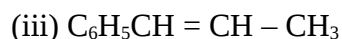
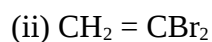
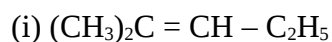


Solution:



Problem 5.

Which of the following compounds will show *cis-trans* isomerism?



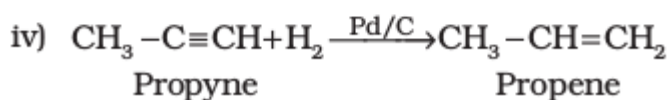
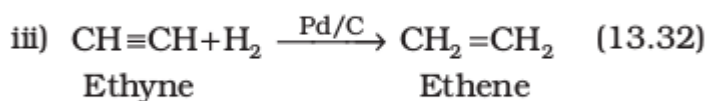
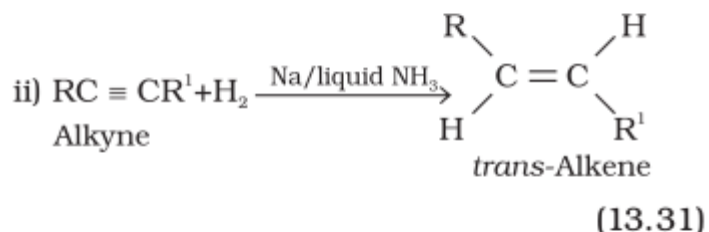
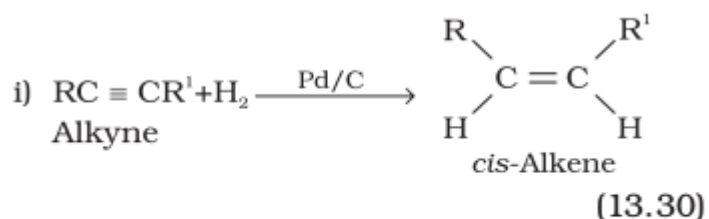
Solution

(iii) and (iv). In structures (i) and (ii), two identical groups are attached to one of the doubly bonded carbon atom.

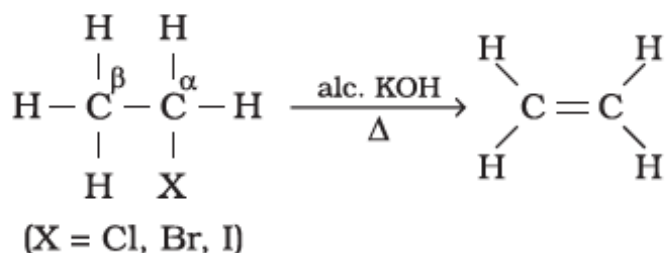
5. Preparation of Alkenes

1. From alkynes: Alkynes on partial reduction with calculated amount of dihydrogen in the presence of *palladised* charcoal partially deactivated with poisons like sulphur compounds or quinoline give alkenes. Partially deactivated palladised charcoal is known as *Lindlar's catalyst*. Alkenes thus obtained are having *cis* geometry. However, alkynes on reduction with sodium in liquid ammonia form *trans* alkenes.

The propene thus obtained does not show geometrical isomerism.

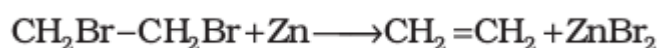


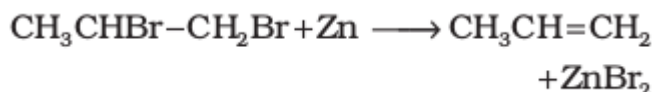
2. From alkyl halides: Alkyl halides (R-X) on heating with alcoholic potash (potassium hydroxide dissolved in alcohol, say, ethanol) eliminate one molecule of halogen acid to form alkenes. This reaction is known as **dehydrohalogenation** i.e., removal of halogen acid. This is an example of **β -elimination reaction**, since hydrogen atom is eliminated from the β carbon atom (carbon atom next to the carbon to which halogen is attached).



Nature of halogen atom and the alkyl group determine rate of the reaction. It is observed that for halogens, the rate is: iodine > bromine > chlorine, while for alkyl groups it is : tert > secondary > primary.

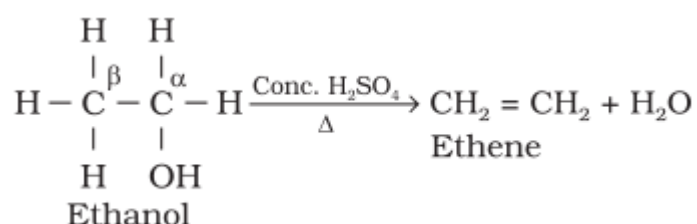
3. From vicinal dihalides: Dihalides in which two halogen atoms are attached to two adjacent carbon atoms are known as *vicinal dihalides*. Vicinal dihalides on treatment with zinc metal lose a molecule of ZnX_2 to form an alkene. This reaction is known as **dehalogenation**.





4. From alcohols by acidic dehydration:

You have read earlier that alcohols are the hydroxy derivatives of alkanes. They are represented by R-OH where, R is $\text{C}_n\text{H}_{2n+1}$. Alcohols on heating with concentrated sulphuric acid form alkenes with the elimination of one water molecule. Since a water molecule is eliminated from the alcohol molecule in the presence of an acid, this reaction is known as **acidic dehydration of alcohols**. This reaction is also the example of β -elimination reaction since -OH group takes out one hydrogen atom from the β -carbon atom.



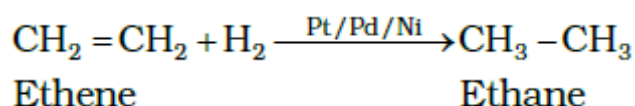
6. Physical Properties of Alkenes

Alkenes as a class resemble alkanes in physical properties, except in types of isomerism and difference in polar nature. The first three members are gases, the next fourteen are liquids and the higher ones are solids. Ethene is a colourless gas with a faint sweet smell. All other alkenes are colourless and odourless, insoluble in water but fairly soluble in nonpolar solvents like benzene, petroleum ether. They show a regular increase in boiling point with increase in size *i.e.*, every $-\text{CH}_2$ group added increases boiling point by 20–30 K. Like alkanes, straight chain alkenes have higher boiling point than isomeric branched chain compounds.

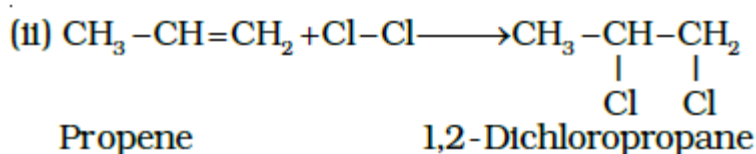
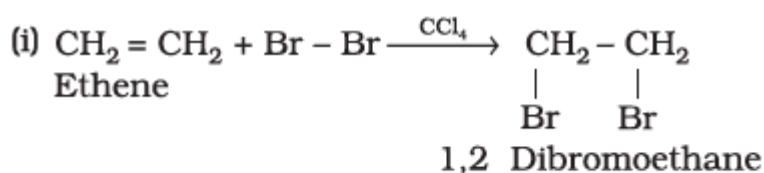
7. Chemical Properties of Alkenes

Alkenes are the rich source of loosely held pi (π) electrons, due to which they show addition reactions in which the electrophiles add on to the carbon-carbon double bond to form the addition products. Some reagents also add by free radical mechanism. There are cases when under special conditions, alkenes also undergo free radical substitution reactions. Oxidation and ozonolysis reactions are also quite prominent in alkenes. A brief description of different reactions of alkenes is given below:

1. Addition of hydrogen: Alkenes add up one molecule of hydrogen gas in the presence of finely divided nickel, palladium or platinum to form alkanes



2. Addition of halogens : Halogens like bromine or chlorine add up to alkene to form vicinal dihalides. However, iodine does not show addition reaction under normal conditions. The reddish orange colour of bromine solution in carbon tetrachloride is discharged when bromine adds up to an unsaturation site. This reaction is used as a test for unsaturation. Addition of halogens to alkenes is an example of electrophilic addition reaction involving cyclic halonium ion formation which you will study in higher classes.

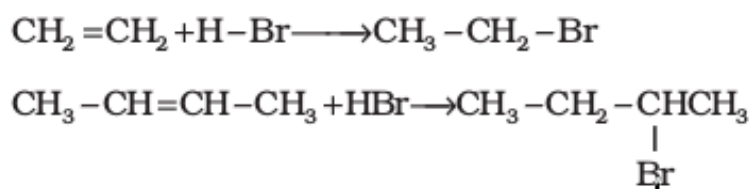


3. Addition of hydrogen halides:

Hydrogen halides (HCl, HBr, HI) add up to alkenes to form alkyl halides. The order of reactivity of the hydrogen halides is $\text{HI} > \text{HBr} > \text{HCl}$. Like addition of halogens to alkenes, addition of hydrogen halides is also an example of electrophilic addition reaction. Let us illustrate this by taking addition of HBr to symmetrical and unsymmetrical alkenes.

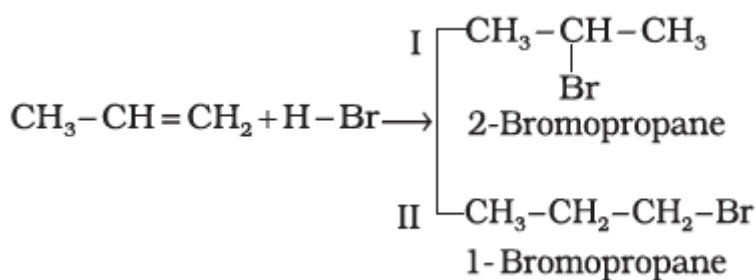
Addition reaction of HBr to symmetrical alkenes

Addition reactions of HBr to symmetrical alkenes (similar groups attached to double bond) take place by electrophilic addition mechanism.



Addition reaction of HBr to unsymmetrical alkenes (Markovnikov Rule)

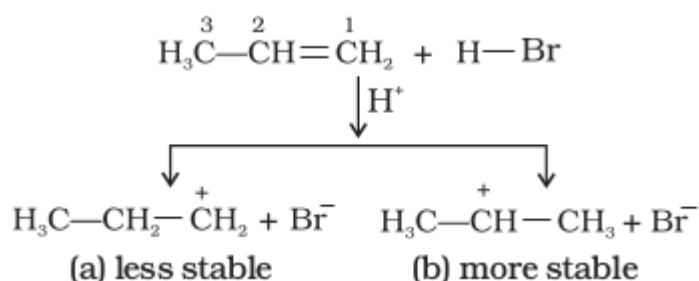
How will $\text{H}-\text{Br}$ add to propene ? The two possible products are I and II.



Markovnikov, a Russian chemist made a generalisation in 1869 after studying such reactions in detail. These generalisations led Markovnikov to frame a rule called **Markovnikov rule**. The rule states that negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms. Thus according to this rule, product I *i.e.*, 2-bromopropane is expected. In actual practice, this is the principal product of the reaction. This generalisation of Markovnikov rule can be better understood in terms of mechanism of the reaction.

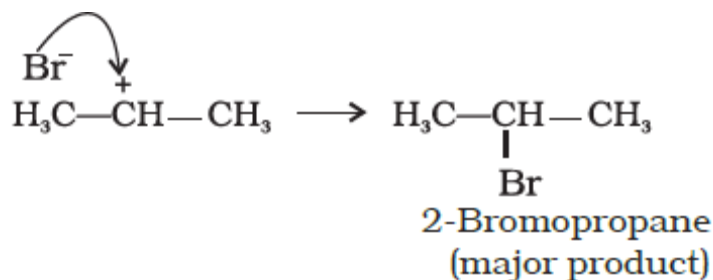
Mechanism

Hydrogen bromide provides an electrophile, H^+ , which attacks the double bond to form carbocation as shown below :



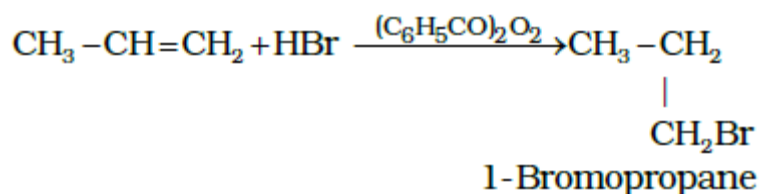
(i) The secondary carbocation (b) is more stable than the primary carbocation (a), therefore, the former predominates because it is formed at a faster rate.

(ii) The carbocation (b) is attacked by Br^- ion to form the product as follows :

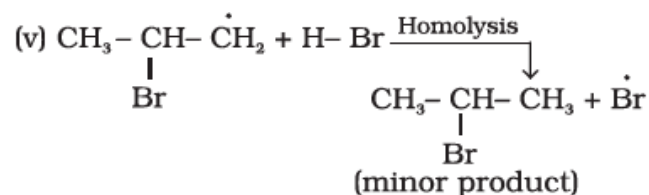
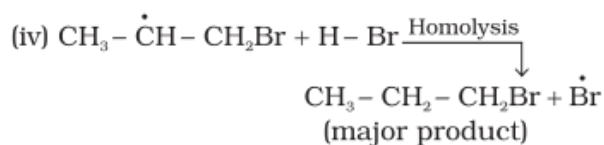
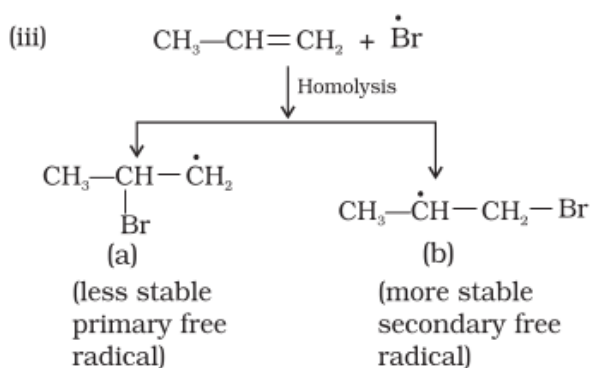
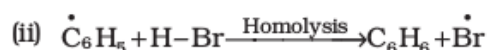
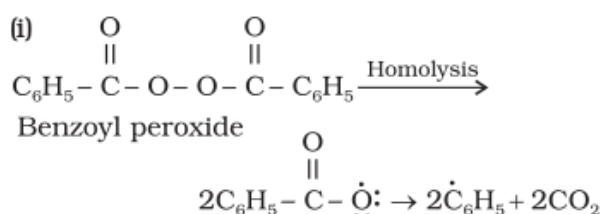


Anti Markovnikov addition or peroxide effect or Kharash effect

In the presence of peroxide, addition of HBr to unsymmetrical alkenes like propene takes place contrary to the Markovnikov rule. This happens only with HBr but not with HCl and HI. This addition reaction was observed by M.S. Kharash and F.R. Mayo in 1933 at the University of Chicago. This reaction is known as *peroxide* or *Kharash* effect or addition reaction anti to Markovnikov rule.



Mechanism : Peroxide effect proceeds via free radical chain mechanism as given below:



The secondary free radical obtained in the above mechanism (step iii) is more stable than the primary. This explains the formation of 1-bromopropane as the major product. It may be noted that the peroxide effect is not observed in addition of HCl and HI. This may be due to the fact

that the H-Cl bond being stronger ($430.5 \text{ kJ mol}^{-1}$) than H-Br bond ($363.7 \text{ kJ mol}^{-1}$), is not cleaved by the free radical, whereas the H-I bond is weaker ($296.8 \text{ kJ mol}^{-1}$) and iodine free radicals combine to form iodine molecules instead of adding to the double bond.

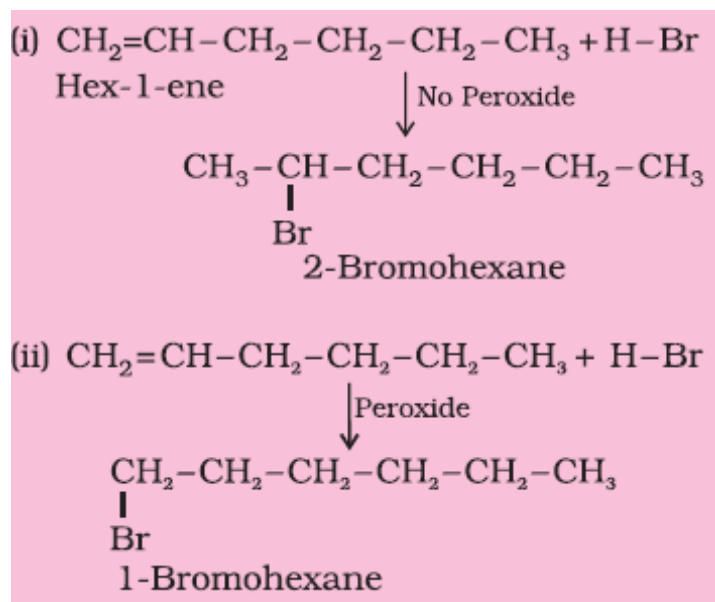
Problem 6.

Write IUPAC names of the products obtained by addition reactions of HBr to hex-1-ene

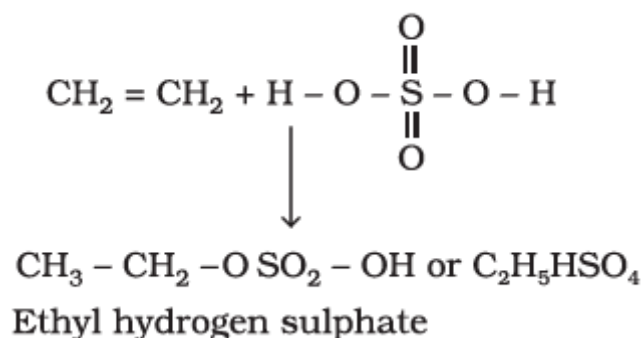
(i) in the absence of peroxide and

(ii) in the presence of peroxide.

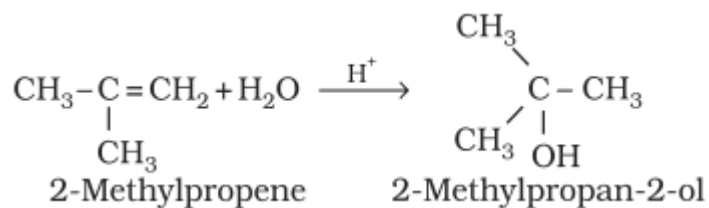
Solution



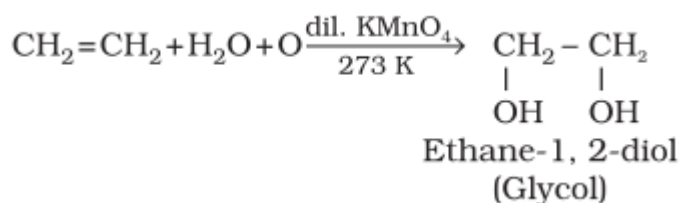
4. Addition of sulphuric acid : Cold concentrated sulphuric acid adds to alkenes in accordance with Markovnikov rule to form alkyl hydrogen sulphate by the electrophilic addition reaction.



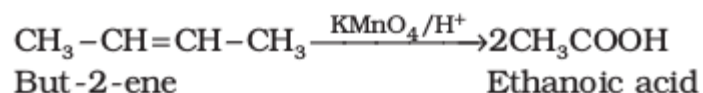
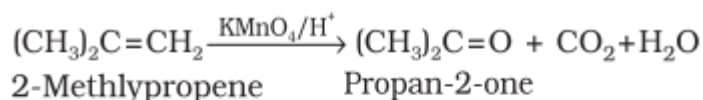
5. Addition of water : In the presence of a few drops of concentrated sulphuric acid, alkenes react with water to form alcohols, in accordance with the Markovnikov rule.



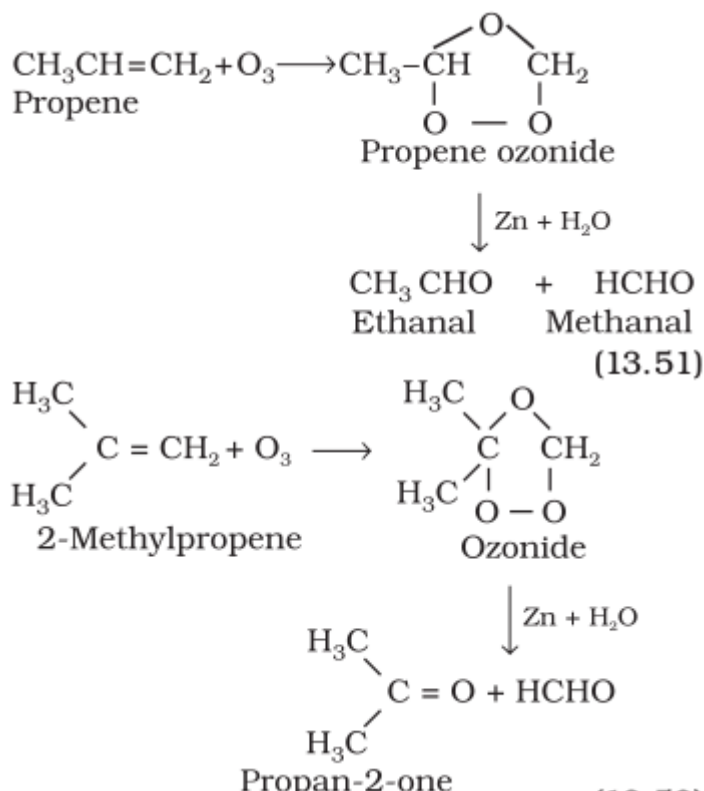
6. Oxidation: Alkenes on reaction with cold, dilute, aqueous solution of potassium permanganate (Baeyer's reagent) produce glycols. Decolorisation of KMnO_4 solution is used as a test for unsaturation.



b) Acidic potassium permanganate or acidic potassium dichromate oxidises alkenes to ketones and/or acids depending upon the nature of the alkene and the experimental conditions

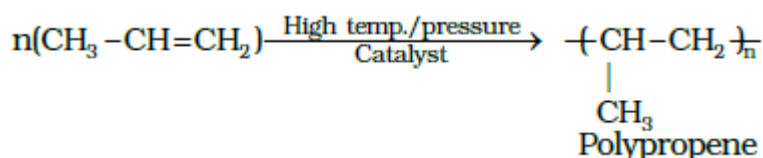
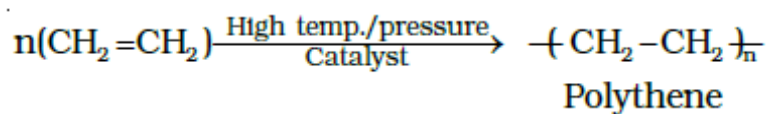


7. Ozonolysis : Ozonolysis of alkenes involves the addition of ozone molecule to alkene to form ozonide, and then cleavage of the ozonide by $\text{Zn-H}_2\text{O}$ to smaller molecules. This reaction is highly useful in detecting the position of the double bond in alkenes or other unsaturated compounds.



8. Polymerisation: You are familiar with polythene bags and polythene sheets.

Polythene is obtained by the combination of large number of ethene molecules at high temperature, high pressure and in the presence of a catalyst. The large molecules thus obtained are called polymers. This reaction is known as **polymerisation**. The simple compounds from which polymers are made are called **monomers**. Other alkenes also undergo polymerisation.



Polymers are used for the manufacture of plastic bags, squeeze bottles, refrigerator dishes, toys, pipes, radio and T.V. cabinets etc. Polypropene is used for the manufacture of milk crates, plastic buckets and other moulded articles. Though these materials have now become common, excessive use of polythene and polypropylene is a matter of great concern for all of us.

8. Summary

Alkenes are unsaturated hydrocarbons containing one or more double bonds. They are generally obtained by the loss of halogen from vicinal dihalides or by the loss of hydrogen halides from haloalkanes. Dehydration of alcohols on heating with conc. sulphuric acid also produce alkenes. Alkenes generally undergo addition reactions which are mainly electrophilic additions. The other important reactions of alkenes are oxidation, ozonolysis (useful for detecting the position of double bond) and polymerization (used for the manufacture of commercially useful products). Alkenes show structural isomerism. They also exhibit geometrical (cis-trans) isomerism due to restricted rotation around the carbon-carbon double bond.