

9.2.4 Conformations

Alkanes contain carbon-carbon sigma (σ) bonds. Electron distribution of the sigma molecular orbital is symmetrical around the internuclear axis of the C-C bond which is not disturbed due to rotation about its axis. This permits free rotation about C-C single bond. This rotation results into different spatial arrangements of atoms in space which can change into one another. Such spatial arrangements of atoms which can be converted into one another by rotation around a C-C single bond are called **conformations** or **conformers** or **rotamers**. Alkanes can thus have infinite number of conformations by rotation around C-C single bonds. However, it may be remembered that rotation around a C-C single bond is not completely free. It is hindered by a small energy barrier of $1-20 \text{ kJ mol}^{-1}$ due to weak repulsive interaction between the adjacent bonds. Such a type of repulsive interaction is called **torsional strain**.

Conformations of ethane : Ethane molecule (C_2H_6) contains a carbon – carbon single bond with each carbon atom attached to three hydrogen atoms. Considering the ball and stick model of ethane, keep one carbon atom stationary and rotate the other carbon atom around the C-C axis. This rotation results into infinite number of spatial arrangements of hydrogen atoms attached to one carbon atom with respect to the hydrogen atoms attached to the other carbon atom. These are called **conformational isomers** (conformers). Thus there are infinite number of conformations of ethane. However, there are two extreme cases. One such conformation in which hydrogen atoms attached to two carbons are as closed together as possible is called **eclipsed** conformation and the other in which hydrogens are as far apart as possible is known as the **staggered** conformation. Any other intermediate conformation is called a **skew** conformation. It may be remembered that in all the conformations, the bond angles and the bond lengths remain the same. Eclipsed and the staggered conformations can be represented by **Sawhorse** and **Newman projections**.

1. Sawhorse projections

In this projection, the molecule is viewed along the molecular axis. It is then projected on paper by drawing the central C-C bond as a somewhat longer straight line. Upper end of the line is slightly tilted towards right or left hand side. The front carbon is shown at the lower end of the line, whereas the rear carbon is shown at the upper end. Each carbon has three lines attached to it corresponding to three hydrogen atoms. The lines are inclined at an angle of 120° to each other. Sawhorse projections of eclipsed and staggered conformations of ethane are depicted in Fig. 9.2.

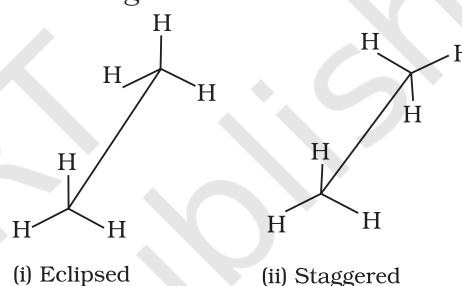


Fig. 9.2 Sawhorse projections of ethane

2. Newman projections

In this projection, the molecule is viewed at the C-C bond head on. The carbon atom nearer to the eye is represented by a point. Three hydrogen atoms attached to the front carbon atom are shown by three lines drawn at an angle of 120° to each other. The rear carbon atom (the carbon atom away from the eye) is represented by a circle and the three hydrogen atoms are shown attached to it by the shorter lines drawn at an angle of 120° to each other. The Newman's projections are depicted in Fig. 9.3.

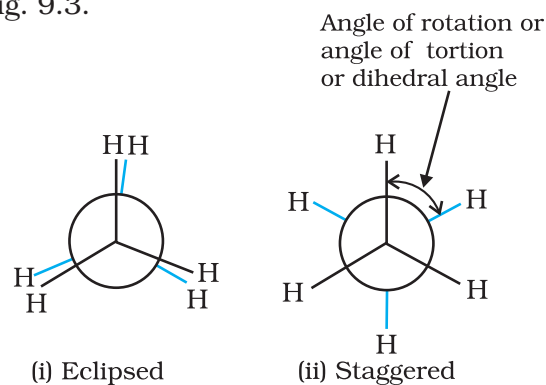


Fig. 9.3 Newman's projections of ethane

Relative stability of conformations: As mentioned earlier, in staggered form of ethane, the electron clouds of carbon-hydrogen bonds are as far apart as possible. Thus, there are minimum repulsive forces, minimum energy and maximum stability of the molecule. On the other hand, when the staggered form changes into the eclipsed form, the electron clouds of the carbon – hydrogen bonds come closer to each other resulting in increase in electron cloud repulsions. To check the increased repulsive forces, molecule will have to possess more energy and thus has lesser stability. As already mentioned, the repulsive interaction between the electron clouds, which affects stability of a conformation, is called **torsional strain**. Magnitude of torsional strain depends upon the angle of rotation about C–C bond. This angle is also called **dihedral angle** or **torsional angle**. Of all the conformations of ethane, the *staggered form has the least torsional strain and the eclipsed form, the maximum torsional strain*. Therefore, staggered conformation is more stable than the eclipsed conformation. Hence, molecule largely remains in staggered conformation or we can say that it is preferred conformation. Thus it may be inferred that rotation around C–C bond in ethane is not completely free. The energy difference between the two extreme forms is of the order of 12.5 kJ mol^{-1} , which is very small. Even at ordinary temperatures, the ethane molecule gains thermal or kinetic energy sufficient enough to overcome this energy barrier of 12.5 kJ mol^{-1} through intermolecular collisions. Thus, it can be said that rotation about carbon-carbon single bond in ethane is almost free for all practical purposes. It has not been possible to separate and isolate different conformational isomers of ethane.

9.3 ALKENES

Alkenes are unsaturated hydrocarbons containing at least one double bond. What should be the general formula of alkenes? If there is one double bond between two carbon atoms in alkenes, they must possess two hydrogen atoms less than alkanes. Hence, 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.

9.3.1 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). You have already read that 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. 9.4 and 9.5.

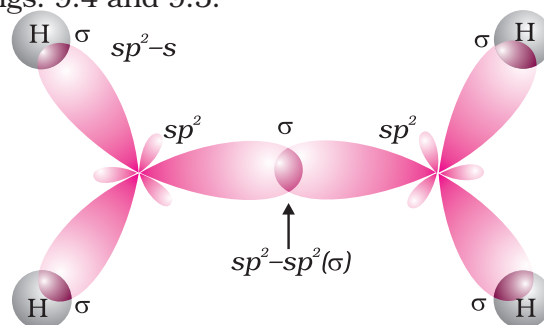


Fig. 9.4 Orbital picture of ethene depicting σ bonds only

9.3.2 Nomenclature

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

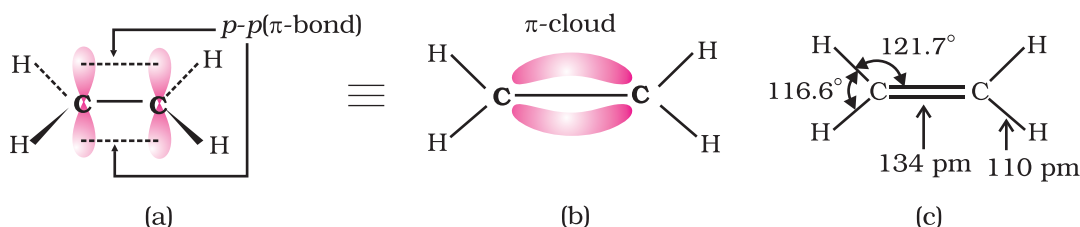


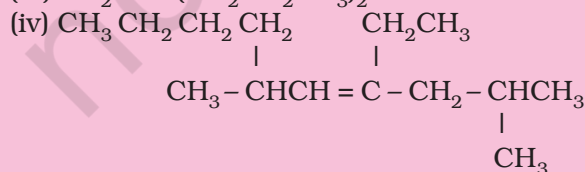
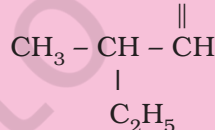
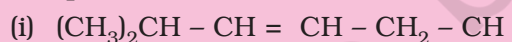
Fig. 9.5 Orbital picture of ethene showing formation of (a) π -bond, (b) π -cloud and (c) bond angles and bond lengths

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
$\text{CH}_2 = \underset{\text{CH}_3}{\text{C}} - \text{CH}_3$	2-Methylprop-1-ene
$\text{CH}_2 = \underset{\text{CH}_3}{\text{CH}} - \text{CH} - \text{CH}_3$	3-Methylbut-1-ene

Problem 9.7

Write IUPAC names of the following compounds:



Solution

- 2,8-Dimethyl-3, 6-decadiene;
- 1,3,5,7 Octatetraene;
- 2- n -Propylpent-1-ene;
- 4-Ethyl-2,6-dimethyl-dec-4-ene;

Problem 9.8

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

Solution

σ bonds : 33, π bonds : 2

σ bonds : 17, π bonds : 4

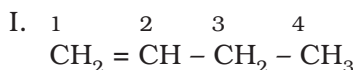
σ bonds : 23, π bond : 1

σ bonds : 41, π bond : 1

9.3.3 Isomerism

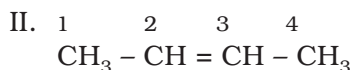
Alkenes show both structural isomerism and geometrical isomerism.

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:



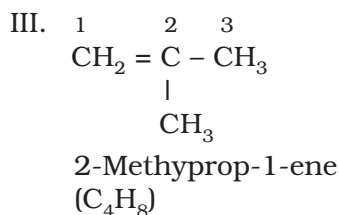
But-1-ene

(C_4H_8)



But-2-ene

(C_4H_8)

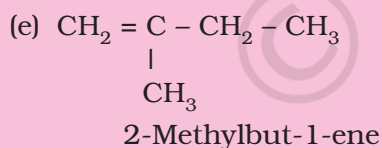
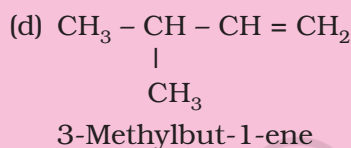
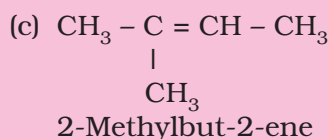
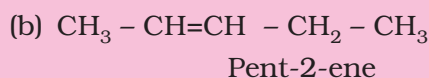
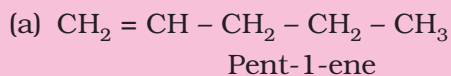


Structures I and III, and II and III are the examples of **chain isomerism** whereas structures I and II are **position isomers**.

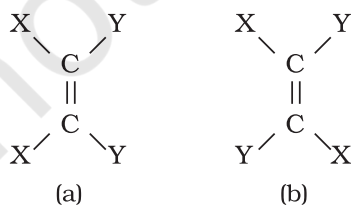
Problem 9.9

Write structures and IUPAC names of different structural isomers of alkenes corresponding to C₅H₁₀.

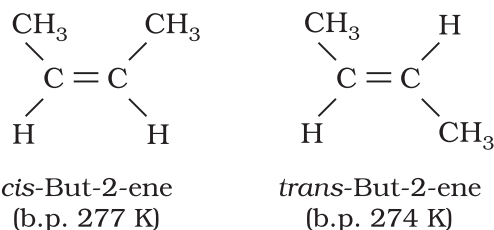
Solution



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 YX C = C XY like structure. YX C = C XY can be represented in space in the following two ways :

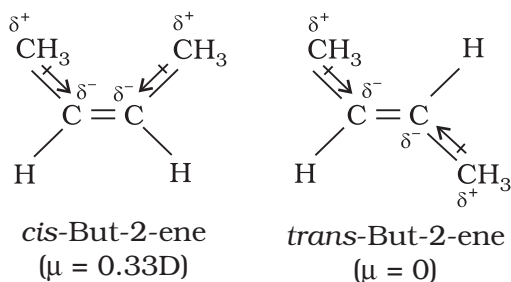


In (a), the two identical atoms *i.e.*, both the X or both the Y lie on the same side of the double bond but in (b) the two X or two Y lie across the double bond or on the opposite sides of the double bond. This results in different geometry of (a) and (b) *i.e.* disposition of atoms or groups in space in the two arrangements is different. Therefore, they are **stereoisomers**. They would have the same geometry if atoms or groups around C=C bond can be rotated but rotation around C=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 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 the *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.

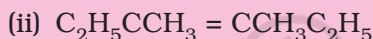


In the case of solids, it is observed that the *trans* isomer has higher melting point than the *cis* form.

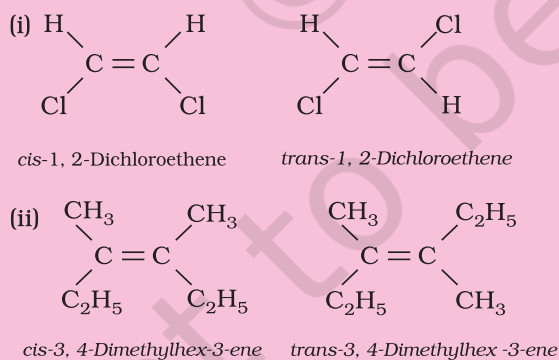
Geometrical or *cis-trans* isomerism is also shown by alkenes of the types $\text{XYC} = \text{CXZ}$ and $\text{XYC} = \text{CZW}$

Problem 9.10

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

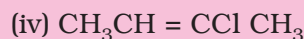
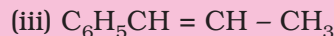
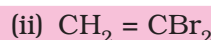
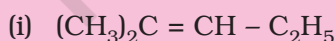


Solution



Problem 9.11

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

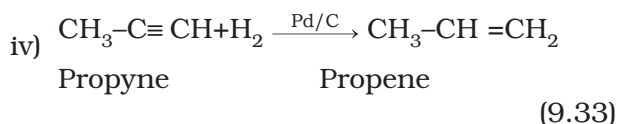
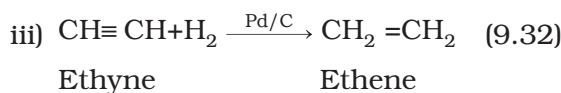
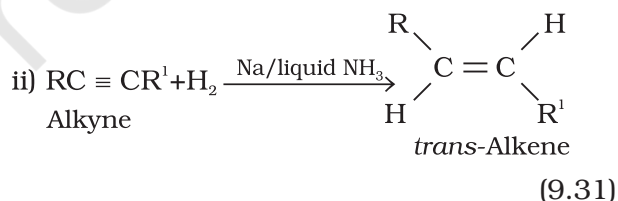
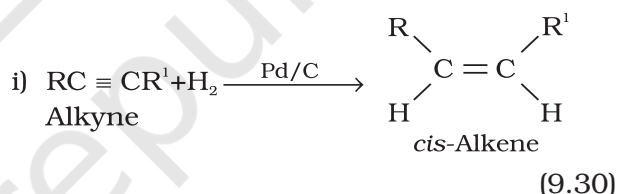


Solution

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

9.3.4 Preparation

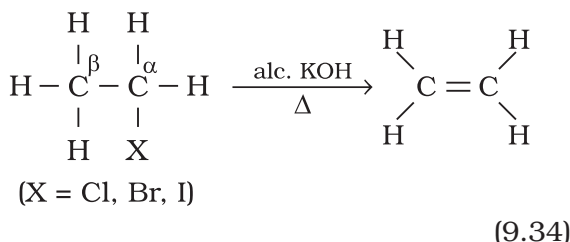
1. **From alkynes:** Alkynes on partial reduction with calculated amount of dihydrogen in the presence of *palladised* charcoal partially deactivated with poisons like sulphur compounds or quinoline give alkenes. Partially deactivated palladised charcoal is known as *Lindlar's catalyst*. Alkenes thus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



Will propene thus obtained show geometrical isomerism? Think for the reason in support of your answer.

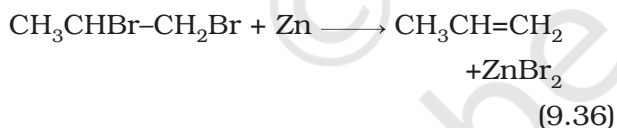
2. **From alkyl halides:** Alkyl halides (R-X) on heating with alcoholic potash (potassium hydroxide dissolved in alcohol, say,

ethanol) eliminate one molecule of halogen acid to form alkenes. This reaction is known as **dehydrohalogenation** i.e., removal of halogen acid. This is 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.

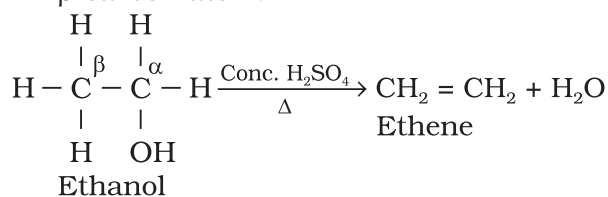
- 3. From vicinal dihalides:** Dihalides in which two halogen atoms are attached to two adjacent carbon atoms are known as *vicinal dihalides*. Vicinal dihalides on treatment with zinc metal lose a molecule of ZnX_2 to form an alkene. This reaction is known as **dehalogenation**.



- 4. From alcohols by acidic dehydration:**

You have read during nomenclature of different homologous series in Unit 12 that alcohols are the hydroxy derivatives of alkanes. They are represented by $\text{R}-\text{OH}$ 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 $-\text{OH}$ group

takes out one hydrogen atom from the β -carbon atom.



(9.37)

9.3.5 Properties

Physical properties

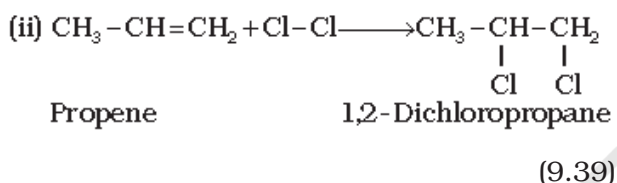
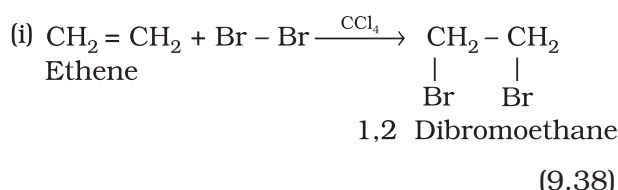
Alkenes as a class resemble alkanes in physical properties, except in types of isomerism and difference in polar nature. The first three members are gases, the next fourteen are liquids and the higher ones are solids. Ethene is a colourless gas with a faint sweet smell. All other alkenes are colourless and odourless, insoluble in water but fairly soluble in non-polar 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.

Chemical properties

Alkenes are the rich source of loosely held π (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 dihydrogen:** Alkenes add up one molecule of dihydrogen gas in the presence of finely divided nickel, palladium or platinum to form alkanes (Section 9.2.2)
- 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

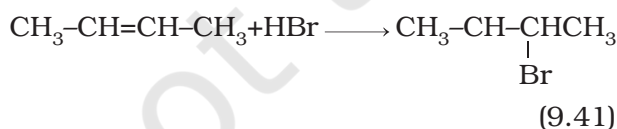
normal conditions. The reddish orange colour of bromine solution in carbon tetrachloride is discharged when bromine adds up to an unsaturation site. This reaction is used as a test for unsaturation. Addition of halogens to alkenes is an example of electrophilic addition reaction involving cyclic halonium 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

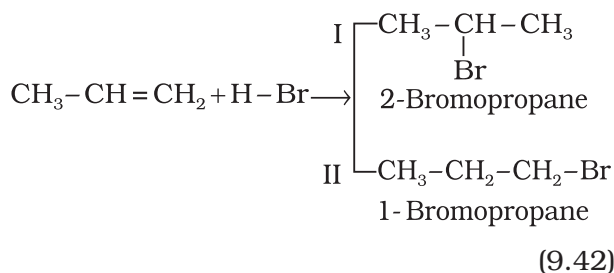
Addition reaction of HBr to symmetrical alkenes

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)

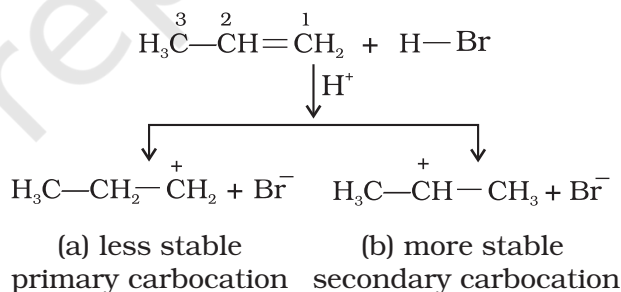
How will $\text{H} - \text{Br}$ add to propene? The two possible products are I and II.



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.

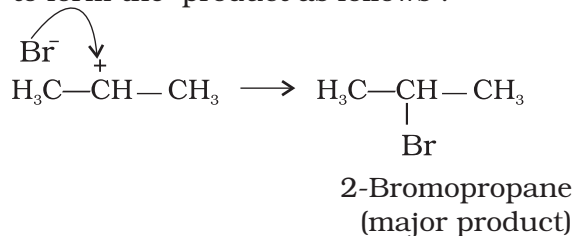
Mechanism

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



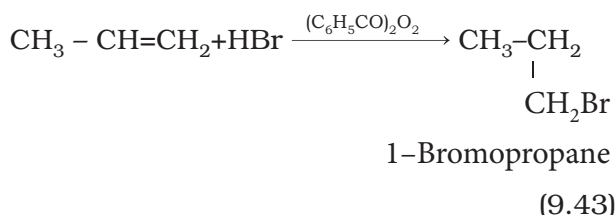
(i) The secondary carbocation (b) is more stable than the primary carbocation (a), therefore, the former predominates because it is formed at a faster rate.

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

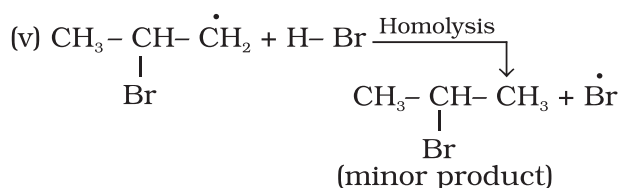
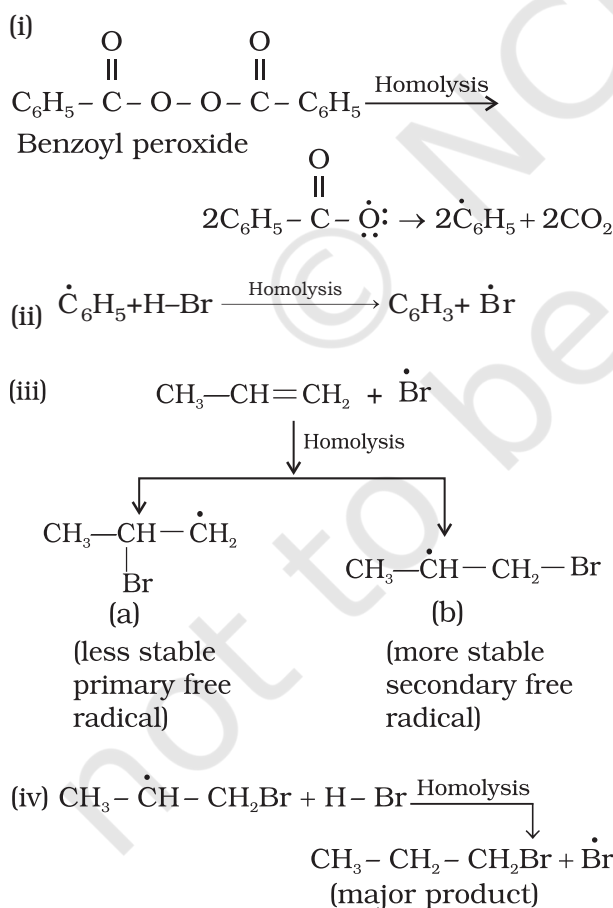


Anti Markovnikov addition or peroxide effect or Kharash effect

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:



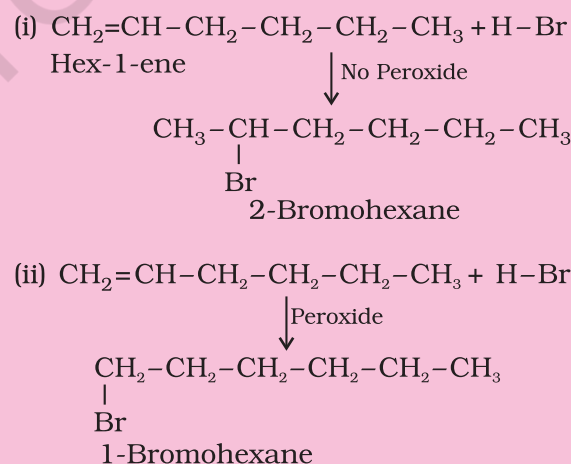
The secondary free radical obtained in the above mechanism (step iii) is more stable than the primary. This explains the formation of 1-bromopropane as the major product. It may be noted that the peroxide effect is not observed in addition of HCl and HI. This may be due to the fact that the H-Cl bond 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 9.12

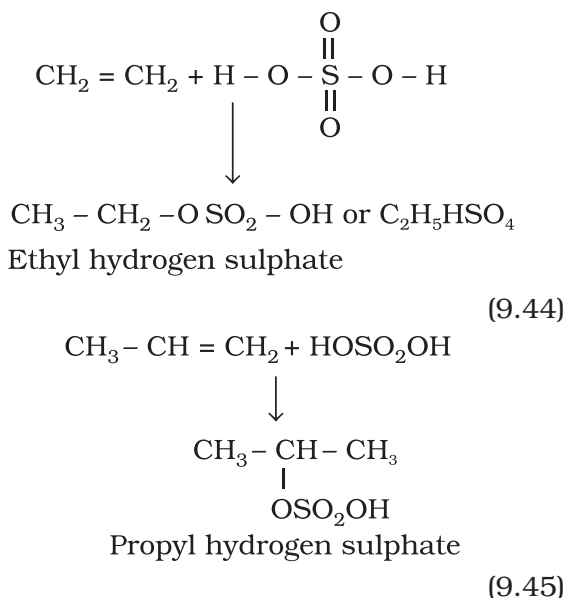
Write IUPAC names of the products obtained by addition reactions of HBr to hex-1-ene

- (i) in the absence of peroxide and
(ii) in the presence of peroxide.

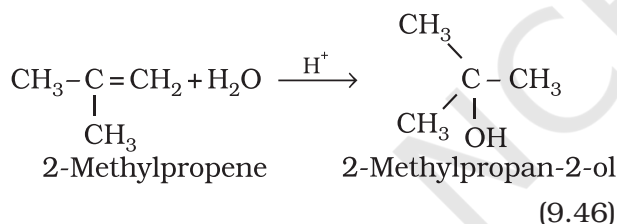
Solution



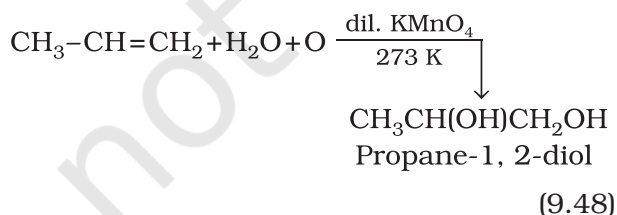
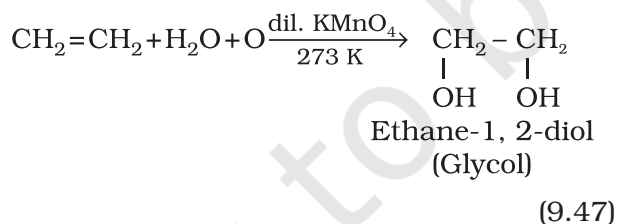
4. Addition of sulphuric acid : Cold concentrated sulphuric acid adds to alkenes in accordance with Markovnikov rule to form alkyl hydrogen sulphate by the electrophilic addition reaction.



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.

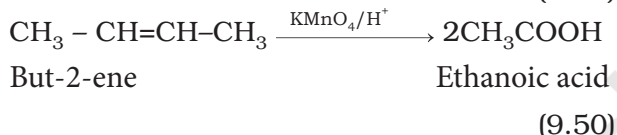
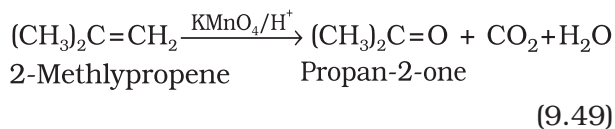


6. Oxidation: Alkenes on reaction with cold, dilute, aqueous solution of potassium permanganate (Baeyer's reagent) produce vicinal glycols. Decolorisation of KMnO_4 solution is used as a test for unsaturation.

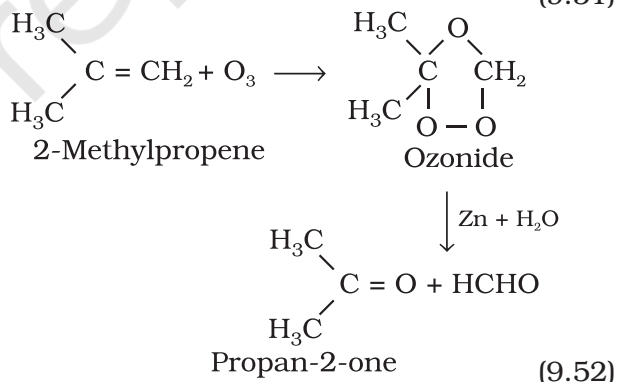
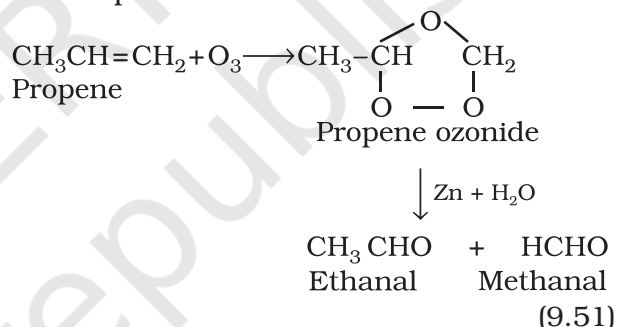


b) Acidic potassium permanganate or acidic potassium dichromate oxidises alkenes to

ketones and/or acids depending upon the nature of the alkene and the experimental conditions

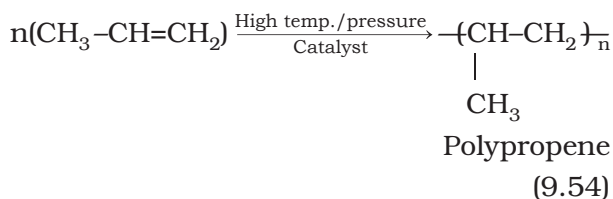
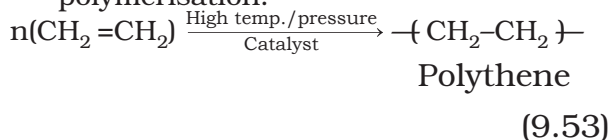


7. Ozonolysis : Ozonolysis of alkenes involves the addition of ozone molecule to alkene to form ozonide, and then cleavage of the ozonide by $\text{Zn-H}_2\text{O}$ to smaller molecules. This reaction is highly useful in detecting the position of the double bond in alkenes or other unsaturated compounds.



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.

9.4 ALKYNES

Like alkenes, alkynes are also unsaturated hydrocarbons. They contain at least one triple bond between two carbon atoms. The number of hydrogen atoms is still less in alkynes as compared to alkenes or alkanes. Their general formula is $\text{C}_n\text{H}_{2n-2}$.

The first stable member of alkyne series is ethyne which is popularly known as acetylene. Acetylene is used for arc welding purposes in the form of oxyacetylene flame obtained by mixing acetylene with oxygen gas. Alkynes are starting materials for a large number of organic compounds. Hence, it is interesting to study this class of organic compounds.

9.4.1 Nomenclature and Isomerism

In common system, alkynes are named as derivatives of acetylene. In IUPAC system, they

are named as derivatives of the corresponding alkanes replacing 'ane' by the suffix 'yne'. The position of the triple bond is indicated by the first triply bonded carbon. Common and IUPAC names of a few members of alkyne series are given in Table 9.2.

You have already learnt that ethyne and propyne have got only one structure but there are two possible structures for butyne – (i) but-1-yne and (ii) but-2-yne. Since these two compounds differ in their structures due to the position of the triple bond, they are known as **position isomers**. In how many ways, you can construct the structure for the next homologue i.e., the next alkyne with molecular formula C_5H_8 ? Let us try to arrange five carbon atoms with a continuous chain and with a side chain. Following are the possible structures :

Structure	IUPAC name
I. $\begin{array}{cccccc} & 1 & 2 & 3 & 4 & 5 \\ \text{HC} & \equiv & \text{C} & - & \text{CH}_2 & - & \text{CH}_2 & - & \text{CH}_3 \end{array}$	Pent-1-yne
II. $\begin{array}{cccccc} & 1 & 2 & 3 & 4 & 5 \\ \text{H}_3\text{C} & - & \text{C} & \equiv & \text{C} & - & \text{CH}_2 & - & \text{CH}_3 \end{array}$	Pent-2-yne
III. $\begin{array}{cccccc} & 4 & 3 & 2 & 1 \\ \text{H}_3\text{C} & - & \text{CH} & - & \text{C} & \equiv & \text{CH} \\ & & & & & & \\ & \text{CH}_3 & & & & & \end{array}$	3-Methylbut-1-yne

Structures I and II are position isomers and structures I and III or II and III are chain isomers.

Problem 9.13

Write structures of different isomers corresponding to the 5th member of alkyne series. Also write IUPAC names of all the isomers. What type of isomerism is exhibited by different pairs of isomers?

Solution

5th member of alkyne has the molecular formula C_6H_{10} . The possible isomers are:

Table 9.2 Common and IUPAC Names of Alkynes ($\text{C}_n\text{H}_{2n-2}$)

Value of n	Formula	Structure	Common name	IUPAC name
2	C_2H_2	$\text{H}-\text{C}\equiv\text{CH}$	Acetylene	Ethyne
3	C_3H_4	$\text{CH}_3-\text{C}\equiv\text{CH}$	Methylacetylene	Propyne
4	C_4H_6	$\text{CH}_3\text{CH}_2-\text{C}\equiv\text{CH}$	Ethylacetylene	But-1-yne
4	C_4H_6	$\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$	Dimethylacetylene	But-2-yne