

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.

13.3 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.

13.3.1 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. 13.4 and 13.5.

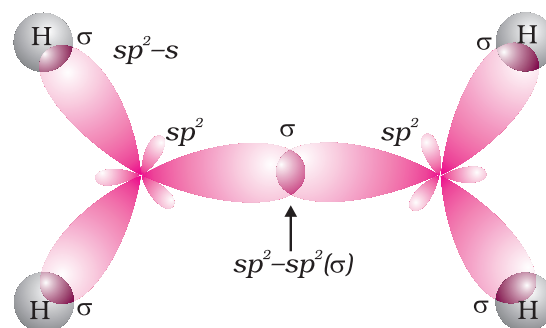


Fig. 13.4 Orbital picture of ethene depicting σ bonds only

13.3.2 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

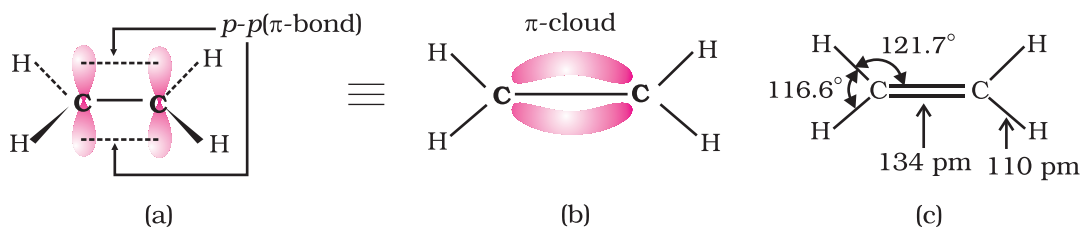


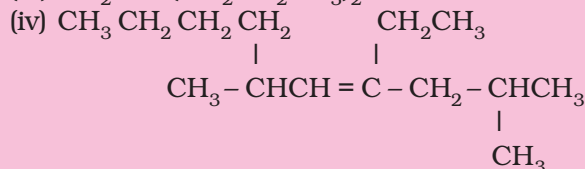
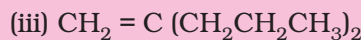
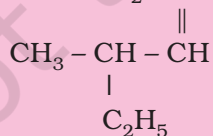
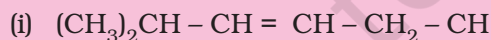
Fig. 13.5 Orbital picture of ethene showing formation of (a) π -bond, (b) π -cloud and (c) bond angles and bond lengths

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
$\text{CH}_2 = \text{C} - \text{CH}_3$ CH_3	2-Methylprop-1-ene
$\text{CH}_2 = \text{CH} - \text{CH} - \text{CH}_3$ CH_3	3-Methylbut-1-ene

Problem 13.7

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 13.8

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

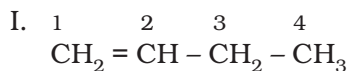
Solution

- σ bonds : 33, π bonds : 2
 σ bonds : 17, π bonds : 4
 σ bonds : 23, π bond : 1
 σ bonds : 41, π bond : 1

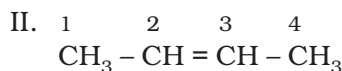
13.3.3 Isomerism

Alkenes show both structural isomerism and geometrical isomerism.

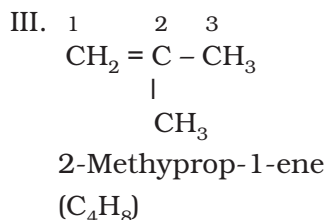
Structural isomerism : As in alkanes, ethene (C_2H_4) and propene (C_3H_6) can have only one structure but alkenes higher than propene have different structures. Alkenes possessing C_4H_8 as molecular formula can be written in the following three ways:



But-1-ene
(C_4H_8)



But-2-ene
(C_4H_8)

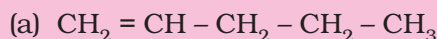


Structures I and III, and II and III are the examples of **chain isomerism** whereas structures I and II are **position isomers**.

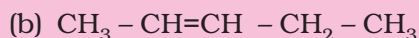
Problem 13.9

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

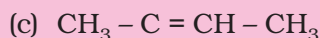
Solution



Pent-1-ene



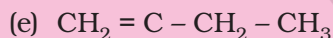
Pent-2-ene



2-Methylbut-2-ene

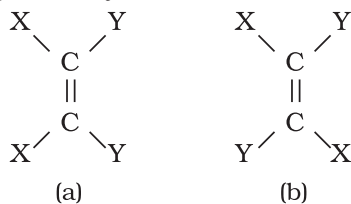


3-Methylbut-1-ene

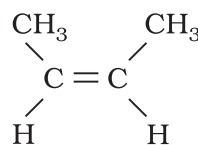


2-Methylbut-1-ene

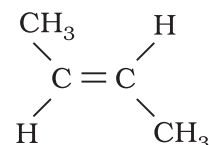
Geometrical isomerism: Doubly bonded carbon atoms have to satisfy the remaining two valences by joining with two atoms or groups. If the two atoms or groups attached to each carbon atom are different, they can be represented by YX C = C XY like structure. YX C = C XY can be represented in space in the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



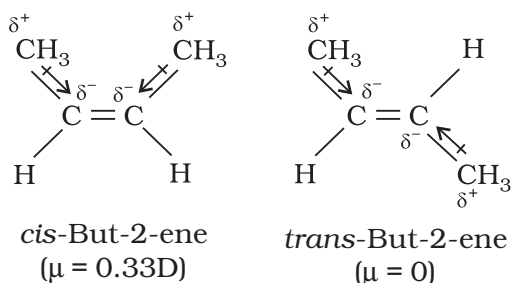
cis-But-2-ene
(b.p. 277 K)



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 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.

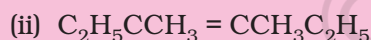


In the case of solids, it is observed that the *trans* isomer has higher melting point than the *cis* form.

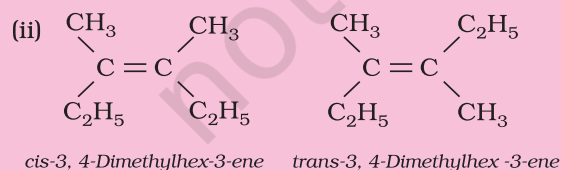
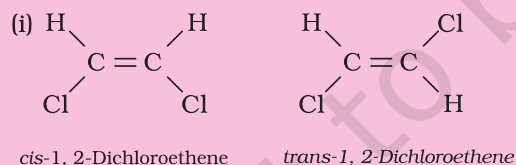
Geometrical or *cis-trans* isomerism is also shown by alkenes of the types XYC = CXZ and XYC = CZW

Problem 13.10

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

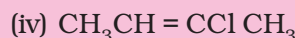
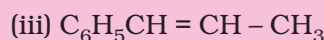
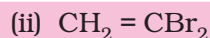
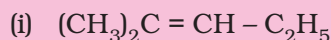


Solution



Problem 13.11

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

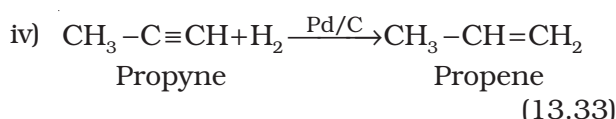
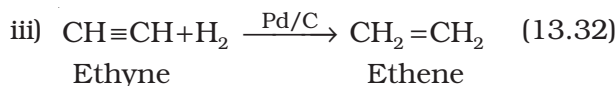
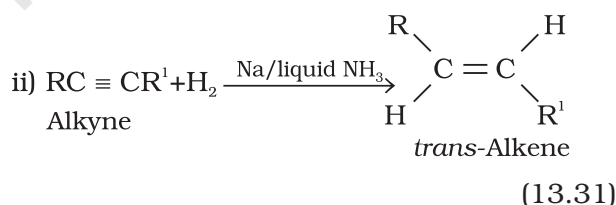
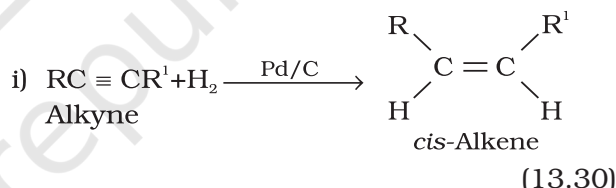


Solution

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

13.3.4 Preparation

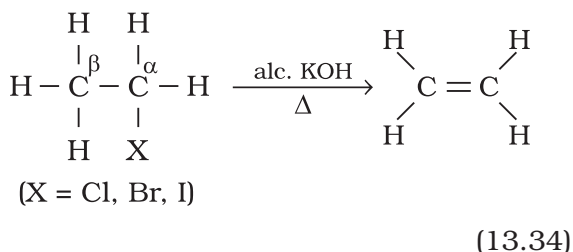
1. From alkynes: Alkynes on partial reduction with calculated amount of dihydrogen in the presence of *palladised* charcoal partially deactivated with poisons like sulphur compounds or quinoline give alkenes. Partially deactivated palladised charcoal is known as *Lindlar's catalyst*. Alkenes thus obtained 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.

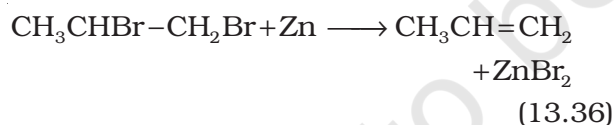
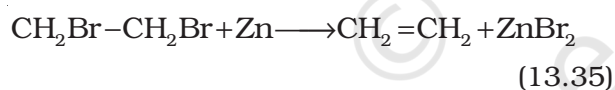
2. From alkyl halides: Alkyl halides (R-X) on heating with alcoholic potash (potassium hydroxide dissolved in alcohol,

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).



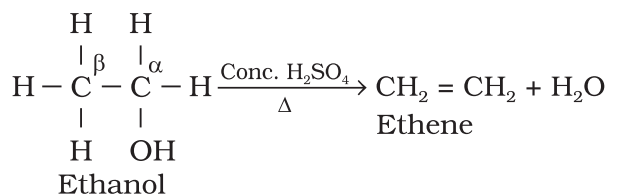
Nature of halogen atom and the alkyl group determine rate of the reaction. It is observed that for halogens, the rate is: iodine > bromine > chlorine, while for alkyl groups it is: tert > secondary > primary.

- 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 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.



(13.37)

13.3.5 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 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 dihydrogen:** Alkenes add up one molecule of dihydrogen gas in the presence of finely divided nickel, palladium or platinum to form alkanes (Section 13.2.2)
- 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