# 11

# HYDROCARBONS

## Student Learning Outcomes [C-11-D-01 to C-11-D-17]

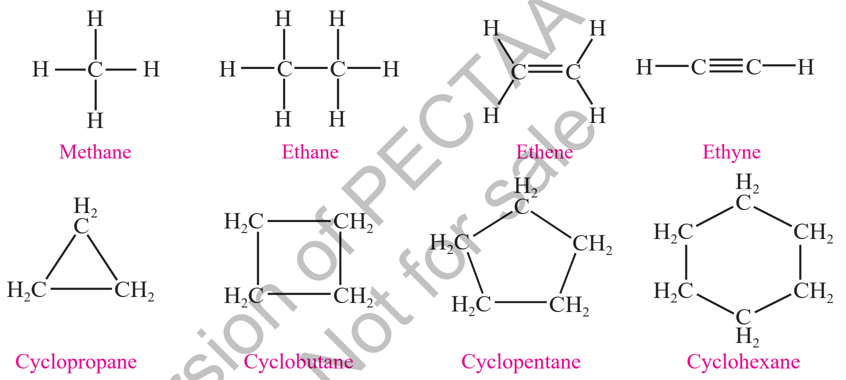
**After studying this chapter, students will be able to:**

- Classify hydrocarbons as aliphatic and aromatic. **(Understanding)**
- Describe the nomenclature of alkanes and cycloalkanes. **(Understanding)**
- Explain the shapes of alkanes and cycloalkanes exemplified by ethane and cyclopropane. **(Understanding)**
- Explain the unreactive nature of alkanes towards polar reagents. **(Understanding)**
- Define homolytic and heterolytic fission, free radical initiation, propagation and termination. **(Understanding)**
- Describe the mechanism of free radical substitution in alkanes exemplified by methane and ethane. **(Understanding)**
- Identify organic redox reactions. **(Understanding)**
- Explain the nomenclature of alkenes. **(Understanding)**
- Explain the shape of the ethene molecule in terms of s and p C-C bonds. **(Understanding)**
- Describe the structure and reactivity of alkenes as exemplified by ethene. **(Understanding)**
- Explain with suitable examples the terms isomerism, stereoisomerism, and structural isomerism. **(Understanding)**
- Explain the dehydration of alcohols and dehydrohalogenation of RX for the preparation of ethene. **(Understanding)**
- Describe the chemistry of alkenes by the following reactions of ethene: hydrogenation, hydrohalogenation, hydration, halogenation, halo hydration, epoxidation, ozonolysis, and polymerization. **(Understanding)**
- Explain the concept of conjugation in alkenes having alternate double bonds. **(Understanding)**
- Describe the mechanism of electrophilic addition in alkenes, using bromine/ ethene and hydrogen bromide propene as examples. **(Understanding)**
- Use the IUPAC naming system for alkenes. **(Understanding)**
- Explain the inductive effects of alkyl groups on the stability of primary, secondary and tertiary cations formed during electrophilic addition (this should be used to explain Markovnikov addition). **(Understanding)**

Hydrocarbons is a class of organic compounds that consists of only carbon and hydrogen. Hydrocarbons are abundantly found in petroleum and natural gas. They are frequently used as domestic and industrial fuels. Generally, hydrocarbons have many synthetic applications. Unsaturated hydrocarbons, especially alkenes, are used as the starting materials for a number of industrial products. Most of the products in the form of medicines, plastics, perfumes, polymers have their origins in hydrocarbons. Hydrocarbons are broadly divided into two classes that is aliphatic and aromatic hydrocarbons.

## 11.1 ALIPHATIC AND AROMATIC HYDROCARBONS

The compounds that are not aromatic are called aliphatic hydrocarbons. Aliphatic compounds may be open chain and cyclic, also they may be saturated or unsaturated. If there are only carbon and hydrogen atoms in an aliphatic compound, it is called aliphatic hydrocarbon. **Alkanes** are acyclic aliphatic hydrocarbons, whereas **cycloalkanes** are cyclic aliphatic hydrocarbons. Alkenes and alkynes are acyclic and unsaturated aliphatic hydrocarbons. **Figure 11.1** shows some examples of aliphatic hydrocarbons.

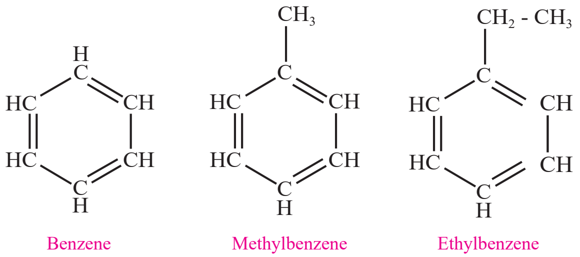


Methane Ethane Ethene Ethyne

Cyclopropane Cyclobutane Cyclopentane Cyclohexane

**Figure 11.1** Aliphatic hydrocarbons

**Aromatic hydrocarbons** is a special class of cyclic hydrocarbons that have high carbon to hydrogen ratio and are based on benzene ($C_6H_6$) or resembling compounds. Benzene is the basic aromatic compound and other compounds such as toluene and phenol are its derivatives. **Figure 11.2** presents the structures of some aromatic hydrocarbons.



Benzene Methylbenzene Ethylbenzene

**Figure: 11.2** Some aromatic hydrocarbons

**Interesting Information!**

The term aromatic was derived from the Greek word ***'aroma'*** meaning "**fragrance**" and is used in organic chemistry for a special class of compounds (aromatic compounds) having characteristic **odour**.

# 11.2 NOMENCLATURE

## 11.2.1 Alkanes or Paraffins

Alkanes are saturated hydrocarbons with the general formula $C_nH_{2n+2}$. Methane ($CH_4$) is the simplest member of this family. The homologous series of alkanes with condensed structural formulae and molecular formulae is shown in **Table 11.1**.

**Did You Know?**

Butane is a fuel used in lighters. Isobutane is used as a propellant in products such as shaving gel.

**Table 11.1** Condensed structural formulae and molecular formulae of alkanes

| IUPAC Name | Molecular formula | Condensed structure |
|---|---|---|
| Methane | $CH_4$ | $CH_4$ |
| Ethane | $C_2H_6$ | $CH_3\ CH_3$ |
| Propane | $C_3H_8$ | $CH_3\ CH_2\ CH_3$ |
| Butane | $C_4H_{10}$ | $CH_3\ CH_2\ CH_2\ CH_3$ |
| Pentane | $C_5H_{12}$ | $CH_3\ CH_2\ CH_2\ CH_2\ CH_3$ |
| Hexane | $C_6H_{14}$ | $CH_3\ CH_2\ CH_2\ CH_2\ CH_2\ CH_3$ |
| Heptane | $C_7H_{10}$ | $CH_3\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_3$ |
| Octane | $C_8H_{18}$ | $CH_3\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_3$ |
| Nonane | $C_9H_{20}$ | $CH_3\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_3$ |
| Decane | $C_{10}H_{22}$ | $CH_3\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_3$ |

What we obtain after the removal of one hydrogen atom from an alkane is called an **alkyl group**. The resulting alkyl groups are named by replacing **–ane** of the alkanes with **–yl**. Few examples are shown in **Table 11.2 & Table 11.3.**

**Table 11.2 Alkyl groups, their names and abbreviations**

| Alkane | Alkyl group | Abbreviation |
|---|---|---|
| $CH_4$<br>Methane | $CH_3$-<br>Methyl | Me– |
| $CH_3$-$CH_3$<br>Ethane | $CH_3$-$CH_2$-<br>Ethyl | Et– |

For alkanes with more than two carbon atoms, more than one alkyl groups can be derived.

Table 11.3 alkyl groups, straight chain and branched and their names

| Alkane | Possible Alkyl Groups | | | |
|---|---|---|---|---|
| $CH_3CH_2CH_3$<br>Propane | $CH_3\,CH_2CH_2$ ——<br>n-Propyl group<br>(Propyl) | $CH_3\overset{|}{C}HCH_3$<br>Iso-Propyl group<br>(1-Methylethyl) | | |
| $H_3CH_2CH_2CH_3$<br>Butane | $CH_3CH_2CH_2CH_2$ —<br>n-Butyl group<br>(Butyl) | $CH_3CH_2\overset{|}{C}HCH_3$<br>sec-Butyl group<br>(1-Methylpropyl) | $CH_3\underset{\underset{CH_3}{|}}{C}HCH_2$—<br>Iso-Butyl group<br>(2-Methylpropyl) | $CH_3\overset{|}{\underset{\underset{CH_3}{|}}{C}}CH_3$<br>tert-Butyl group<br>(1,1-Dimethylpropyl) |

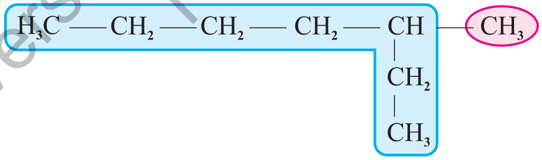
## 11.2.2 Nomenclature of Alkanes

Branched chain alkanes are named according to the following rules:

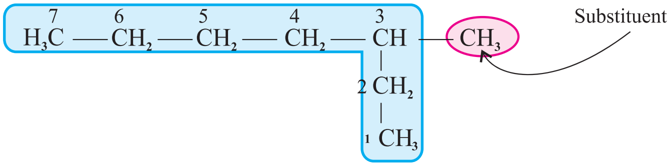
1. Locate the longest continuous chain of carbon atoms; this chain determines the parent name for the alkane. We designate the following compound as a hexane because the longest continuous chain contains six carbon atoms, that is, a bent chain.

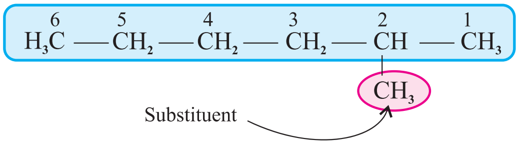
$$H_3C—CH_2—CH_2—CH_2—\underset{\underset{CH_3}{|}}{CH}—CH_3$$

The longest continuous chain may not always be obvious from the way the formula is written. Notice, for example, that the following alkane is designated as a heptane because the longest chain contains seven carbon atoms.



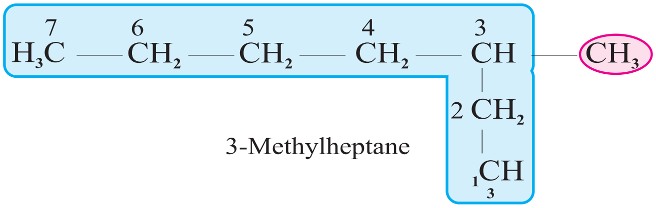
2. Number the longest chain beginning from the end nearest to the substituent. Applying this rule, we number the two alkanes shown below in the following way.



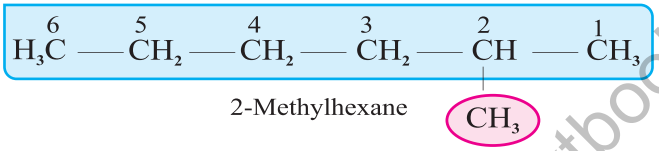


$$\overset{6}{H_3C}—\overset{5}{CH_2}—\overset{4}{CH_2}—\overset{3}{CH_2}—\underset{\underset{CH_3}{|}}{\overset{2}{CH}}—\overset{1}{CH_3}$$

3. Use the numbers obtained by applying rule 2 to designate the location of the substituent group. The parent name is placed last, and the substituent group, preceded by the number designating its location on the chain, is placed first. For example:

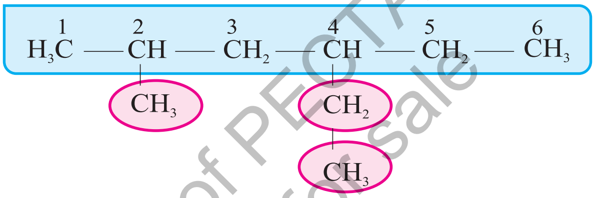

$H_3C-CH_2-CH_2-CH_2-CH(CH_3)-CH_2-CH_3$

3-Methylheptane


$H_3C-CH_2-CH_2-CH_2-CH(CH_3)-CH_3$

2-Methylhexane

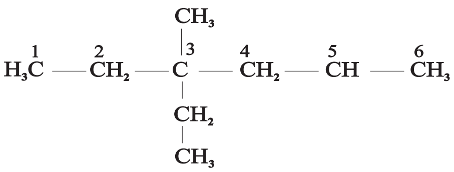
4. When two or more substituents are present, give each substituent a number corresponding to its location on the longest chain. For example, we designate the following compound as 4-Ethyl-2-methylhexane.


$H_3C-CH(CH_3)-CH_2-CH(CH_2CH_3)-CH_2-CH_3$

4-Ethyl-2-methylhexane

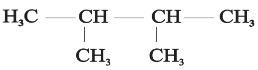
The substituent groups should be listed alphabetically (i.e. ethyl before methyl). While deciding on alphabetical order ignore multiplying prefixes such as “di” and “tri”.

5. When two substituents are present on the same carbon atom, use that number twice.

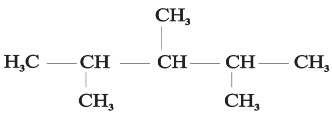

$H_3C-CH_2-C(CH_3)(CH_2CH_3)-CH_2-CH_2-CH_3$

3-Ethyl-3-methylhexane

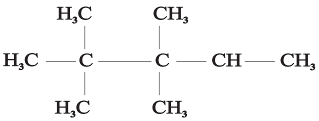
6. When two or more substituents are identical, indicate this by the prefixes di, tri, tetra, and so on. Then make certain that each and every substituent has a number.


$H_3C-CH(CH_3)-CH(CH_3)-CH_3$

2, 3-Dimethylbutane


$H_3C-CH(CH_3)-CH(CH_3)-CH(CH_3)-CH_3$

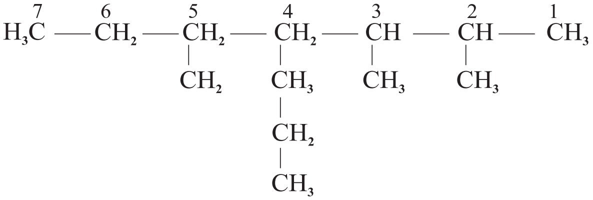
2,3,4 Trimethyl butane


$H_3C-C(CH_3)_2-C(CH_3)_2-CH-CH_3$

2, 2, 3, 3-Tetramethyl butane

Applying these six rules allows us to name most of the alkanes that we shall encounter. Two other rules, however, may be required occasionally.

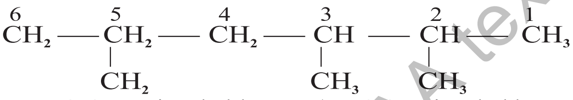
7. When two chains of equal length compete for selection as the parent chain, choose the chain with the greater number of substituents.



$$\overset{7}{H_3C}-\overset{6}{CH_2}-\overset{5}{CH_2}(CH_2)-\overset{4}{CH_2}(CH_3CH_2CH_3)-\overset{3}{CH}(CH_3)-\overset{2}{CH}(CH_3)-\overset{1}{CH_3}$$

2, 3, 5-Trimethyl-4-propylheptane

8. When branching first occurs at an equal distance from either end of the longest chain, choose the name that gives the lower number at the first point of difference.

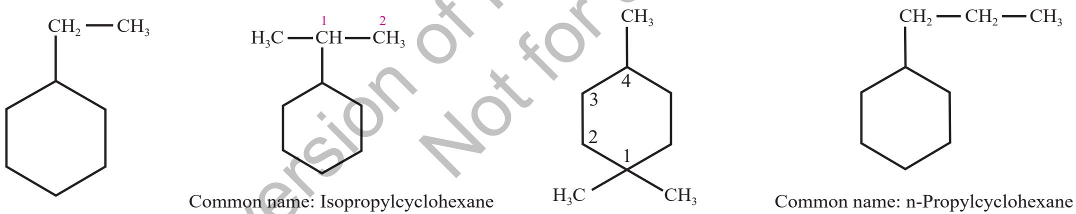


$$\overset{6}{CH_2}-\overset{5}{CH_2}(CH_2)-\overset{4}{CH_2}-\overset{3}{CH}(CH_3)-\overset{2}{CH}(CH_3)-\overset{1}{CH_3}$$

2, 3, 5-Trimethyl-hexane (not-2,4,5 trimethyl hexane)

## 11.2.3 Nomenclature of cycloalkanes

Cycloalkanes are named by attaching the prefix 'cyclo' to the names of the alkanes possessing the same number of carbon atoms as in **Figure 11.3**



Ethylcyclohexane

Common name: Isopropylcyclohexane
IUPAC name: 1-Methylethylcyclohexane

1,1,4-Trimethylcyclohexane

Common name: n-Propylcyclohexane
IUPAC name: Propyclcyclohexane

**Figure 11.3** Naming cycloalkanes

**Quick Check 11.1**

**a)** Write down the structural formulas for 2-Methylbutane and 2,2-Dimethylpropane.

**b)** Write down displayed formula of 2,3,3-Trimethylhexane and Methylcyclohexane.

**c)** Give two differences between molecules of cyclopentane and pentane.

**d)** Eicosane is a straight chain alkane whose molecules contain 20 carbon atoms. What is the molecular formula of eicosane?

## 11.2.4 Shapes of Alkanes and Cycloalkanes

The carbon atom in an alkane has four $sp^3$ hybridized orbitals and forms four single bonds that are equidistant from each other as in **Figure 11.4**. Alkane molecules have a tetrahedral shape around carbon atoms.

Carbon atoms in alkane molecules form sigma bonds with surrounding carbon and hydrogen atoms.

As a result, carbon atoms in alkanes are surrounded by 4 pairs of bonding electrons which equally repel each other to form 109.5° bond angles and a C-C bond length of 1.54 Å. The shapes of organic molecules are generally represented using ball and stick formula. The shapes of some straight chain alkanes are shown in **Table 11.4**.

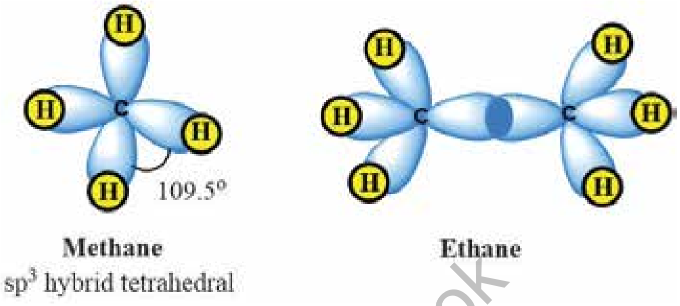
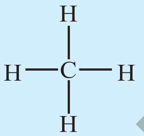
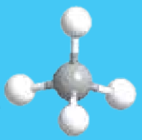
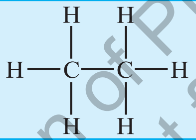
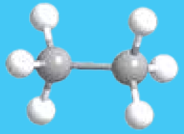
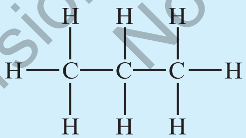
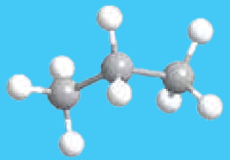
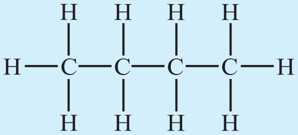
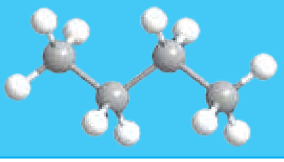


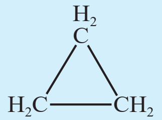
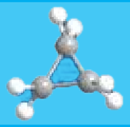
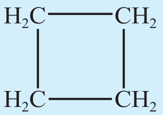
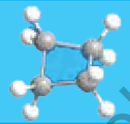
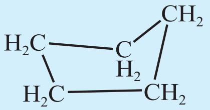
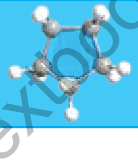
**Figure 11.4** $sp^3$ hybridised methane and ethane

**Table 11.4** Shapes of some straight chain alkanes

| IUPAC name & Molecular formula | Structural formula | 3D Structure |
|---|---|---|
| Methane<br>$CH_4$ |  $\mathrm{H}-\overset{\displaystyle\mathrm{H}}{\underset{\displaystyle\mathrm{H}}{\mathrm{C}}}-\mathrm{H}$ |  |
| Ethane<br>$C_2H_6$ |  $\mathrm{H}-\overset{\displaystyle\mathrm{H}}{\underset{\displaystyle\mathrm{H}}{\mathrm{C}}}-\overset{\displaystyle\mathrm{H}}{\underset{\displaystyle\mathrm{H}}{\mathrm{C}}}-\mathrm{H}$ |  |
| Propane<br>$C_3H_8$ |  $\mathrm{H}-\overset{\displaystyle\mathrm{H}}{\underset{\displaystyle\mathrm{H}}{\mathrm{C}}}-\overset{\displaystyle\mathrm{H}}{\underset{\displaystyle\mathrm{H}}{\mathrm{C}}}-\overset{\displaystyle\mathrm{H}}{\underset{\displaystyle\mathrm{H}}{\mathrm{C}}}-\mathrm{H}$ |  |
| Butane<br>$C_4H_{10}$ |  $\mathrm{H}-\overset{\displaystyle\mathrm{H}}{\underset{\displaystyle\mathrm{H}}{\mathrm{C}}}-\overset{\displaystyle\mathrm{H}}{\underset{\displaystyle\mathrm{H}}{\mathrm{C}}}-\overset{\displaystyle\mathrm{H}}{\underset{\displaystyle\mathrm{H}}{\mathrm{C}}}-\overset{\displaystyle\mathrm{H}}{\underset{\displaystyle\mathrm{H}}{\mathrm{C}}}-\mathrm{H}$ |  |

Cycloalkanes are cyclic, meaning that the carbon atoms of the molecule are arranged in the form of a ring. Cycloalkanes are also saturated, meaning that all of the carbons atoms that make up the ring are singly bonded to other atoms. The structural shapes of cyclopropane, cyclobutane and cyclopentane are shown below **(Table 11.5)**

Table 11.5 Shapes of few cycloalkanes

| IUPAC name & Molecular formula | Structural formula | 3D Structure |
|---|---|---|
| Cyclopropane<br>$C_3H_6$ |  |  |
| Cyclobutane<br>$C_4H_8$ |  |  |
| Cyclopentane<br>$C_4H_{10}$ |  |  |

## 11.2.5 Physical Properties of Alkanes

1. Alkanes containing upto four carbon atoms are gases while pentane to heptadecane ($C_5$ to $C_{17}$) are liquids. The higher members from $C_{18}$ onwards are waxy solids. Alkanes are colourless and odourless.
2. Alkanes are non-polar or very weakly polar and are insoluble in polar solvents like water, but soluble in non-polar solvents, such as hexane, benzene, ether, etc.
3. Their physical constants, e.g. boiling points, melting points, density, etc increase with the increase in number of carbon atoms, whereas solubility decreases with the increase in molecular mass. The boiling points of alkanes having branched chain structures are lower than their isomeric normal chain alkanes, e.g. straight chain butane has a higher boiling point -0.50 ºC than 2-Methylpropane (isobutane, -11.7 °C).

**Quick Check 11.2**

**a)** Why do branched alkanes have lower boiling points than the straight-chain alkanes?

**b)** Explain why alkanes have a tetrahedral shape.

**c)** Draw the shapes of cyclopropane and cyclopentane.

## 11.3 REACTION MECHANISM AND MODES OF BOND BREAKING

Reaction mechanism is the series of steps that take place in the course of the overall reaction. Like all chemical reactions, organic reactions involve the breaking of chemical bonds. There are two ways in which covalent bonds can break.

### (a) Homolytic Fission

Homolytic fission occurs when the covalent bond breaks evenly to produce free radicals. Free Radical is a species that contains an unpaired electron and is very reactive. Free radicals are extremely reactive because of the tendency of unpaired electrons to become paired.

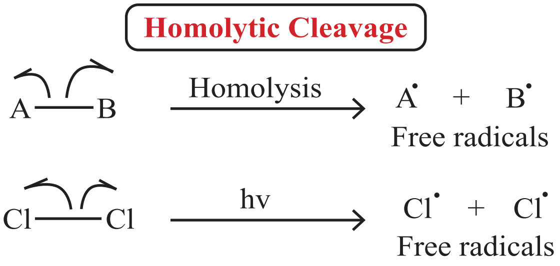


**Figure 11.5** Homolytic fission and free radical formation

### (b) Heterolytic Fission

Heterolytic fission occurs when the covalent bond breaks in such a way that the originally shared pair of electrons is gained by one atom only and oppositely charged ions are produced. This bond fission is shown by full curly arrows in mechanisms.

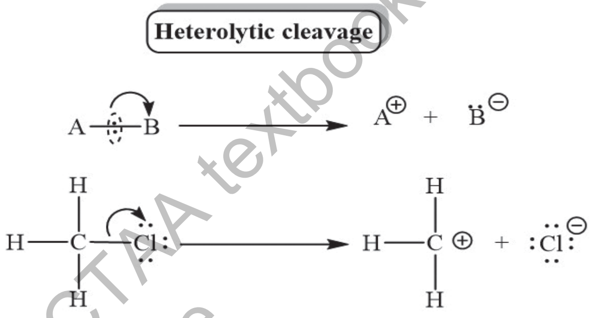


**Figure 11.6** Heterolytic fission and formation of ions

## 11.4 UNREACTIVE NATURE OF ALKANES TOWARDS POLAR REAGENTS

The alkanes or paraffins (Latin: *parum* = little, *affins* = affinity) are inert towards acids, alkalis, oxidizing and reducing agents under ordinary conditions. The lack of reactivity of alkanes under normal conditions may be explained on the basis of the non-polarity of the bonds forming them. The electronegativity values of carbon (2.5) and hydrogen (2.1) do not differ appreciably and the bonding electrons between C–H and C–C are equally shared making them almost non-polar and generally unreactive.

**Did You Know?**

Hydrocarbon combustion produces $CO_2$, a greenhouse gas contributing to climate change. Incomplete combustion can release carbon monoxide (CO) and particulate matter, which have serious health and environmental consequences.

The unreactive nature of alkanes can also be explained on the basis of inertness of a sigma bond. In a sigma bond the electrons are very tightly held between the nuclei which makes it a very stable bond. A lot of energy is required to break it.

## 11.5 REACTIONS OF ALKANES

Under high temperature or suitable conditions, alkanes undergo two types of reactions.

*i.* Thermal and catalytic reactions ,e.g. Combustion and cracking

*ii.* Free Radical substitution reactions are the reactions that involve replacement of one atom, or group of atoms by another through the free radical mechanism.

### 11.5.1 Free radical Substitution Reactions

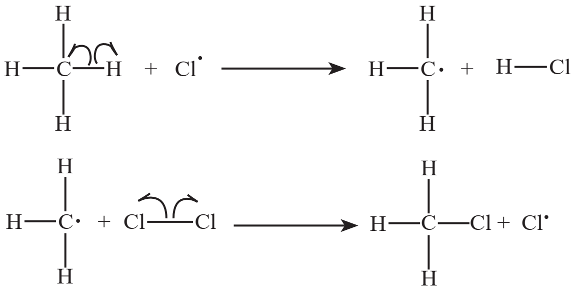
Substitution reactions of alkanes take place in the presence of light energy through the formation of highly reactive free radicals. An example is the substitution of a halogen atom with a hydrogen of an alkane, called **halogenation**. Alkanes react with chlorine and bromine in the presence of sunlight or UV light resulting in the successive replacement of hydrogen atoms with halogens. The extent of halogenation depends upon the amount of halogen used. Reaction of alkanes with fluorine is highly violent and results in a mixture of carbon, fluorinated alkanes and hydrofluoric acid. Iodine does not substitute directly because the reaction is too slow and reversible. The order of reactivity of halogens is:

$$\mathbf{F_2 > Cl_2 > Br_2 > I_2}$$

Halogenation involves the following three steps:

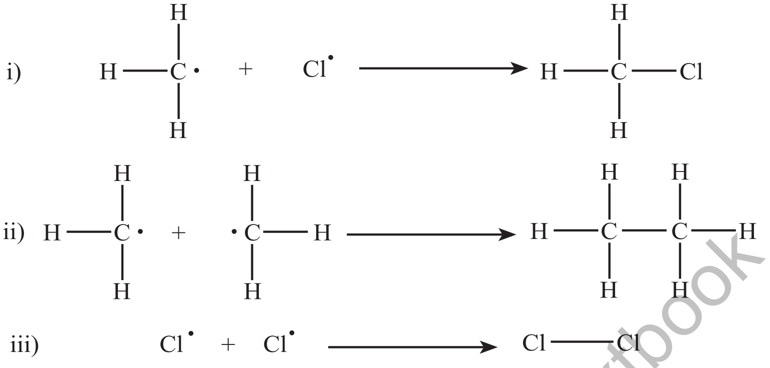
**i) Initiation step** is the first step in the mechanism of free radical substitution of alkanes by halogens. It involves breaking the halogen-halogen bond homolytically using energy from the UV light.

**ii) Propagation step** is the second step in the free radical substitution in which the initially formed radicals attack the alkane molecule generating more free radicals.



**iii) Termination step** is the final step in a free radical substitution in which two free radicals react together to form a product. The termination may take place in different ways. The chloride and alkyl radicals may combine to form a chloroalkanes or two chloride radicals may also react to make the chlorine molecule.

Another termination mode is the formation of alkane with double number of carbon atoms which takes place when two alkyl radicals merge together. This type of termination is rare and the alkanes with double carbon atoms are formed in traces. However, its presence is evident of free radical substitution mechanism.



i) $\mathrm{H{-}\overset{H}{\underset{H}{C}}{\cdot}} + \mathrm{Cl^{\bullet}} \longrightarrow \mathrm{H{-}\overset{H}{\underset{H}{C}}{-}Cl}$

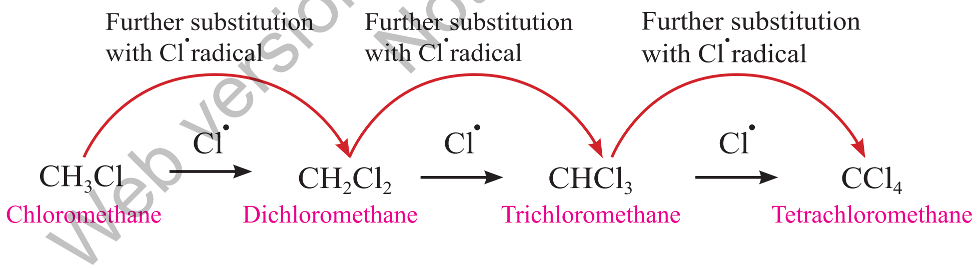
ii) $\mathrm{H{-}\overset{H}{\underset{H}{C}}{\cdot}} + \mathrm{{\cdot}\overset{H}{\underset{H}{C}}{-}H} \longrightarrow \mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}H}$

iii) $\mathrm{Cl^{\bullet}} + \mathrm{Cl^{\bullet}} \longrightarrow \mathrm{Cl{-}Cl}$

By repetition of step (ii), propagation step, a mixture of halogen substituted products (chloroalkanes) is obtained. The more the chlorine gas in reaction mixture to start with, the greater the proportions of chlorine atoms in the chloroalkane molecules formed. Trichloromethane is also known as chloroform and tetrachloromethane is also known as carbon tetrachloride.

### Interesting Information!

Haloalkanes are anaesthetic in nature. The anesthetic power of a haloalkane increases with the number of halogen atoms. Use of these as organic solvents in lab is strictly monitored due to their toxic nature.



$$CH_3Cl \xrightarrow{Cl^{\bullet}} CH_2Cl_2 \xrightarrow{Cl^{\bullet}} CHCl_3 \xrightarrow{Cl^{\bullet}} CCl_4$$

## Quick Check 11.3

**a)** Explain why alkanes have high stability?

**b)** What are major types of reactions that alkanes undergo?

**c)** How the termination step occurs in the halogenation of alkanes?

**d)** State the conditions under which a mixture of halogenoalkanes is obtained from the halogenation of alkanes.

**e)** Predict the products of the free radical chlorination of ethane.

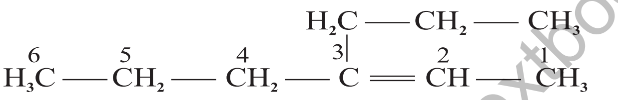
## 11.6 ALKENES

### 11.6.1 Nomenclature of Alkenes:

Alkenes are unsaturated hydrocarbons, *unsaturated hydrocarbons* are compounds of hydrogen and carbon only whose molecules contain carbon to carbon double bonds (or triple bonds). Alkenes have two hydrogen atoms less than the corresponding saturated hydrocarbons with general formula $C_nH_{2n}$.

The IUPAC rules for naming alkenes are similar in many respects to those for naming alkanes.

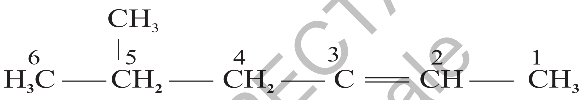
1. Select the longest continuous chain that contains the C = C as the parent chain. Change the ending of the name of the alkane of identical length from — ane to — ene, e.g.,



$$\overset{6}{H_3C}-\overset{5}{CH_2}-\overset{4}{CH_2}-\overset{H_2C-CH_2-CH_3}{\overset{|}{\overset{3}{C}}}=\overset{2}{CH}-\overset{1}{CH_3}$$

3-Propyl 2-hexene

2. Number the chain so as to include both carbon atoms of the double bond. Numbering begins from the end nearer to the double bond.



$$\overset{6}{H_3C}-\overset{CH_3}{\overset{|}{\overset{5}{CH_2}}}-\overset{4}{CH_2}-\overset{3}{C}=\overset{2}{CH}-\overset{1}{CH_3}$$

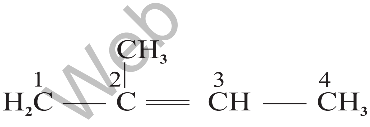
5-Methyl-2-hexene

3. Designate the location of the double bond by using the number of the first atom of the double bond as a prefix.

$$\overset{1}{H_2C}=\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{4}{CH_3} \qquad \overset{1}{H_2C}=\overset{2}{CH}\ \overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_3}$$

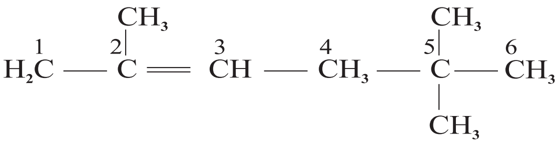
1-Butene 1-Pentene

4. Indicate the locations of the substituent groups by the numbers of the carbon atoms to which they are attached.



$$\overset{1}{H_2C}-\overset{CH_3}{\overset{|}{\overset{2}{C}}}=\overset{3}{CH}-\overset{4}{CH_3}$$

2-Methyl-2-butene



$$\overset{1}{H_2C}-\overset{CH_3}{\overset{|}{\overset{2}{C}}}=\overset{3}{CH}-\overset{4}{CH_3}-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{\overset{5}{C}}}}}-\overset{6}{CH_3}$$

2, 5, 5-Trimethyl-2-hexene

### 11.6.2 Preparation of Alkenes

Alkenes are prepared by the removal of small atoms (H, OH, X) from the adjacent carbon atoms of the saturated compounds, so as to create a double bond between carbon atoms. These reactions are known as **elimination reactions**. In such reactions, a small molecule such as $H_2O$ or HCl, is removed from adjacent carbons in an organic molecule. Preparation of ethene through various methods is being discussed below:

### i) Dehydration of Alcohols

Ethene is prepared by heating a mixture of ethanol and excess of concentrated sulphuric acid at 180°C. The reaction involves the removal of a water molecule from the alcohol molecule.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{heat}]{H_2SO_4} \underset{\text{Ethene}}{CH_2=CH_2} + \underset{\text{water}}{H_2O}$$

In the first step, ethyl hydrogen sulphate is formed which decomposes on heating to produce ethene.

$$CH_3–CH_2OH + H_2SO_4 \xrightarrow{180^{\circ}C} CH_3–CH_2–OSO_3H + H_2O$$

$$CH_3–CH_2OSO_3H \xrightarrow{\text{heat}} H_2C=CH_2 + H_2SO_4$$

### ii) Dehydrohalogenation of Alkyl Halides

On heating, ethyl bromide with alcoholic KOH, ethene is formed. Removal of hydrogen and halogen takes place from adjacent carbon atoms to create a double bond.

$$H_3C–CH_2–Br + KOH_{(alcoholic)} \xrightarrow{\text{heat}} H_2C=CH_2 + KBr + H_2O$$

## 11.6.3 Physical Properties

*i.* First three members i.e. ethene, propene and butene are gases at room temperature while $C_5$ to $C_{15}$ are liquids and the higher members are solids.

*ii.* They are insoluble in water but soluble in alcohol.

*iii.* They have characteristic smell and burn with luminous flame.

*iv.* Unlike alkanes, they show weakly polar properties because of $sp^2$ hybridization

**Quick Check 11.4**

**a)** Give the reactions of propanol with $H_2SO_4$, write down all the reaction involved:

**b)** Name the following alkenes:

i) $CH_3C(CH_3)=CH-CH_3$ ii) $CH_2=CHCH(CH_3)_2$

**c)** Draw the structural formulas of the following alkenes:

i) 3-Methyl-2-butene ii) 2-Methyl-4-ethyl-2-pentene

**d)** Give the dehydrohalogenation reaction of bromopropane.

**e)** Can propanol undergo dehydration? If yes give reactions involving dehydration.

# 11.7 STRUCTURE AND REACTIVITY OF ALKENES

## 11.7.1 Structure of Alkenes

Ethene ($C_2H_4$) is the simplest alkene. Each carbon atom in ethene is $sp^2$ hybridized and forms three equivalent $sp^2$ hybrid orbitals which lie in the same plane. The unhybrid *p*-orbital lies perpendicular (90º) to the plane of hybrid orbitals as shown in **Figure 11.7**.

These $sp^2$ orbitals are formed by mixing of the 2*s* orbital with two 2*p* orbitals leaving one unhybrid *p* orbital. In ethene, each carbon uses two $sp^2$ orbitals to form two C–H bonds each. The remaining $sp^2$ orbital on each carbon is used to form a carbon-carbon σ bond by linear overlap as in **Figure 11.8**.

The unhybrid *p*-orbitals of each carbon atom which are parallel to each other overlap laterally to form another carbon-carbon bond. This bond formed by the lateral overlap of *p*-orbitals is called a π bond.

### Interesting Information!

Plants produce ethene as a natural ripening hormone. For efficientharvesting and transportation to market, fruits and vegetables are often picked unripe and exposed to ethene so they could ripen in short time.

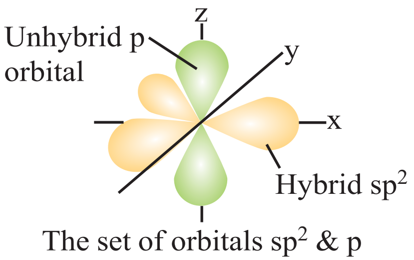


**Figure 11.7** $sp^2$ hybrid & unhybrid p orbitals of C

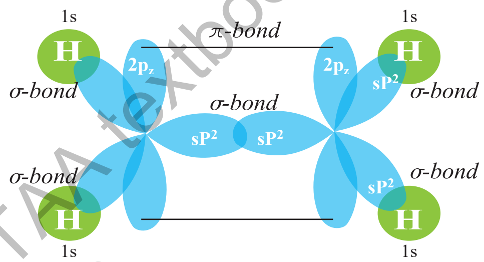


**Figure11.8** Bond formation of carbons in ethene

The two carbon atoms forming a double bond and the four atoms attached directly to them lie in the same plane. The remaining p-orbital on each carbon is used to form the π bond.

The sp² hybridization results in a trigonal planar arrangement around each carbon atom. The bond angles are approximately 120º, leading to a planar molecule as shown in **Figure 11.9.**

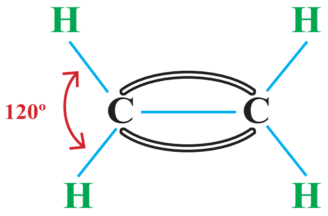


**Figure 11.9** Structure of ethene

## 11.7.2 Reactivity of π bond

Alkenes are more reactive than alkanes due to the presence of the double bond. The probability of finding electrons is away from the line joining the two nuclei. Due to this reason π-electrons are less firmly held between the nuclei. A π bond is, therefore, a weak bond as compared to a σ-bond. During a reaction it breaks comparatively easily rendering alkenes as reactive group of compounds. Moreover, the loosely held π-electrons are more exposed to attack by the electrophilic reagents. Alkenes, therefore, undergo electrophilic addition reactions very easily.

### Did You Know?

*Electrophile* is a species that can act as electron pair acceptor, it is represented by $\mathbf{E^+}$. Alkenes act as nucleophile because they contain π electrons. *Nucleophile* is a species that can act as a donor of a pair of electrons, it is represented by **Nü**.

**Quick Check 11.5**

**a)** How does an alkane differ from an alkene in stability?

**b)** Which of the following species is likely to act as a nucleophile? Why?

i) $H_2$ ii) $H^+$ iii) $OH^-$

**c)** Which of the following species is likely to act as an electrophile? Why?

i) $H_2$ ii) $H^+$ iii) $OH^-$

The reactions of alkenes mostly proceed through the formation of carbocations. Therefore, before studying the addition reactions of alkenes, the concept of carbocations and their stability is very important.

### 11.7.3 Carbocation Stability and Inductive Effect of Alkyl group

Carbocation is an alkyl group with a single positive charge on one of its carbon atoms. Carbocations are classified into following types.

*i.* Carbocation which is bonded to H only is named as methyl carbocation.

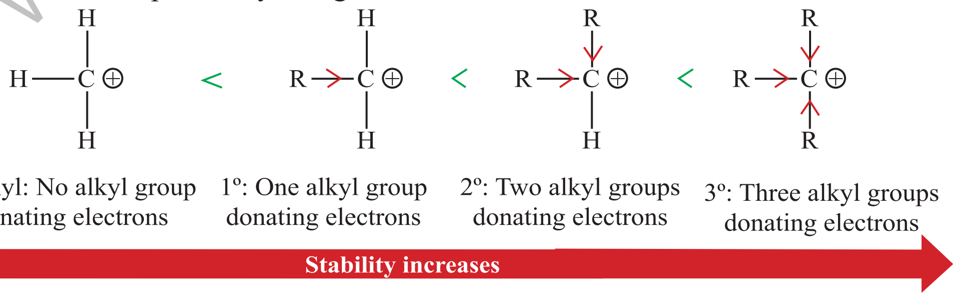
*ii.* If carbocation is bonded to one C or alkyl substituent, it is named as primary 1° carbocation.

*iii.* If it is bonded to 2 carbons (alkyl substituent) directly, it is named as secondary 2° carbocation.

*iv.* If it is directly bonded to 3 carbons (alkyl substituent), it is as tertiary 3° carbocation

The inductive effect of alkyl groups plays an important role in the stability of carbocation. The polarization of a σ bond due to electron withdrawing or electron donating effect of adjacent groups or atoms is referred to as inductive effect. Alkyl groups have a slightly electron donating inductive effect. Electron donating species, are said to have positive inductive effect (+I), whereas electron withdrawing species, such as a halogen atom, have a negative inductive effect (-I).

The alkyl groups attached to the positively charged carbon atoms are **electron donating groups**. Due to the positive charge on the carbon atom, carbocation is electrophile. The inductive effect is shown by the arrowheads on the bonds to show the alkyl groups pushing electrons towards the positively charged carbon.



Methyl: No alkyl group donating electrons

1°: One alkyl group donating electrons

2°: Two alkyl groups donating electrons

3°: Three alkyl groups donating electrons

**Figure 11.10** Inductive effect and Stability of carbocation

As a result, the carbocation become less positively charged which makes it energetically more stable. The stability of carbocation ions increases with a number of alkyl groups due to their +I effect. This means that tertiary carbocation is the most stable as they have three electron-donating alkyl groups which energetically stabilize the carbocation **Figure 11.10**.

### 11.7.4 Electron Withdrawing Inductive Effect

Electron withdrawing groups, such as a halogen atom, have a negative inductive effect (-I). Halogen withdraws bonded electrons from carbon to carbon bond and thus displays negative inductive effect. This causes a permanent dipole to arise in the molecule wherein the halogen atom holds a negative charge and carbon become partial positive **Figure 11.11**.

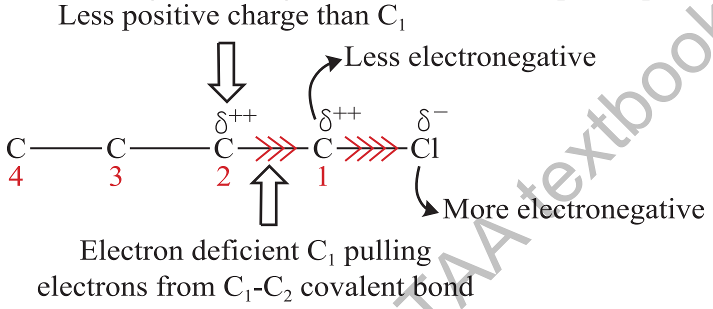


**Figure 11.11** Inductive effect and polarization of sigma bond

## 11.8 REACTIONS OF ALKENES

Alkenes are unsaturated hydrcarbons and they undergo electrophilic addition reactions mostly. Other minor types of reactions include oxidation, combustion and polymerization reactions.

### 11.8.1 Electrophilic Addition Reactions

The reactions in which an electrophile is added to the double bond of an alkene is called electrophilic addition reaction.

#### Mechanism of electrophilic addition in alkenes

The C=C in alkenes is a region of high electron density making susceptible to attack by electrophiles. Alkenes reacts with an electrophile to give a carbocation intermediate that then reacts with a nucleophile. In the generalized mechanism as in **Figure 11.12**, $X^+$ represents an electrophile and $Y^-$ represents a nucleophile.

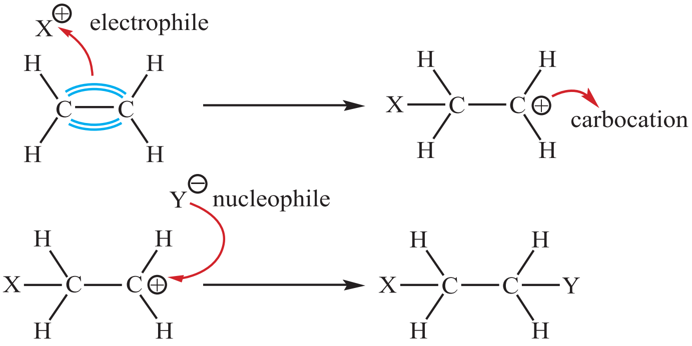


**Figure 11.12** Generalized mechanism of electrophilic addition

**Quick Check 11.6**

**a)** How do alkenes react with an electrophile?

**b)** Why the order of stability of carbocation is 3° > 2° > 1°?

### 1. Halogenation

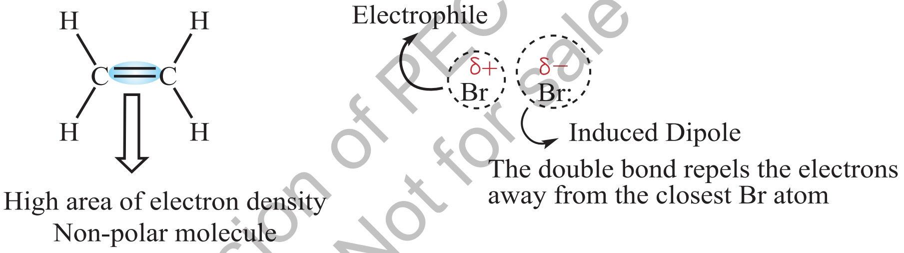
Halogenation means addition of halogens like chlorine or bromine. When bromine water (a solution of bromine in water having red-brown colour) is added to ethene in an inert solvent like carbon tetrachloride, its reddish brown colour is discharged at once. This reaction is used to identify the unsaturation of an organic compound.

$$CH_2=CH_2 + Br_2 \xrightarrow{CC\ell_4} Br\text{-}CH_2\text{-}CH_2\text{-}Br$$

**Mechanism**

The above reaction proceeds through a three–steps mechanism as given below:

i) Bromine ($Br_2$) is a non-polar molecule, however, when a bromine molecule gets closer to the double bond of an alkene, the high electron density in the double bond repels the electron pair in Br-Br away from the Br atom. As a result of this, the Br atom closest to the double bond is slightly positive and acts as an electrophile.



ii) The $\delta^+$ bromine of $Br_2$ is attacked by the π electrons in the double bond and the partial positive bromine accepts a pair of electrons from the C=C bond in the alkene. This results in the formation of a highly reactive carbocation intermediate.

iii) This carbocation intermediate reacts with the $Br^-$ (nucleophile) to make the product. Mechanism is shown below **Figure 11.13.**

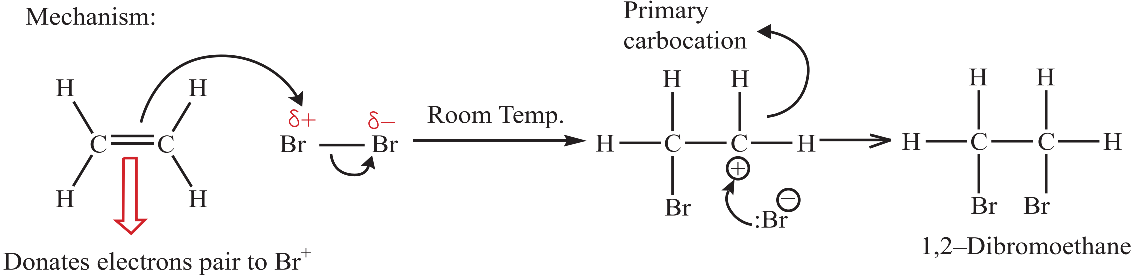


**Figure 11.13** Electrophilic addition mechanism of ethene and $Br_2$

## 2. Hydrohalogenation

When an alkene reacts with dry gaseous hydrogen halide at room temperature, the product is a halogenoalkane.

$$\underset{\text{Ethene}}{CH_2=CH_2+HBr} \longrightarrow \underset{\text{Bromoethane}}{CH_3-CH_2-Br}$$

Hydrogen halides are among the simplest examples of polar substances having permanent dipoles that add to alkenes as in **Figure 11.14.** All hydrogen halides (HBr,HCl,HI,HF) give this reaction and add across C=C exactly the same way. But, the rate of reaction increases from HF to HI. The actual product formed depends upon whether the alkene is symmetrical or unsymmetrical.

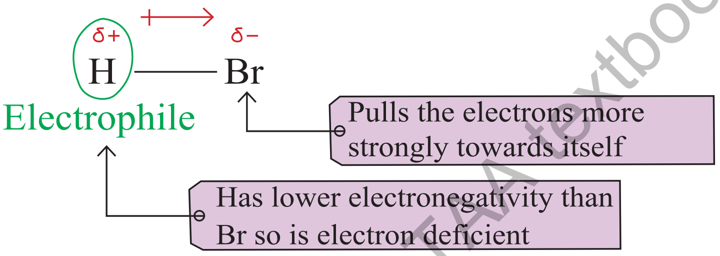


**Figure 11.14** HBr molecule polarity

### i) Addition to symmetrical alkenes

When the alkene (e.g. ethene) is symmetrical only one product is theoretically possible. Let us look at the mechanism of addition of HBr to ethene.

**Mechanism**

*i.* Nucleophilic pi-bond attacks the hydrogen in hydrogen halide. Hydrogen bromide gives a bromide ion ($Br^-$). Ethene is converted to carbocation by adding hydrogen to one of the double bonded carbons.

*ii.* The bromide ion (nucleophile) attacks the carbocation to give the addition product as in **Figure 11.15**.

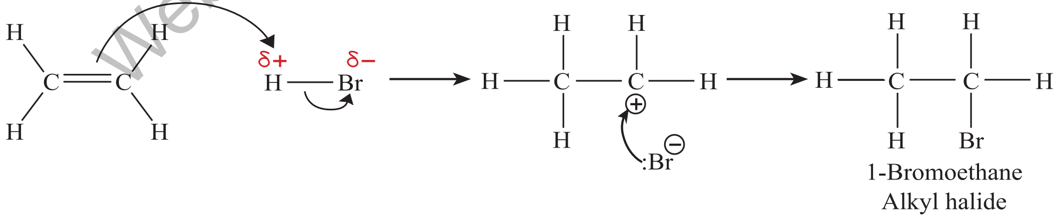


**Figure 11.15** Electrophilic addition mechanism of HBr to ethene

### ii) Addition to unsymmetrical alkenes

When the alkene is unsymmetrical, two products are theoretically possible. For example, the addition of HBr to propene can give two products. But experimentally, it has been found that under these conditions, the major product is 2-bromopropane and the minor product is 1-bromopropane.

**Markovnikov's Rule** is applicable for addition reactions in alkenes. According to this rule, "When a polar reagent adds to an unsymmetrical alkene, the negative part of the reagent attach to the double bonded carbon which bears the lesser number of hydrogen."

## Mechanism

Propene reacts with HBr in two ways. The mechanism of this reaction involves the following steps.

*i.* The pi electrons of C=C attacks on partial positive end of H-Br. Hydrogen bromide breaks heterolytically creating bromide ion (electrophile) and hydrogen is added to double bonded carbon with more number of hydrogen, creating a 2° carbocation.

*ii.* The bromide ion attacks the secondary carbocation to give the major product. The minor product is formed by the attack on primary carbocation as in **Figure 11.16**.

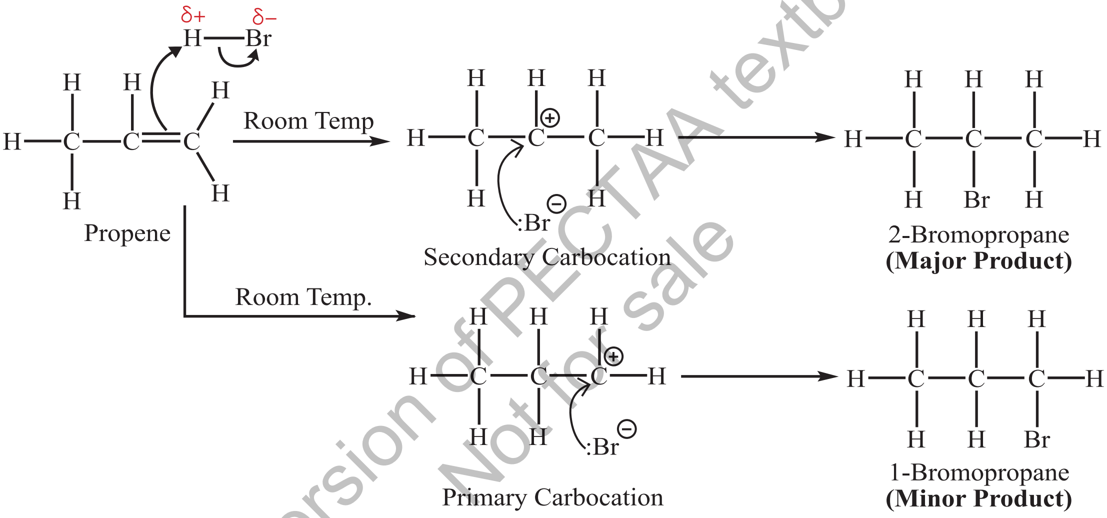


**Figure 11.16** Electrophilic addition mechanism of HBr to propene

**Quick Check 11.7**

- **a)** Compare and explain the relative rates of addition to alkenes (reactivities) of HCl, HBr and HI.
- **b)** Explain the difference between an addition reaction and an elimination reaction.
- **c)** How alkene react with an electrophile?
- **d)** Explain how Markovnikove's rule is applied in addition of HBr to 2-pentene.

### 3. Hydrogenation

Hydrogenation means addition of molecular hydrogen to an alkene in the presence of a catalyst (Ni/ Pt) to form a saturated compound at 250-300 $^0$C.

$$H_2C=CH_2 + H_2 \xrightarrow[250\text{–}300\ ^\circ C]{Ni} H_3C-CH_3$$

On industrial scale, this reaction is used to convert vegetable oil into margarine (Banaspati ghee).

$$\text{Oil} + H_2 \xrightarrow{Ni} \text{Margarine (Banaspati ghee)}$$

## 4. Hydration

Gaseous alkenes react with steam at high temperature and pressure in the presence of concentrated acid ($H_2SO_4$) as the catalyst to form alcohols.

$$H_2C=CH_2 + H_2O \xrightarrow{H_2SO_4} C_2H_5OH$$

Similar to hydrohalogenation, the alkene forms a carbocation intermediate, which is then attacked by $OH^-$.

## 5. Halohydration

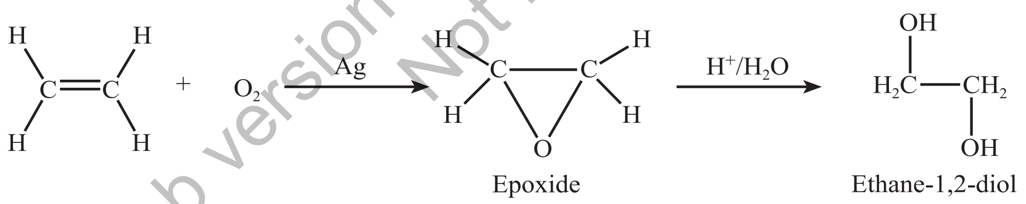
Halohydration is a reaction where an alkene reacts with a halogen (such as bromine or chlorine) in the presence of water to form a halohydrin. For **ethene ($C_2H_4$),** the reaction specifically produces a bromohydrin or chlorohydrin, depending on the halogen used.

$$H_2C=CH_2+Br_2+H_2O \longrightarrow CH_3-CH(Br)(OH) + HBr$$

1-Bromoethanol

## 6. Epoxidation

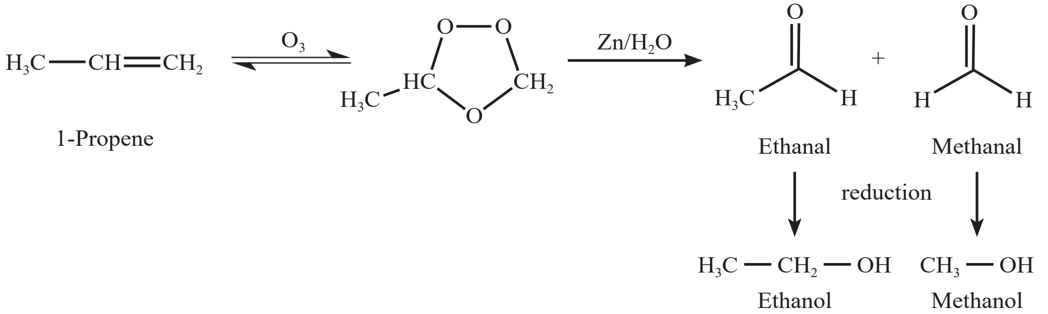
The epoxidation of alkenes gives an oxygen-containing three-membered cyclic ether called **epoxide.** In the case of ethene ($C_2H_4$), this reaction can be accomplished using various oxidizing agents. Ethene can also be converted to ethylene oxide using molecular oxygen and metal catalysts. A transition metal catalyst facilitates the reaction, forming an epoxide directly from the alkene. The epoxides can be converted in to diols by acid hydrolysis.



## 7. Ozonolysis

Ozonolysis is a method of oxidative cleavage of alkenes using ozone ($O_3$), a reactive allotrope of oxygen. This reaction is often used to identify the structure of unknown alkenes by breaking them down into smaller, more easily identifiable pieces. Alkenes react with ozone ($O_3$) to form ozonides, which can be further reduced to carbonyl compounds (aldehydes or ketones), and ultimately to alcohols.

$$C_2H_4 + O_3 \longrightarrow C_2H_4O_3 \longrightarrow 2CH_2O$$



## Quick Check 11.8

**a)** Write the equation for the ozonolysis of ethene.

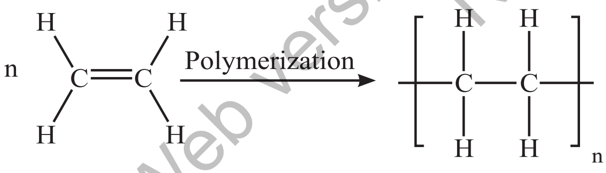
**b)** Give the epoxidation reaction of 2-Butene.

**c)** How ozonolysis can indicate the position of a double bond in an alkene? Explain it with the help of an example.

## 8. Polymerization

Polymerization is the formation of extremely long molecules (polymers) from small reactive molecules that join together (monomers). Addition polymerization is one of the most important addition reactions of alkenes which form the basis of the plastics industry. Addition polymerization is the reaction in which many monomers containing at least one C=C double bond form long chains of polymers as the only product.

Just like in other addition reactions of alkenes, the π-bond in each C=C bond breaks and then the monomers link together to form new C-C single bonds. A polymer is a long-chain molecule that is made up of many repeating units.

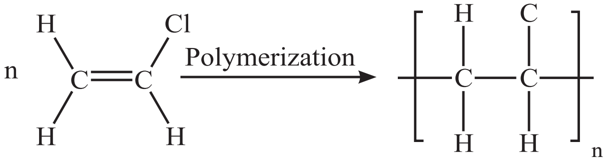


Ethene
**Monomer**

Poly (ethene)
**Polymer**

### Interesting Information!

Alkenes, like ethene and propene, are used to create plastics through polymerization. Ethene, for instance, is polymerized to make polyethylene, one of the world's most common plastics used in bags, bottles, and packaging.



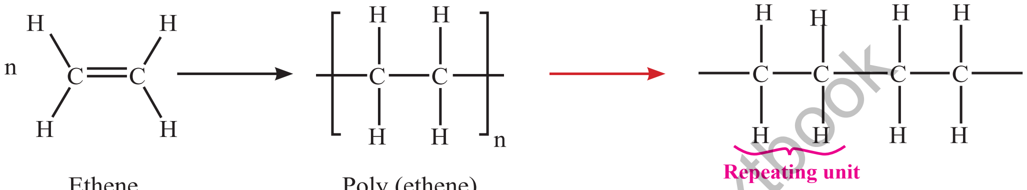
Chloroethene
**Monomer**

Poly(chloroethene) (PVC)
**Polymer**

This ball pen is made of PVC

### Deducing repeating units

- A **repeating unit** is the smallest group of atoms that when connected one after the other make up the polymer chain. It is represented by **square brackets** in the displayed and general formula.
- In **poly(alkenes)** (such as poly(ethene)) and **substituted poly(alkenes)** (such as PVC) made of **one type of monomer,** the repeating unit is the same as the monomer except that the C=C double bond is changed to a C-C single bond.



Ethene
**Monomer**

Poly (ethene)
**Polymer**

**Quick Check 11.9**

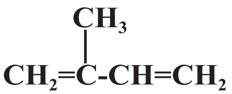
**a)** Ethene is a monomer used in the polymerization process to create polyethylene.
  (i) Discuss how the chemical structure of ethene makes it suitable for polymerization.
  (ii) Discuss the change in hybridization and bond angle during this reaction.
**b)** Explain why an addition reaction increases the saturation of a molecule.

## 11.9 CONJUGATED DIENES

As the name indicates, a diene is a molecule containing two double bonds (C=C). In a **Conjugated diene,** the double bonds in the carbon chain are separated by a single bond. The adjacent double bonds in conjugated dienes allow for the overlap of p-orbitals on three or more adjacent atoms. This overlap leads to a delocalization of electrons, which can stabilize the molecule and affect its reactivity. In conjugated dienes, π-bond overlap extends over the entire system.

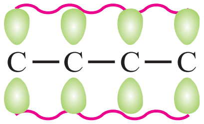
**$CH_2=CH\text{-}CH=CH_2$**

But-1,3-diene



$$CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}\text{-}CH=CH_2$$

2-Methylbut-1,3-diene (Isoprene)



Delocalization of pie electrons
of the conjugated bonds

Conjugated alkenes are an important class of compounds in organic chemistry, featuring unique properties due to the arrangement of their double bonds. Conjugated dienes like 1,3-butadiene are used in the production of synthetic rubber. The conjugated structure allows for polymerization, leading to long chains that exhibit rubber-like properties.

**Quick Check 11.10**

**a)** Draw the structure of simple conjugated dienes such as Penta-1,3-diene.

**b)** Illustrate the delocalization of electrons in conjugated dienes.

## 11.10 ISOMERISM

The concept of isomerism is an important feature of organic compounds. Two or more compounds having the same molecular formula but different structural formulae and properties are said to be isomers and the phenomenon is called **isomerism**. The structural formula of a compound shows the arrangement of atoms and bonds present in it.

The simplest hydrocarbon to have structural isomers is butane ($C_4H_{10}$). If we study the structural formula of butane or other higher hydrocarbons of the alkane family, we will observe that it is possible to arrange the atoms present in the molecule in more than one way to satisfy all valencies. This means that it is possible to have two or more different arrangements for the same molecular formula. For example, chlorobutane molecule can have two different arrangements as represented by the following structural formulas:

$CH_3CH_2CH_2CH_2Cl$ and $CH_3CHClCH_2CH_3$

1-Chlorobutane 2-Chlorobutane

This fact has been supported by an experimental evidence that there are two compounds with different physical properties but with the same molecular formula of $C_4H_9Cl$. Isomerism is not only possible but common if the compound contains more than three carbon atoms. As the number of carbon atoms in a hydrocarbon increases, the number of possible isomers increase very rapidly. The five carbon compound, pentane, has three isomers.

### 11.10.1 Types of Isomerism

### A. Structural Isomerism

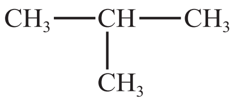
The structural isomerism is not confined to hydrocarbons only. In fact, all classes of organic compounds and their derivatives show the phenomenon of structural isomerism. The structural isomerism arises due to the difference in the arrangement of atoms within the molecule. The structural isomerism can be exhibited in five different ways.

#### i) Chain isomerism

This type of isomerism arises due to the difference in the nature of the carbon chain. For example, for pentane ($C_5H_{12}$) and butane ($C_4H_{10}$), the following arrangements are possible.

$CH_3-CH_2-CH_2-CH_3$

Butane

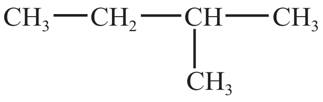


$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$$

2-Methylpropane
(Isobutane)

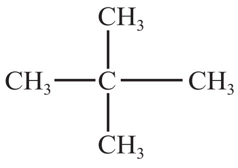
$CH_3-CH_2-CH_2-CH_2-CH_3$

Pentane



$$CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$$

2-Methylbutane
(Isopentane)



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3$$

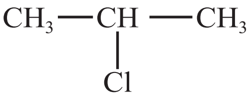
2,2-Dimethylpropane
(Neopentane)

### ii) Position Isomerism

This type of isomerism arises due to the difference in the position of the same functional group on the carbon chain. The arrangement of carbon atoms remains the same. For example: chloropropane and butene ($C_4H_8$) can have two positional isomers.

$$CH_3-CH_2-CH_2-Cl$$

1-Chloropropane



$$CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$$

2-Chloropropane

$$CH_3-CH_2-CH=CH_2$$

But-1-ene

$$CH_3-CH=CH-CH_3$$

But-2-ene

### iii) Functional Group Isomerism

The compounds having the same molecular formula but different functional groups are said to exhibit functional group isomerism. For example, there are two compounds having the same molecular formula $C_2H_6O$ , but different arrangement of atoms.

$$H_3C-O-CH_3$$

Methoxy methane

$$H_3C-CH_2-OH$$

Ethanol

### iv) Metamerism

This type of isomerism arises due to the unequal distribution of carbon atoms on either side of the functional group. Such compounds belong to the same homologous series. For example, diethyl ether and methoxy propane.

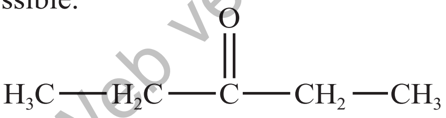
$$H_3C-H_2C-O-CH_2-CH_3$$

Ethoxy ethane

$$H_3C-O-CH_2-CH_2-CH_3$$

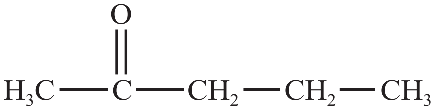
Methoxy propane

For a ketonic compound having the molecular formula $C_5H_{10}O$, the following two metamers are possible.



$$H_3C-H_2C-\overset{\displaystyle O}{\overset{||}{C}}-CH_2-CH_3$$

3-Pentanonone

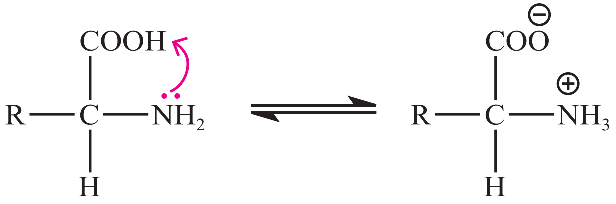


$$H_3C-\overset{\displaystyle O}{\overset{||}{C}}-CH_2-CH_2-CH_3$$

2-Pentanone

### v) Tautomerism

This type of isomerism arises due to shifting of proton from one atom to another within the same molecule. This is commonly seen in amino acids. They exist as zwitterions which are formed when a proton is shifted from the carboxylic acid end of amino acid molecule to the amine group.



$$R-\overset{\displaystyle COOH}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C}}}}-\ddot{N}H_2 \rightleftharpoons R-\overset{\displaystyle COO^{\ominus}}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C}}}}-\overset{\oplus}{N}H_3$$

Amino acid

Zwitterion

### B. Stereoisomerism

Stereoisomers are such compounds which possess the same structural formula, but differ with respect to the positions of the identical groups in space.

There are two types of stereoisomerism;

*i.* Geometrical or cis trans isomerism

*ii.* Optical isomerism

## 11.11 ORGANIC REDOX REACTIONS

Oxidation-Reduction reactions that involve organic compounds are called organic redox reactions. These reactions are characterized by the addition or removal of atoms/bonds. Normally, during organic oxidation, oxygen is added or hydrogen is removed. During organic reduction, hydrogen is added or oxygen is removed. Some examples of oxidation and reduction reactions are given below:

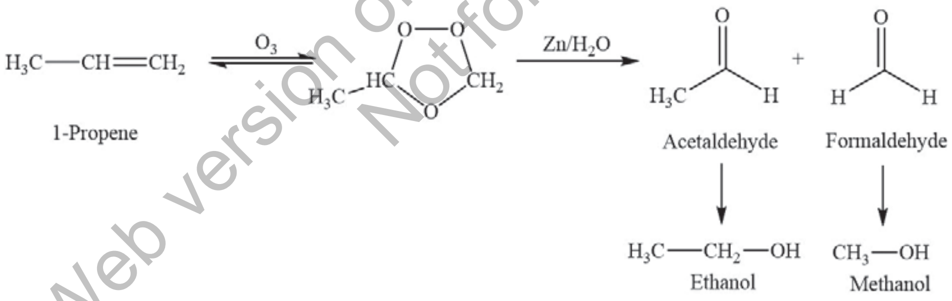
### 11.11.1 Oxidation

Oxidation of organic compounds involving reaction with oxygen is usually the combustion reaction:

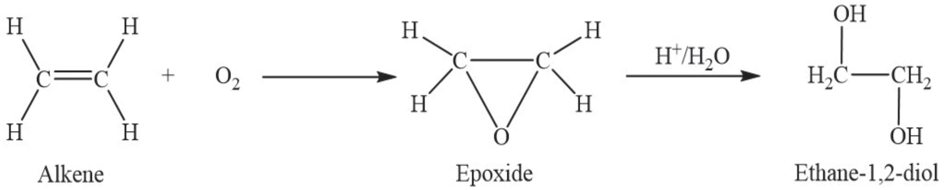
$$2C_2H_6 + 7O_2 \longrightarrow 4CO_2 + 6H_2O$$

Reactions of organic compounds with oxidizing agents.e.g.

i) Ozonolysis is a method of oxidative cleavage of alkenes using ozone ($O_3$).



ii) The epoxidation of **alkene is also example of oxidation reaction. In** this reaction various oxidizing agents can be used like molecular oxygen and metal catalysts.

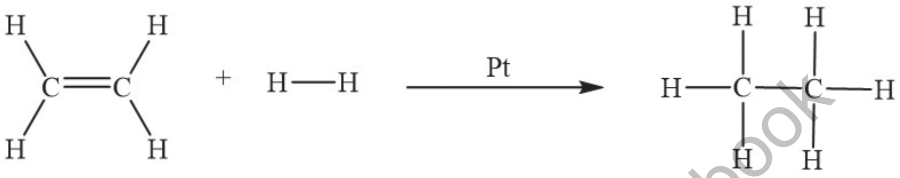


iv) Reaction of primary alcohols with acidified $K_2Cr_2O_7$ to make carboxylic acids, detail will be discussed in class 12 syllabus.

$$C_2H_5OH + 2[O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COOH + H_2O$$

### 11.11.2 Reduction

Addition of hydrogen to carbon-carbon double bond to form alkane is an example of organic reduction reaction.



Ethene Ethane

Various reducing agents are used in Organic synthesis. e.g; $LiAlH_4$, $NaBH_4$, Sn + conc.HCl. Reduction of nitriles to amines, amides to amines, carboxylic acid to primary alcohols, nitrobenzene to phenylamine are all examples of reduction.

$$H_3C\text{–}\overset{\overset{\displaystyle O}{||}}{C}\text{–}H + 2[H] \xrightarrow[\Delta]{LiAlH_4} CH_3\text{–}\overset{\overset{\displaystyle OH}{|}}{C}H_2$$

**Quick Check 11.11**

**a)** Draw the displayed formula and names of isomers of $C_4H_8$ that could be an example of positional isomerism?

**b)** What type of isomers are ethoxy methane ($CH_3OC_2H_5$) and propanol ($C_3H_7OH$)?

**c)** What are the different types of structural isomerism in alkenes?

**d)** Write down different isomers of the compound, $C_4H_9NH_2$.

## EXERCISE

## MULTIPLE CHOICE QUESTIONS

### Q.1 Four choices are given for each question. Select the correct choice.

**I. An alkene undergoes ozonolysis followed by reduction with zinc dust and water to yield propanone and methanal. The alkene is:**

a) 1-Butene b) 2-Butene

c) 2-Methylpropene d) 2-Methyl-2-butene

**II. Which of the following reagents is typically used for the acid-catalyzed hydration of alkenes to form alcohols?**

a) $H_2/Ni$
b) $O_3$ followed by $Zn/H_2O$
c) Dilute $H_2SO_4$
d) $Br_2$ in $CCl_4$

**III. Halogenation of alkanes is an example of:**

a) Electrophilic substitution
b) Nucleophilic substitution
c) Free-radical substitution
d) Oxidation

**IV. Which of the following reactions can an alkane undergo?**

a) Addition
b) Substitution
c) Polymerization
d) Nitration

**V. What is the first step in the electrophilic addition reaction of alkenes?**

a) Formation of a carbocation
b) Attack by a nucleophile
c) Attack by an electrophile on the double bond
d) Formation of a free radical

**VI. The addition of unsymmetrical reagent to an unsymmetrical alkene is in accordance with the rule/principle?**

a) Markovnikov's rule
b) Hund's rule
c) Le Chatelier's principle
d) Aufbau principle

**VII. The most stable carbonium ion among the following is:**

a) $CH_3^+$
b) $CH_3CH_2^+$
c) $(CH_3)_2CH^+$
d) $(CH_3)_3C^+$

**VIII. Markownikov's rule is applicable to :**

a) $CH_2 = CH_2$
b) $CH_3 — CH_2 — CH_3$
c) $CH_3 — CH = CH—CH_3$
d) $(CH_3)_2 — C = CH_2$

**IX. What intermediate is formed during the electrophilic addition of HBr to an alkene?**

a) Carbocation
b) Carbanion
c) Radical
d) Epoxide

**X. The enhanced stability of conjugated dienes compared to isolated dienes is primarily attributed to:**

a) Inductive effects of the double bonds.
b) Increased s-character of the hybridised orbitals.
c) Delocalisation of $\pi$ electrons across the conjugated system.

d) Steric hindrance between the double bonds.

**XI. Which of the following carbocations would be the *least* stable?**

a) $(CH_3)_2CH^+$
b) $CH_3CH_2^+$
c) $CH_3^+$
d) $(CH_3)_3C^+$

**XII. Which of the following is the repeating unit in the polymer poly(ethene)?**

a) $-CH_2CH_3-$
b) $-CH=CH-$
c) $-CH_2CH_2-$
d) $-CH(CH_3)CH_2-$

# SHORT ANSWER QUESTIONS

## Q.2 Attempt the following short-answer questions:

**a.** Define the following:

i) Cycloalkanes ii) Isomerism iii) Conjugated dienes iv) Inductive effect

**b.** Differentiate between:

i) Aliphatic and Aromatic hydrocarbons
ii) Homolytic and Heterolytic Fission
iii) Electrophile and Nucleophile

**c.** Explain why alkanes do not undergo addition reactions.

**d.** How elimination reaction is considered the opposite of an addition reaction?

**e.** Compare the carbocation stability in propene and 2-Butene.

**f.** Given the molecular formula $C_5H_{10}$, list all possible structural isomers that are alkenes.

**g.** When propene ($C_3H_6$) undergoes electrophilic addition with HBr, it forms 2-bromopropane as the major product. Explain why 2-bromopropane is favored over 1-bromopropane, using the concept of carbocation stability.

**h.** Explain why conjugated alkenes may show different reactivity compared to isolated alkenes.

**i.** Explain how inductive effects from alkyl groups stabilize carbocations in alkenes.

**j.** Write the equation for each reaction.

i. $CH_3CH_2CH=CH_2$ with $H_2$ (Ni catalyst)
ii. $CH_3CH=CH_2$ with $Cl_2$
iii. $CH_3CH_2CH=CHCH_2CH_3$ with $H_2O$ ($H_2SO_4$ catalyst)

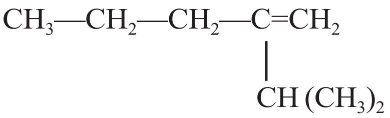
**k.** Write structural formulas for each of the following compounds:

i) Isobutylene
ii) 2,3,4,4-Tetramethyl-2-pentene
iii) 2 ,5-Heptadiene
iv) 4,5-Dimethyl-2-hexene

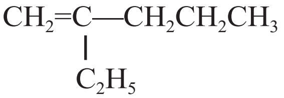
v) Vinylacetylene
vi) 1,3-Pentadiene
vii) 1-Butyne
viii) 3-n-Propyl-1, 4-pentadiene
ix) Vinyl bromide
x) But-1 -en.3 -yne
xi) 4-Methyl-2-pentyne
xii) Isopentane

**I.** Write down names of the following compounds according to IUPAC system:

i) $H_3C—CH{=}CH(CH_2)_2CH_3$
ii) $(CH_3)\ C{=}CH_2$

iii) 
$CH_3—CH_2—CH_2—\underset{\underset{\textstyle CH\,(CH_3)_2}{|}}{C}{=}CH_2$

iv) $CH_2{=}CH—CH{=}CH_2$

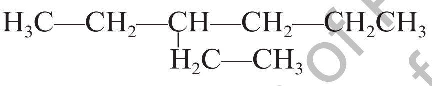
v) 
$CH_2{=}\underset{\underset{\textstyle C_2H_5}{|}}{C}—CH_2CH_2CH_3$

vi) $(CH_3CH_2)_3CH$

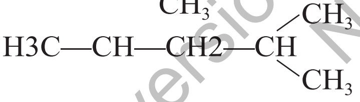
vii) $CH_3CH_2C(CH_3)_2CH(CH_2CH_3)CH_3$
Viii) $CH_2{=}CH—C{=}C—CH{=}CH_2$

ix) $(CH_3)\ C—CH_2—C(CH_3)_3$
x) $CH_2{=}CH—C{=}CH$

xi) $CH_3C(CH_3)_2(CH_2)CH_3$

a) 
$H_3C—CH_2—\underset{\underset{\textstyle H_2C—CH_3}{|}}{CH}—CH_2—CH_2CH_3$

b) 
$(CH_3)_2CH—\underset{\underset{\textstyle CH_3}{|}}{CH}—CH\ (CH_3)_2$

c) 

## DESCRIPTIVE QUESTIONS

**Q.3** Describe the free radical halogenation of methane using $Cl_2$ as an example.

**Q.4** Describe the following methods for the preparation of alkenes:

i) Dehydrohalogenation of alkyl halides

ii) Dehydration of alcohols

**Q.5** Describe the mechanism of electrophilic addition of hydrogen halides to alkenes. Discuss Markovnikov's rule in the context of hydrogen halide addition.

**Q.6** Explain the following reactions of alkenes with examples:

a) Halogenation
b) Ozonolysis
c) Epoxidation
d) Polymerization