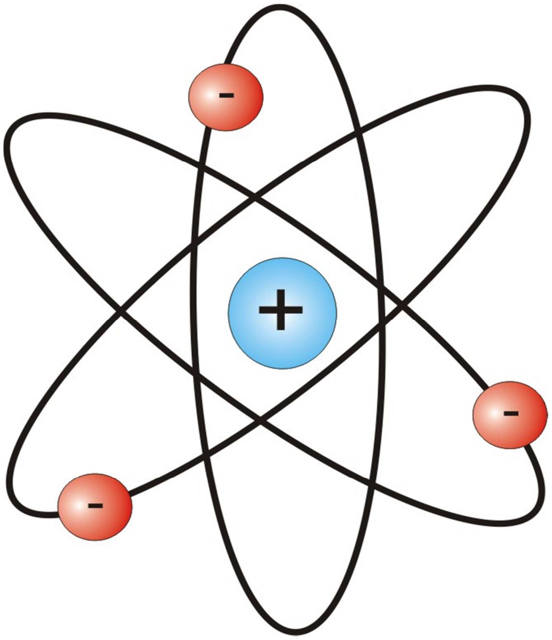
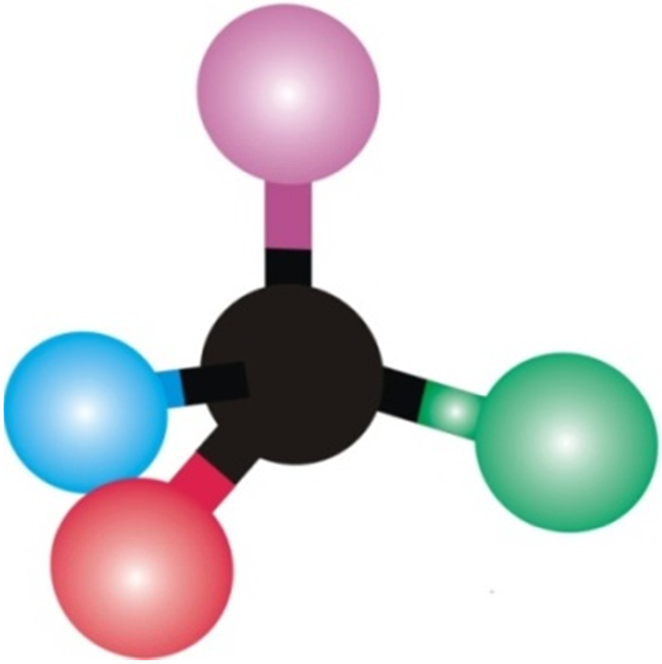
ignou
THE PEOPLE'S
UNIVERSITY

Indira Gandhi National
Open University
School of Sciences

BCHCT-131

ATOMIC STRUCTURE, BONDING, GENERAL ORGANIC CHEMISTRY AND ALIPHATIC HYDROCARBONS





HYDROCARBONS

4

Indira Gandhi National
Open University
School of Sciences

BCHCT-131

ATOMIC STRUCTURE, BONDING, GENERAL ORGANIC CHEMISTRY AND ALIPHATIC HYDROCARBONS

Block

4

HYDROCARBONS

Course Design Committee

Prof. H. B. Singh (Retd.)
Dept. of Chemistry,
University of Delhi, Delhi

Prof. A.K. Bakhshi
Dept. of Chemistry,
University of Delhi,
Delhi

Prof. Amir Azam
Dept. of Chemistry,
Jamia Millia Islamia,
New Delhi

Prof. Tabrez Alam
Dept. of Chemistry,
Jamia Millia Islamia,
New Delhi

Prof. J.M. Khurana
Dept. of Chemistry,
University of Delhi, Delhi

School of Sciences,
IGNOU

Prof. Vijayshri
Prof. Sunita Malhotra
Prof. Javed A. Farooqi
Dr. Lalita S. Kumar

Block Preparation Team

Prof. Javed A. Farooqi
School of Sciences, IGNOU

Prof. B. S. Saraswat (Retd.) (Editor)
School of Sciences, IGNOU

Course Coordinators: Prof. Sunita Malhotra and Prof. Javed A. Farooqi

Production

Mr. Sunil Kumar
Assistant Registrar (Pub.)

Acknowledgements: Prof. Bharat Inder Fozdar, Prof. Sunita Malhotra and Prof. Lalita S. Kumar for comments on Units. Mr. Sarabjeet Singh for word processing, art work and CRC preparation; Mr. Deepak Kumar for word processing.

The utilisation of some content of Units 6, 7, 8 and 9 of Organic Chemistry (CHE 05) course is gratefully acknowledged.

July, 2019

ISBN: 978-93-88980-97-5

Further information on Indira Gandhi National Open University courses may be obtained from the University's office at Maidan Garhi, New Delhi-110 068 or IGNOU website www.ignou.ac.in.

Printed and published on behalf of Indira Gandhi National Open University, New Delhi by Prof. M.S. Nathawat, Director, School of Sciences.

Printed at: Raj Printers, A-9. Sector B-2, Tronica City, Loni (Gzb.)

BLOCK 4 : HYDROCARBONS

In the third block of this course, you have studied the stereochemistry and structure-reactivity relationships of organic compounds. There are about 1 million organic compounds known. Among all the compounds hydrocarbons play key role in organic chemistry. In this block, you will learn about the hydrocarbons. These compounds provide the skeleton for all organic compounds.

The term hydrocarbon is used to designate organic compounds of carbon and hydrogen. On the basis of structure, the hydrocarbons can be divided into two main categories: aliphatic and aromatic. The aliphatic hydrocarbons can be further divided into four families: alkanes, alkenes, alkynes and their cyclic analogues. Alkanes are saturated aliphatic hydrocarbons. Alkenes and alkynes are unsaturated aliphatic hydrocarbons.

This block contains five units. In Unit 15, which is the first unit of this block, we shall discuss chemistry of alkanes. Alkanes are saturated open or branched chain hydrocarbons. They can be prepared from alkenes, alkynes, alkyl halides or carboxylic acids. These compounds are generally unreactive. Alkanes undergo mainly substitution reactions, and that too at a high temperature and pressure or UV light. In addition to this, you will study about petroleum.

In Unit 16, you will study the characteristic features of alkenes. Open or branched chain hydrocarbons containing one or more carbon-carbon double bond(s) are known as alkenes. Alkenes can be prepared from alkyl halides, alcohols and ketones. The characteristic reactions of alkenes involve addition to C=C bond which you will study in Unit 17.

In Unit 18, you will learn another kind of hydrocarbons, known as alkynes, which contain carbon-carbon triple bond. Alkynes can be prepared by the alkylation of terminal alkynes or by two-fold elimination of HX from dihalides or dehalogenation of tetrahalides. Alkynes react with electrophilic reagents in a manner similar to that of alkenes. In addition to electrophilic reactions, alkynes undergo reduction and oxidation reactions.

Unit 19 deals with aromaticity. In this unit, you will study nomenclature of aromatic hydrocarbons, physical properties and structure of benzene along with resonance and aromaticity concepts.

Expected Learning Outcomes

After studying this block, you should be able to:

- classify the types of hydrocarbons;
- list the physical properties of hydrocarbons;
- discuss different methods for the preparation of hydrocarbons; and
- discuss the important chemical reactions of hydrocarbons.

UNIT 15

ALKANES

Structure

15.1 INTRODUCTION

Alkanes are saturated aliphatic hydrocarbons. You have already learnt in your earlier classes that the saturated aliphatic hydrocarbons have the general formula, C_nH_{2n+2}, Because of their zig-zag patterns due to the tetrahedral geometry of sp^3 hybridised carbon, carbon atoms which are close together often join up with expulsion of two hydrogen atoms to form a ring. Such ring compounds are referred to as cyclic aliphatic hydrocarbons and also called alicyclic hydrocarbons or cycloalkanes, which have the general formula, C_nH_{2n}.

Alkanes are also known as *paraffins*. The name paraffin comes from two Latin words, "*Paraum* and *affinis*", which mean "little affinity". This name was suggested because these hydrocarbons were apparently unreactive. It is observed that under ordinary conditions, alkanes are inert towards reagents such as: acids, alkalies, oxidizing and reducing agents. However, under suitable conditions, alkanes undergo different types of reactions like halogenation, pyrolysis, aromatization, etc. Many of these reactions proceed through the formation of highly reactive free radicals.

In this unit, first we shall discuss the composition of petroleum, as it is the main source of alkanes. Then, we shall discuss the physical properties of alkanes. Finally, we shall study method of preparation and some chemical reactions of alkanes and cycloalkanes.

Expected Learning Outcomes

After studying this unit, you should be able to:

- describe the composition of petroleum;
- explain octane number and cetane number;
- discuss the physical properties of alkanes;
- list the methods of preparation of alkanes and cycloalkanes; and
- discuss the important chemical reactions of alkanes and cycloalkanes.

15.2 PETROLEUM: A SOURCE OF ALKANES

Petroleum is an oily, viscous, inflammable and usually dark coloured liquid. Petroleum is a mixture of alkanes and occurs abundantly in various natural deposits in the earth. Few alkanes are also found in plants and animals.

The biggest oil-producing country of the world is the USA. The other major oil producing countries are Russia, Venezuela, Iran, Gulf countries, Romania, Myanmar, Pakistan, India and Canada.

Petroleum industry in India has made headway only after independence. In the last 40 years, petroleum production and refining levels have increased by more than 100 times whereas the consumption has increased by around 15 times. It is worth mentioning that even with this increased productivity, only less than one-fourth of our needs are satisfied.

Petroleum can be separated into various fractions known as gasoline, naphtha, kerosene, etc. In the following section, we will study the composition of petroleum in detail.

15.2.1 Composition of Petroleum

The composition of petroleum varies with the location of its occurrence, but all samples contain mixtures of alkanes ranging in size from methane, with only one carbon atom, to long chain hydrocarbons containing upto 40 carbon atoms. Cyclohexane, naphthalene and other aromatic hydrocarbons are also present in small amounts. In addition to hydrocarbons, oxygen, nitrogen and sulphur containing compounds may also be present in petroleum. In fact, as many as 500 compounds have sometimes been detected in a single sample of petroleum.

Natural gas whose major components are methane (80%) and ethane (10%) is found along with petroleum. Small amount of mixture of higher hydrocarbons are also present. Besides hydrocarbons, natural gas also contains carbon dioxide and nitrogen.

15.2.2 Fractionation of Petroleum

The first step in the refining of petroleum involves its separation into fractions of different boiling ranges by fractional distillation. Crude petroleum is heated in a furnace at, 650 K and the hot liquid is then passed through a flash chamber where the low boiling fractions are volatilised by lowering the pressure. The vapours are then passed through a tall bubble tower. This tower is filled with horizontal stainless steel trays. Bach tray is provided with chimneys covered with a loose cap called **bell cap**. As the vepours ascend, they become gradually cooler and, therefore, various fractions condense at different heights. The higher boiling fractions condense in the lower portion of the tower. This permits the separation of 'crude petroleum vapours into a number of fractions, each condensing within a definite temperature range. Each fraction is a mixture of different hydrocarbons. Therefore, it has to be purified prior to use.

The important petroleum fractions along with their boiling ranges and chief uses are given in Table 15.1.

Table 15.1: Fractionation of Petroleum

Name	B.P. (K)	Approximate composition	Uses
Natural gas		C_1–C_4	Refinery and domestic fuel
Light petrol	293-373	C_5–C_7	Solvent
Benzene	343-363	C_6–C_7	Dry cleaning
Ligroin	353-393	C_6–C_8	Solvent
Petrol (gasoline)	343-473	C_6–C_{11}	Motor fuel
Kerosene (paraffin oil)	473-573	C_{12}–C_{16}	Lighting
Gas oil (heavy oil)	above 573	C_{13}–C_{18}	Fuel oil
Lubricating oil (mineral oil)	above 573	C_{16}–C_{20}	Lubricants
Greases, Vaseline, Petroleum	above 573	C_{18}–C_{22}	Pharmaceutical preparations
Paraffin wax (hard wax)	above 573	C_{20}–C_{30}	Candles, waxed paper, etc.
Residue (asphaltic bitumen)	above 573	C_{30}–C_{40}	Asphalt tar, petroleum coke

With the development of civilization and the growth of industry, the demand of gasoline and petroleum products is increasing day by day. The natural resources are limited and it is feared that they will soon be exhausted. Keeping this in mind, the chemists have tried different methods of manufacturing synthetic fuels.

15.2.3 Octane Number

The most commonly used fuel for automobiles is gasoline, not all fuel are equally good. Let us see how we can differentiate between good quality and bad quality fuels. This can be done by comparing their octane numbers. Octane number is a measure of the quality of gasoline: the higher the octane number, the better the fuel.

The 2,2,4-trimethylpentane (*iso*-octane), which is considered a good fuel, is given an octane number of 100 whereas *n*-heptane, a very poor fuel, is given an octane number of zero. Mixture of these two compounds is used to define octane numbers between 0 and 100. Octane number is the percentage of 2, 2, 4-trimethylpetane present in a mixture of 2,2,4-trimethylpentane and *n*-heptane which has similar ignition properties as the fuel under examination. For example, a fuel that performs as well as a 1:1 mixture of 2,2,4-trimethylpentane and *n*-heptane has an octane number 50. Commercial gasoline has octane number 81, 74 and 65 for the premium, regular and third grade gasoline. Good quality motor fuels used in modern automobiles have octane number in the 87-95 range.

It has been observed that:

- branching of the hydrocarbon chain increases octane number.
- octane number decreases as the chain length increases.
- unsaturated hydrocarbons have higher octane number than saturated hydrocarbons.
- cycloalkanes have higher octane number than the corresponding acyclic alkanes.

15.2.4 Cetane Number

The working of diesel engine differs from that of gasoline engine. In diesel engines, fuels have a lower octane number are much more useful than those having a higher octane number. In other words, the straight chain hydrocarbons constitute a superior fuel than the branched chain hydrocarbons. Quality of diesel fuel is expressed in terms of a number called **cetane number.**

The hexadecane (cetane, $C_{16}H_{34}$), considered a good fuel, is given a cetane number 100 whereas α-methylnaphthalene, a very poor fuel, is given a cetane number zero. Cetane number is defined as the percentage of hexadecane in a mixture of hexadecane and *α*-methylnaphthalene which has similar ignition properties as the fuel under examination. Good quality diesel fuels required for modern diesel engine having cetane number greater than 45.

15.2.5 Liquefied Petroleum Gas (LPG) and Compressed Natural Gas (CNG)

In 1912 an American scientist, Dr. Walter Snelling discovered LPG and realised that these gases can be changed into liquid and stored in a cylinder. The main components of liquefied petroleum gas (LPG) are propane and butane. In addition to these very small amount of other hydrocarbons may also be present. At normal temperature and pressure LPG is a gas. It can be liquefied at a low temperature and high pressure. LPG is stored in liquid form in a cylinder. When we start using the gas, pressure of the cylinder is released.The liquid gas gets converted into vapours. Propane and butane are colourless and odorless gases at room temperature to which foul-smelling mereaptan is added so that leak can easily be detected.

Liquefied petroleum gas (LPG) contains a mixture of propane and butane.

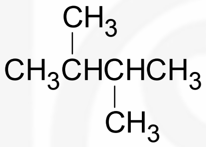
Compressed Natural Gas (CNG) is best alternative to petrol for automotive industries. The main component of CNG is methane. In addition to CNG, Liquefied Natural Gas (LNG) is also a good alternative fuel for motor vehicles.

SAQ 1

State which compound has better octane rating in each of the following pairs?

a) $CH_3(CH_2)_4CH_3$; $CH_3CH_2CH_2CH_3$

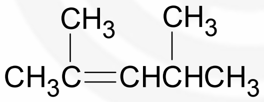
b)



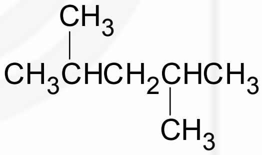
$CH_3\overset{CH_3}{\overset{|}{C}}H\underset{\underset{CH_3}{|}}{C}HCH_3$; $CH_3(CH_2)_4CH_3$

c) $H_2C{=}CHCH_2CH_3$; $CH_3CH_2CH_2CH_3$

d)



$CH_3\overset{CH_3}{\overset{|}{C}}{=}CH\overset{CH_3}{\overset{|}{C}}HCH_3$;

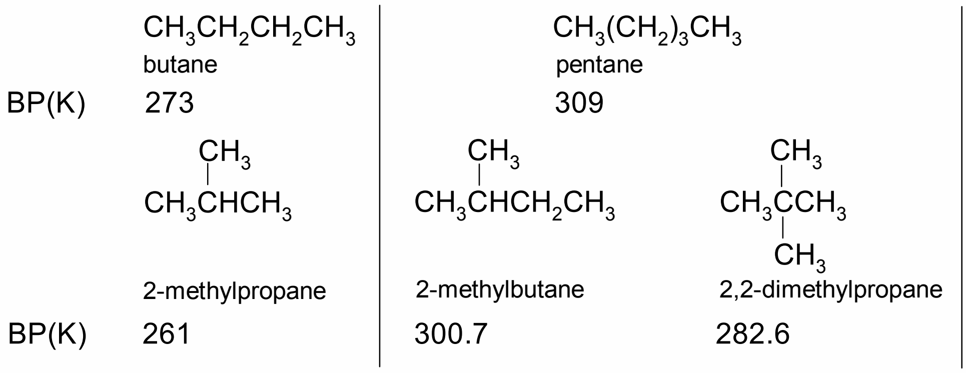


$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2\underset{\underset{CH_3}{|}}{C}HCH_3$

15.3 PHYSICAL PROPERTIES

Here, we will discussed about physical properties like boiling point, density etc. Covalent bonds of an alkane molecule are either carbon-carbon bonds or bonds between carbon and hydrogen atoms that differ very little in electronegativity. Therefore, the alkanes are either non-polar or very weakly polar. Their physical constants like boiling points, densities, etc., increase with increase in the number of carbon atoms. Except for the first few members, the boiling point increases by 20 to 30 degrees for each CH_2 unit that is added to the chain. The boiling point of a covalent substance depends upon the intermolecular forces. Intermolecular forces, in turn, depend upon the number of electrons, surface area of the molecule and its dipole moment. The intermolecular forces increase with the increase in the number of electrons or in the value of the dipole moment and surface area.

The stronger the intermolecular forces, the higher the boiling point. In a particular series, with the increase in the number of carbon atoms, the surface area increases and hence, the intermolecular forces and boiling points also increase. Branching in a chain reduces the surface area and, therefore, decreases the boiling point.



$CH_3CH_2CH_2CH_3$ butane, BP(K) 273

$CH_3(CH_2)_3CH_3$ pentane, BP(K) 309

$CH_3\overset{CH_3}{\overset{|}{C}}HCH_3$ 2-methylpropane, BP(K) 261

$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_3$ 2-methylbutane, BP(K) 300.7

$CH_3\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_3$ 2,2-dimethylpropane, BP(K) 282.6

Unlike boiling points, the melting points of alkanes do not show a regular increase. It has been found that molecules with an odd number of carbon atoms have lower melting point than those with an even number of carbon atoms. A possible explanation of this is given here. The carbon atoms in alkanes are sp^3 hybridised state with a bond angle of 109°28’. The terminal carbon atoms in a carbon chain with an odd number of carbon atoms lie on the same side, whereas those in carbon chain with an even number of carbon atoms lie on the opposite. This means that the packing efficiency and the interaction between the molecules in the solid state is less in alkanes containing odd number of carbon atoms as compared to those with an even number of carbon atoms. The maximum density of alkanes is about 0.8, thus, all alkanes are lighter than water. Alkanes are soluble in non-polar solvents but insoluble in polar solvents. Some important physical properties of alkanes are given in Table 15.2.

Table 15.2: Physical properties of some alkanes

Number of carbons	Alkane	Melting point (K)	Boiling point (K)	Density (g/mL)
1	Methane	91	109	0.5547
2	Ethane	89.7	184.4	0.509
3	Propane	83.3	230.9	0.5005
4	Butane	134.7	272.5	0.5788
5	Pentane	143.3	336.1	0.6262
6	Hexane	178	341.9	0.6603
7	Heptane	182.4	371.4	0.6837
8	Octane	216.2	398.7	0.7025
9	Nonane	222	423.8	0.7176
10	Decane	243.3	447.1	0.7300
4	Isobutene	113.6	261.3	0.579
5	Isopentane	113.4	300.8	0.6201
5	Neopentane	256.5	282.5	0.6135
8	Isooctane	165.6	372.3	0.6919

SAQ 2

Fill in the blanks:

a) Alkane molecules are very less polar or non-polar because there is very little………… difference between the carbon and hydrogen atoms.

b) Boiling point of alkanes…………… with the increase in the length of the carbon chain.

c) Branching in the carbon chain……………….. the boiling point.

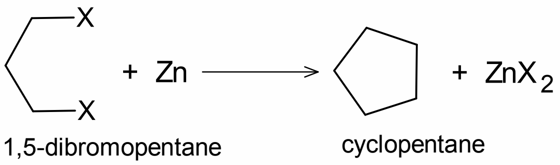
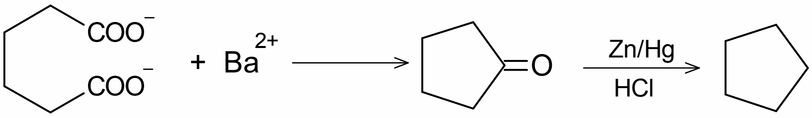
d) Alkanes are soluble in ……………. solvents.

15.4 PREPARATION OF ALKANES AND CYCLOALKANES

Alkanes are generally obtained from natural sources: petroleum and natural gas. However, synthetic methods are more practical when a pure alkane is required. Alkanes can be prepared from: (a) alkenes or alkynes, (b) alkyl halides, and (c) carboxylic acids. You have already studied about the preparation of alkanes and cycloalkanes in your earlier classes. Here, we recall only the important methods. The general methods for the preparation of alkanes and cycloalkanes are summarised in Table 15.1.

Table 15.1: General methods for the preparation of alkanes and cycloalkanes

ALKANES	
i)	**Wurtz reaction** $2RX + 2Na \longrightarrow RR + 2NaX$
ii)	**Kolbe's electrolytic method** $R'COOK + RCOOK \longrightarrow \underbrace{R'R + 2\,CO_2}_{\text{at anode}} + \underbrace{H_2 + 2\,KOH}_{\text{at cathode}}$
iii)	**Hydrogenation of unsaturated hydrocarbons** $RCH{=}CHR + H_2 \xrightarrow{\text{catalyst}} RCH_2CH_2R$
iv)	**Reduction of alkyl halides** $RX \xrightarrow[\text{agent}]{\text{reducing}} RH$ $RX + Mg \xrightarrow{\text{ether}} RMgX \xrightarrow[H_2O]{H^+} RH + Mg(OH)X$
v)	**Decarboxylation of carboxylic acids** $RCOONa + NaOH \longrightarrow RH + Na_2CO_3$

CYCLOALKANES	
i)	
ii)	

Now let us study these methods in brief.

15.4.1 Wurtz Reaction

In Wurtz reaction, an alkyl halide is treated with sodium in dry ether. The result is the joining of the two alkyl groups from two molecules of alkyl halide to form an alkane.

$$2RX + 2Na \longrightarrow RR + 2NaX$$

This reaction is useful only when two identical alkyl halide molecules are used. When a mixture of two different alkyl halides is used, a mixture of three different alkanes is obtained. For example, if you take a mixture of bromomethane and bromoethane, you will get three different products, viz.,

$$\underset{\text{bromo-methane}}{CH_3Br} + \underset{\text{bromo-ethane}}{C_2H_5Br} + 2Na \longrightarrow \underset{n\text{-propane}}{CH_3{-}C_2H_5} + 2NaBr$$

$$\underset{\text{bromo-methane}}{CH_3Br} + \underset{\text{bromo-methane}}{CH_3Br} + 2Na \longrightarrow \underset{\text{ethane}}{CH_3{-}CH_3} + 2NaBr$$

$$\underset{\text{bromo-ethane}}{C_2H_5Br} + \underset{\text{bromo-ethane}}{C_2H_5Br} + 2Na \longrightarrow \underset{n\text{-butane}}{C_2H_5{-}C_2H_5} + 2NaBr$$

The separation of such a mixture into individual alkanes is quite difficult. Thus, the Wurtz reaction between two different alkyl halides is normally useless in practice. When a single alkyl halide is used, the synthesised hydrocarbon contains an even number of carbon atoms. In other words, we can say that Wurtz reaction is suitable for the preparation of only those alkanes which contain an even number of carbon atoms. As shown above, the main difficulty with the Wurtz reaction is the formation of many side products when an alkane with odd number of carbon atoms is desired.

15.4.2 Kolbe's Electrolytic Method

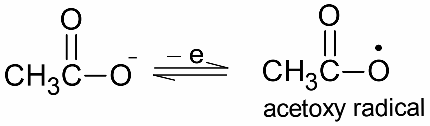
When a concentrated solution of sodium or potassium salt of a carboxylic acid is electrolyzed, an alkane is formed. This method is known as Kolb's electrolytic method.

$$RCOOK + RCOOK + H_2O \longrightarrow \underset{\text{at anode}}{RR + 2CO_2} + \underset{\text{at cathode}}{H_2 + 2KOH}$$

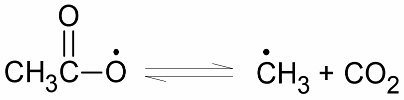
The following mechanistic pathway illustrates this method:

At anode

$$CH_3COOK \rightleftharpoons CH_3COO^- + K^+$$



$$CH_3\overset{O}{\overset{||}{C}}-O^- \xrightleftharpoons{-e} \underset{\text{acetoxy radical}}{CH_3\overset{O}{\overset{||}{C}}-\dot{O}}$$



$$CH_3\overset{O}{\overset{||}{C}}-\dot{O} \rightleftharpoons \dot{C}H_3 + CO_2$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow H_3C-CH_3$$

At cathode

$$2H_2O + 2\bar{e} \rightleftharpoons H_2 + 2\bar{O}H$$

$$2K^+ + 2\bar{O}H \longrightarrow 2KOH$$

In case, a mixture of salts of two carboxylic acids is electrolysed, a mixture of alkanes is formed:

$$R'COOK + R''COOK \longrightarrow \begin{array}{l} R'R' \\ \quad + \\ R'R'' + CO_2 + H_2 + KOH \\ \quad + \\ R''R'' \end{array}$$

Like Wurtz reaction, this reaction also has limited synthetic applications because of the formation of many side products as a result of other reactions of the free radicals formed.

15.4.3 Hydrogenation of Unsaturated Hydrocarbons

Alkanes or cycloalkanes can be prepared by hydrogenation of unsaturated hydrocarbons using platinum or palladium as catalyst. You may remember that the manufacture of vegetable fat involves hydrogenation of double bonds in present in vegetable oil. The general reaction for the reduction of unsaturated hydrocarbons is:

$$\underset{\text{alkene}}{RCH{=}CHR} + H_2 \xrightarrow{\text{Pt or Pd}} \underset{\text{alkane}}{RCH_2CH_2R'}$$

$$\underset{\text{alkyne}}{RC{\equiv}CR} + 2H_2 \xrightarrow{\text{Pt or Pd}} \underset{\text{alkane}}{RCH_2CH_2R}$$

Like alkenes, alkynes also undergo catalytic addition of hydrogen which takes place in two steps. The first addition result is the formation of alkenes. Since, an alkene can also undergo catalytic hydrogenation, the second addition gives the alkane.

Sabatier-Senderens’ Reaction

Hydrogenation of an alkene can also be carried out by using nickel catalyst, but relatively higher temperature and pressure are required for this reaction. This reaction is called **Sabatier-Senderens’** reaction. An example is given the below:

$$\underset{\text{I-propene}}{CH_3CH{=}CH_2} + H_2 \xrightarrow{Ni} \underset{\text{propane}}{CH_3CH_2CH_3}$$

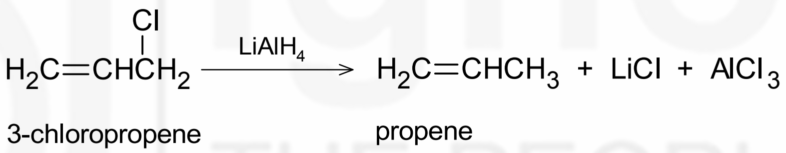
This is a very useful synthetic method and the yield is nearly 100%.

15.4.4 Reduction of Alkyl Halides

Alkanes can also be prepared by the reduction of alkyl halides by various methods. Reducing agents like zinc and acetic acid and zinc-copper couple give good yields of alkanes.

$$RX \xrightarrow[\text{agent}]{\text{Reducing}} RH$$

Lithium aluminium hydride, $LiAlH_4$, is an excellent reducing agent. Though it reduces many unsaturated functional groups, such as CO, C≡N, etc., it does not attack isolated double bond or triple bond. Dry ether is the commonly used solvent. For example,



$$\underset{\text{3-chloropropene}}{H_2C{=}CH\overset{\overset{\displaystyle Cl}{|}}{C}H_2} \xrightarrow{LiAlH_4} \underset{\text{propene}}{H_2C{=}CHCH_3} + LiCl + AlCl_3$$

Alkyl halides are widely used, to prepare Grignard reagents (organomagnesium halides), RMgX. These reagents are among the most useful classes of compounds in organic synthesis. The Grignard reagent is generally prepared by reaction between magnesium and alkyl or aryl halides. Grignard reagents on treatment with water or dilute acid decompose to give alkanes.

$$RX + Mg \xrightarrow{\text{ether}} RMgX \xrightarrow[H_2O]{H^+} RH + Mg(OH)X$$

where R=alkyl or aryl group and

X = Cl, Br or I

The Grignard reagents are highly reactive compounds because the carbon-magnesium bond is strongly polarised making carbon atom both nucleophilic and strongly basic. Grignard reagents are used to prepare a large variety of organic compounds and preparation of alkanes is one of them.

Alkanes are prepared by reaction of Grignard reagents with water, alcohols, ammonia, amines etc.

$$RMgX + \underset{\text{water}}{H_2O} \longrightarrow \underset{\text{alkane}}{RH} + Mg(OH)X$$

$$RMgX + \underset{\text{alcohol}}{R'OH} \longrightarrow \underset{\text{alkane}}{RH} + Mg(OR')X$$

$$RMgX + \underset{\text{ammonia}}{NH_3} \longrightarrow \underset{\text{alkane}}{RH} + Mg(NH_2)X$$

$$RMgX + \underset{\text{amine}}{R'NH_2} \longrightarrow \underset{\text{alkane}}{RH} + Mg(NHR')X$$

SAQ3

Fill in the following blanks:

a) Lithium aluminium hydride does not attack on the ………….. double bonds.

b) The Grignard reagent gives alkane on treatment with ……………..

c) Sabatier-Senderens' reaction gives almost …………… % alkane.

15.4.5 Decarboxylation of the Carboxylic Acids

Alkanes may be prepared through decarboxylation of carboxylic acids by heating a mixture of the sodium salt of a carboxylic acid with soda lime:

$$RCOONa + NaOH \longrightarrow RH + Na_2CO_3$$

This process of eliminating CO_2 from a carboxylic acid is known as decarboxylation. The alkanes so produced contain one carbon atom less than the original acid. The new hydrogen atom in the product is derived from soda lime.

Soda lime is a mixture of NaOH and CaO. The active ingredient is NaOH,CaO helps in keeping the reaction mixture porous.

Although methane is obtained from ethanoic acid in good yield, other acids give only 10-20% of the corresponding hydrocarbon.

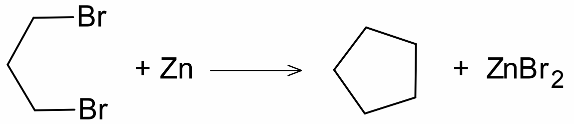
Sometimes decarboxylation of the acid itself is more effective than that of its salt. The direct decarboxylation of carboxylic acid can be carried out by heating it with an organic base, such as pyridine using copper chromate ($CuO.Cr_2O_3$) as catalyst.

$$\underset{\text{propanoic acid}}{CH_3CH_2COOH} + \underset{\text{pyridine}}{C_5H_5N} \xrightarrow{CuO.Cr_2O_3} \underset{\text{ethane}}{CH_3{-}CH_3} + CO_2$$

Next, we discuss two methods of preparation of cycloalkanes.

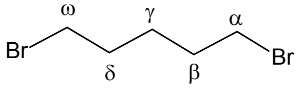
15.4.6 Preparation of Cycloalkanes

i) When 1, 5-dihalogen derivatives of alkanes are treated with sodium or zinc, the corresponding cycloalkane is formed, e.g., 1, 5-dibromopentane would form the cyclopentane:

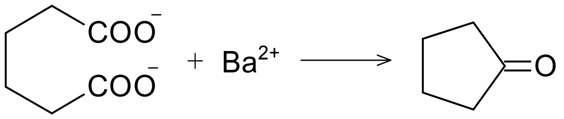


1,5-dibromopentane cyclopentane

In common names, Greek letters have long been used to designate position on a carbon skeleton, relative to a functional group e.g., 1,5-dibromopentane is also called α, ω-dibromopentane.

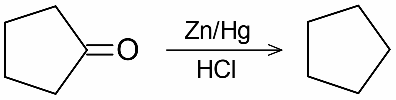


ii) When the calcium or barium salt of a dicarboxylic acid is distilled, a cyclic ketone is formed, e.g. barium adipate gives cyclopentanone



salt of dicarboxalic acid cyclopentanone

A cyclic ketone can be reduced into the corresponding cycloalkane using zinc amalgam and concentrated hydrochloric acid (Clemmensen reduction).



cyclopentanone cyclopentane

SAQ 4

Write the equation showing synthesis of the following alkanes from the starting materials indicated.

a) Cyclohexane from cyclohexene

b) Undecane from the sodium salt of dodecanoic acid, $CH_3(CH_2)_{10}COOH$

c) Cyclopropane from 1,3-dibromopropane

d) Butane from 1-chlorobutane

15.5 REACTIONS OF ALKANES

Alkanes are relatively unreactive or do not react with most of the common reagents. It is difficult to define the terms “reactive” and “unreactive”, since a compound may be reactive under one set of conditions and unreactive under another. This reactivity or unreactivity may be explained by considering the nature of C−C and C−H bonds present in their molecules. Since the electronegativities of carbon and hydrogen do not differ appreciably, the bonded electrons in C−H are more or less equally shared between them. Thus, C−H bonds present in alkanes are almost non-polar and the same is true of C−C bonds. Thus, polar and ionic reagents find no sites to attack an alkane molecule. Alkanes undergo mainly substitution reactions, which can be explained using free radical mechanism. These reactions take place in the presence of UV light or at a high temperature or in the presence of certain free radical initiators such as peroxides. In substitution reactions, one or more of the hydrogen atom(s) of alkanes are substituted by halogen or some other groups. Some important reactions of alkanes are given in Table 15.3.

Table 15.3: Reactions of alkanes

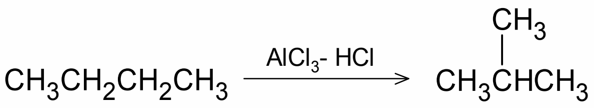
i) Halogenation

$$RH + X_2 \xrightarrow[\text{or } \Delta]{h\nu} RX + HX$$

ii) Nitration

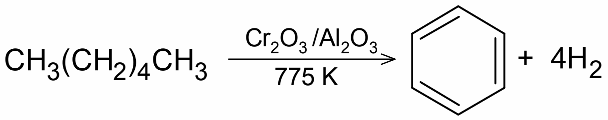
$$RH + HNO_3 \longrightarrow RNO_2 + H_2O$$

iii) Isomerisation



$$CH_3CH_2CH_2CH_3 \xrightarrow{AlCl_3\text{- }HCl} CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_3$$

iv) Aromatisation



v) Pyrolysis

$$CH_3CH_2CH_2 \longrightarrow CH_4 + H_2C{=}CH_2$$

$$\downarrow$$

$$CH_3CH{=}CH_2 + H_2$$

Let us discuss these reactions in detail.

15.5.1 Halogenation

Halogenation is one of the most important reactions of alkanes. It is defined as the replacement of hydrogen atom(s), from an alkane molecule, by halogen atom(s).

$$RH + X_2 \xrightarrow{\Delta / h\nu} RX + HX$$

The reaction does not take place in dark but a vigorous reaction occurs when the mixture of alkane and halogen is exposed to light or heated to a high temperature. But in most cases, the reaction is of limited synthetic value because a mixture of products is obtained. Multiple substitutions may occur. For example, chlorination of methane produces a mixture of chloromethane, dichloromethane, trichloromethane and tetrachloromethane.

$$\underset{\text{methane}}{CH_4} + Cl_2 \xrightarrow{h\nu} \underset{\text{chloromethane}}{CH_3Cl}$$

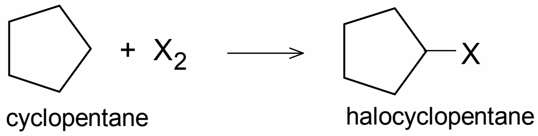
$$\underset{\text{chloro-methane}}{CH_3Cl} + Cl_2 \xrightarrow{h\nu} \underset{\text{dichloromethane}}{CH_2Cl_2}$$

$$\underset{\text{dichloro-methane}}{CH_2Cl_2} + Cl_2 \xrightarrow{h\nu} \underset{\text{trichloromethane}}{CH_3Cl}$$

$$\underset{\text{trichloro-methane}}{CHCl_3} + Cl_2 \xrightarrow{h\nu} \underset{\text{tetrachloromethane}}{CCl_4}$$

The yield of the monosubstituted product may increase by using an excess of alkane.

Similarly, a cycloalkane reacts with halogens to give halocycloalkane, e.g.,



The mechanism of halogenations involves the following steps;

i) In the first step, the halogen molecule undergoes homolysis forming free radicals. This step is called chain initiation:

$$X_2 \xrightarrow{\Delta / h\nu} 2\dot{X}$$

ii) In the next step, the halogen atom abstracts a hydrogen atom from the alkane molecule thereby producing an alkyl radical.

$$RH + \dot{X} \longrightarrow HX + \dot{R}$$

iii) The alkyl radical on collision with another molecule of halogen abstracts a halogen atom from it generating a molecule of the alkyl halide and a halogen atom. These two steps are called chain propagation. They are repeated in sequence till the reactants are consumed.

$$X_2 + \dot{R} \longrightarrow RX + \dot{X}$$

iv) Finally, the above chain may be terminated by coupling of any two radicals. This step is known as termination.

$$\dot{X} + \dot{X} \longrightarrow XX$$

$$\dot{R} + \dot{R} \longrightarrow RR$$

$$\dot{R} + \dot{X} \longrightarrow RX$$

The order of reactivity of halogens in halogenation of alkanes is:

$$F_2 > Cl_2 > Br > I_2$$

The fluorination reaction is too violent to be practical, and iodine actually does not react at all.

SAQ 5

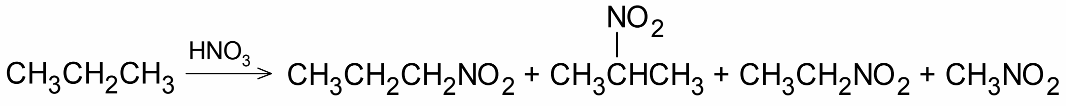
What are the limitations of halogenation of alkanes?

15.5.2 Nitration

Alkanes, especially the higher members, can be nitrated with nitric acid at 675-775K. Like halogenation, it is also a free radical reaction.

$$RH + HNO_3 \longrightarrow RNO_2 + H_2O$$

In this reaction, the product is usually a mixture of nitroalkanes including those with smaller carbon chain than the parent alkane.

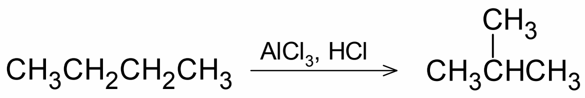


$$\mathrm{CH_3CH_2CH_3 \xrightarrow{HNO_3} CH_3CH_2CH_2NO_2 + CH_3\overset{\overset{NO_2}{|}}{C}HCH_3 + CH_3CH_2NO_2 + CH_3NO_2}$$

propane 1-nitropropane 2-nitropropane nitroethane nitromethane

15.5.3 Isomerisation

The molecular arrangement of one compound into another compound is called isomerisation. The straight chain alkanes are converted into branched chain isomers in the presence of aluminium chloride and hydrogen chloride.



$$\mathrm{CH_3CH_2CH_2CH_3 \xrightarrow{AlCl_3,\ HCl} CH_3\overset{\overset{CH_3}{|}}{C}HCH_3}$$

butane 2-methylpropane

Similarly, other less branched alkanes isomerise to more branched ones.
Thus,

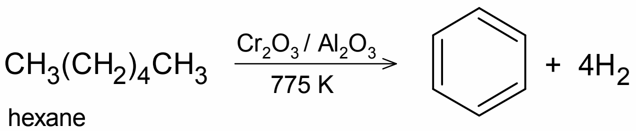
$$\mathrm{CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_2CH_3 \longrightarrow CH_3\overset{\overset{CH_3}{|}}{C}H{-}\overset{\overset{CH_3}{|}}{C}HCH_3}$$

2-methylpentane 2,3-dimethylbutane

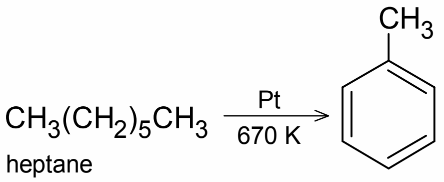
Isomerisation is used to increase the branching of alkanes. Branched chain alkanes are more valuable than straight chain alkanes as a motor fuel.

15.5.4 Aromatisation

This is a process of converting aliphatic or alicyclic compounds to aromatic hydrocarbons. Alkanes with six or more carbon atoms, when heated strongly under pressure in the presence of a catalyst, give aromatic hydrocarbons. This process involves cyclisation, isomerisation and dehydrogenation.
Aromatisation of gasoline increases their octane number from 40 to 95, and we know that unsaturated hydrocarbons are better fuels.



hexane benzene



heptane toluene

Catalytic aromatisation in the presence of platinum is sometimes referred to as platforming or hydroreforming. This process also constitutes a valuable method for commercial production of these hydrocarbons.

15.5.5 Pyrolysis

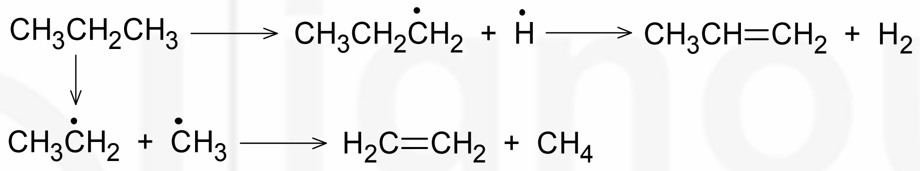
This is a process of decomposing an organic substance by heating at high temperature in the absence of oxygen. The word **pyrolysis** is taken from the Greek words *pyro* (fire) and *lysis* (disintegration). The pyrolysis of alkanes, particularly where petroleum is concerned, is known as **cracking**. When an alkane is heated to about 775-875 K, it decomposes into smaller molecules. For example, on cracking propane, the possible products are:

$$\underset{\text{propene}}{CH_3CH{=}CH_2} + H_2 \longleftarrow \underset{\text{propane}}{CH_3CH_2CH_3} \longrightarrow \underset{\text{methane}}{CH_4} + \underset{\text{ethene}}{H_2C{=}CH_2}$$

Large quantities of high boiling fractions of petroleum are converted into low boiling gasoline by cracking. Propene and hydrogen are produced from propane as a result of fission of C-H linkages. In the case of higher alkanes, fission of C-C linkages occurs more readily. The presence of catalysts like oxides of chromium, vanadium and molybdenum, however, accelerates the fission of C-H linkage. Pyrolysis in the presence of a catalyst is used in the manufacture of alkenes.

The sp^3 orbitals of the carbon atoms in cyclopropane cannot undergo complete overlap with each other because the angles between the carbon atoms of cyclopropane are geometrically required to be 60°. The ring sigma bonds of cyclopropane are therefore, less stable than sp^3 sigma bonds that have the normal tetrahedral angle.

The mechanism of cracking follows a free radical mechanism as illustrated below:



$$CH_3CH_2CH_3 \longrightarrow CH_3CH_2\dot{C}H_2 + \dot{H} \longrightarrow CH_3CH{=}CH_2 + H_2$$

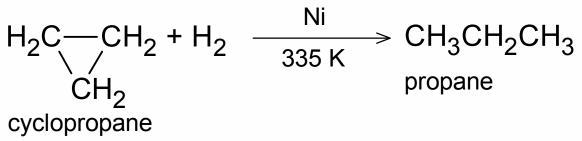
$$CH_3CH_2CH_3 \longrightarrow CH_3\dot{C}H_2 + \dot{C}H_3 \longrightarrow H_2C{=}CH_2 + CH_4$$

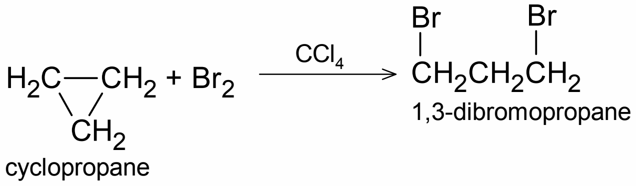
The products formed during cracking of alkanes depend upon: (i) the structure of alkane and (iii) the presence or absence of a catalyst.

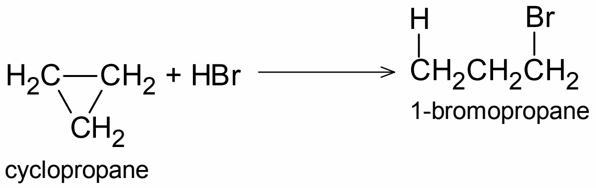
15.5.6 Reactions of Small Ring Compounds

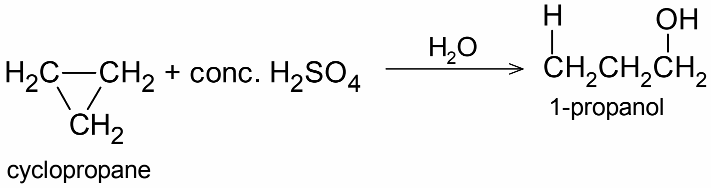
Let us now study the reactions characteristic of small ring compounds, such as cyclopropane and cyclobutane.

Besides, the free radical substitution reactions that are characteristic of cycloalkanes and of alkanes, in general, cyclopropane and, to some extent, cyclobutane undergo certain addition reactions. You will recall from your earlier classes that the bonding in cyclopropane and cyclobutane is not as strong as that in their higher homologues. Hence, the bonds in cyclopropane and cyclobutane are vulnerable to attack by certain reagents. These addition reactions destroy the cyclopropane and cyclobutane ring system and yield an open chain product. Some examples are given below:



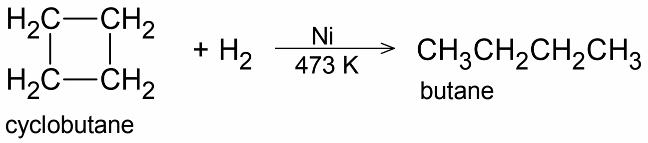






In each of these reactions, a carbon-carbon bond is broken and the two atoms of reagent appear at the terminal carbon atoms in the product.

Cyclobutane does not undergo most of the ring opening reactions of cyclopropane unlike cyclopropane, cyclobutane do not react with Br_2 or HBr or H_2SO_4; it gets hydrogenated under vigorous conditions.



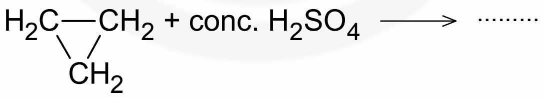
So you can see that cyclobutane undergoes addition reactions less readily than cyclopropane.

SAQ 6

Complete the following reactions:

a) $CH_3CH_2Cl_2 \xrightarrow{h\nu}$ ....

b) $CH_3CH_3 + HNO_3 \longrightarrow$ ....

c) 

d) $CH_3(CH_2)_5CH_3 \xrightarrow[670\ K]{Pt}$ ....

15.6 SUMMARY

In this unit, you have learnt that:

- alkanes are compounds having the general formula C_nH_{2n+2}. Cycloalkanes contain a ring of carbon atoms and have the general formula C_nH_{2n}.
- the chief source of alkanes is petroleum.
- alkanes are non-polar compounds. The physical constants like boiling point, density, etc., increase with increase in number of carbon atom.
- branching in the chain of the alkane decreases the boiling point.

- alkanes are prepared byi) Wurtz reaction, (ii) Kolbe's electrolytic method, (iii) hydrogenation of unsaturated hydrocarbons, (iv) decarboxylation of carboxylic acids, (v) reduction of alkyl halides, and (vi) hydrolysis of Grignard reagents.
- halogenation of alkanes gives multiple substitutions. The order of reactivity of halogens is $F_2 > Cl_2 > Br_2$. Iodine does not react at all.
- an alkane can be converted into its corresponding branched chain isomer in the presence of aluminium chloride and hydrogen chloride.
- when an alkane is heated to a high temperature, it decomposes into small molecules. This process is known as pyrolysis.
- when alkanes with six or more carbon atoms are heated under pressure in the presence if a catalyst, aromatic hydrocarbons are produced.

15.7 TERMINAL QUESTIONS

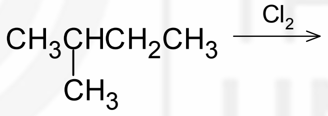
1. Give the products of the following reactions;

   a) $CH_3CH_2Br + CH_3CH_2Br \xrightarrow{Na}$

   b) $CH_3CH_2CH_3 \xrightarrow{LiAlH_4}$

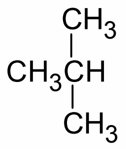
   c) $CH_3CH{=}CHCH_2Cl \xrightarrow{H_2/Pt}$

   d) $CH_3CH_3 + Cl_2 \xrightarrow{h\nu}$

   e) 

   $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3 \xrightarrow{Cl_2}$

2. Starting with $CH_2{=}CHCH_2Br$ or $(CH_3)_3CCl$, how would you prepare the following compounds:

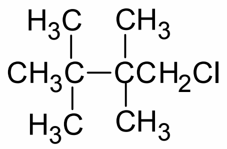


$CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}H$

a)

$CH_3(CH_2)_4CH_3$

b)

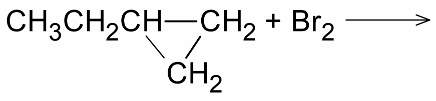


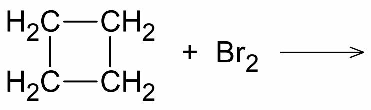
$CH_3\overset{\displaystyle H_3C}{\underset{\displaystyle H_3C}{\overset{|}{\underset{|}{C}}}}{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}CH_2Cl$

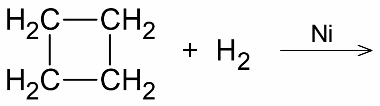
c)

3. Write the equation to show Wurtz reaction.

4. Complete the following reactions:

   a) 

   b) 

c) 
$$\begin{array}{c} H_2C-CH_2 \\ |\qquad | \\ H_2C-CH_2 \end{array} + H_2 \xrightarrow{Ni}$$

5. Write the steps involved in the mechanism of halogenation of alkanes.

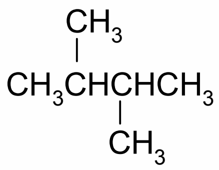
6. What are the limitations of Wurtz reaction?

7. What is Sabatier-Senderens' Reaction? Give one example.

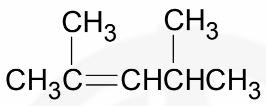
15.8 ANSWERS

Self-Assessment Questions

1. a) $CH_3CH_2CH_2CH_3$

   b) 
   $$\begin{array}{c} CH_3 \\ | \\ CH_3CHCHCH_3 \\ | \\ CH_3 \end{array}$$

   c) $H_2C{=}CHCH_2CH_3$

   d) 
   $$\begin{array}{c} CH_3 \quad CH_3 \\ | \qquad | \\ CH_3C{=}CHCHCH_3 \end{array}$$

2. a) electronegativity

   b) Increases

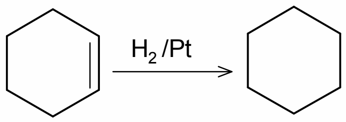
   c) decreases

   d) non-polar

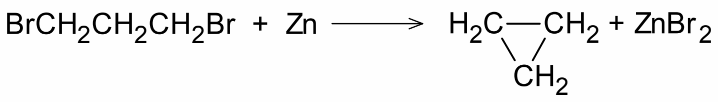
3. a) Isolated

   b) water or dilute acid or ROH or NH_3 or RNH_2

   c) 100%

4. a) 

   b) $CH_3(CH_2)_{10}COOH + C_5H_5N \xrightarrow{CuO.Cr_2O_3} CH_3(CH_2)_9CH_3$

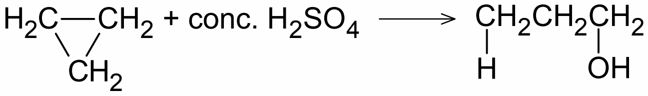
   c) 
   $$BrCH_2CH_2CH_2Br + Zn \longrightarrow \begin{array}{c} H_2C-CH_2 \\ \diagdown\ \diagup \\ CH_2 \end{array} + ZnBr_2$$

   d) $CH_3CH_2CH_2CH_2Cl \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_3$

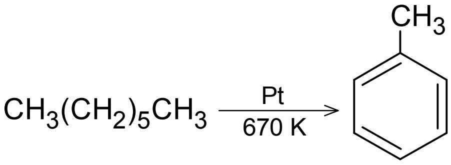
5. The reaction is of limited synthetic value because a mixture of products is obtained. Multiple substitutions may occur.

6. a) $CH_3CH_3 + Cl_2 \xrightarrow{hv} CH_3CH_2Cl$

b) $CH_3CH_3 + HNO_3 \longrightarrow CH_3CH_2NO_2$

c) 

$\underset{H}{C}H_2CH_2\underset{OH}{C}H_2$

d) 

Terminal Questions

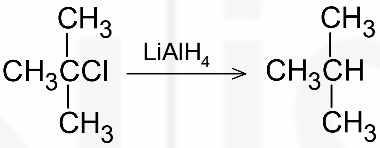
1. a) $CH_3CH_2CH_2CH_3$

b) No reaction

c) CH_3CH_2Cl

d) CH_3CH_2Cl

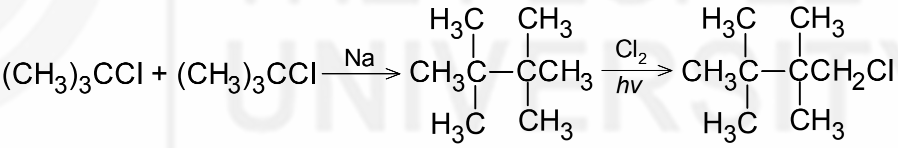
e) No reaction

2. a) 

$$CH_3\overset{CH_3}{\underset{CH_3}{C}}Cl \xrightarrow{LiAlH_4} CH_3\overset{CH_3}{\underset{CH_3}{C}}H$$

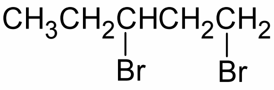
b) $H_2C{=}CHCH_2Br + H_2C{=}CHCH_2Br \xrightarrow{Na} H_2C{=}CHCH_2CH_2CH{=}CH_2$

$\xrightarrow{H_2 / Pt} CH_3(CH_2)_4CH_3$

c) 

$$(CH_3)_3CCl + (CH_3)_3CCl \xrightarrow{Na} CH_3\overset{H_3C}{\underset{H_3C}{C}}-\overset{CH_3}{\underset{CH_3}{C}}CH_3 \xrightarrow[hv]{Cl_2} CH_3\overset{H_3C}{\underset{H_3C}{C}}-\overset{CH_3}{\underset{CH_3}{C}}CH_2Cl$$

3. $CH_3Br + CH_3Br \xrightarrow{2Na} CH_3CH_3 + 2\,NaBr$

4. a) 

$$CH_3CH_2\underset{Br}{C}HCH_2\underset{Br}{C}H_2$$

b) No reaction

c) $CH_3CH_2CH_2CH_3$

5. i) $\dot{X}_2 \xrightarrow{\Delta / h\nu} 2\dot{X}$

ii) $RH + \dot{X} \longrightarrow HX + \dot{R}$

iii) $X_2 + \dot{R} \longrightarrow RX + \dot{X}$

iv) $\dot{R} + \dot{X} \longrightarrow RX$

6. Wurtz reaction is suitable for the preparation of only those alkanes which contain an even number of carbon atoms. The main difficulty with the Wurtz reaction is the formation of many side products when an alkane with odd number of carbon atoms is desired (for detail see subsection 15.4.1).

7. Hydrogenation of an alkene can be carried out by using nickel catalyst but relatively higher temperature and pressure are required for this reaction. This reaction is called **Sabatier-Senderens'** reaction. An example is given below:

$$CH_3CH{=}CH_2 + H_2 \xrightarrow{Ni} CH_3CH_2CH_3$$

UNIT 16

ALKENES –I

Structure

16.1 INTRODUCTION

In the preceding unit, we discussed the chemistry of alkanes and mentioned briefly about the alkenes. In this unit and in the following unit, we shall discuss chemistry of alkenes in detail. Alkenes occur abundantly in nature and have important consequences in biology. In this unit, we will discuss briefly different types of alkenes, their structures and their physical properties. Then, we will learn different methods of their preparation. In the next unit, we will discuss the important reactions of alkenes.

Expected Learning Outcomes

After studying this unit, you should be able to:

- classify the types of alkenes;
- explain the structures of monoenes and dienes;
- list the physical properties of alkenes; and
- list the different methods of their preparation.

16.2 ALKENES AND THEIR CLASSIFICATION

Ethene, the simplest alkene, was known to chemists in the eighteenth century and was obtained in pure form in 1795. Alkenes, also called olefins, are hydrocarbons which contain one or more carbon-carbon double bond(s). Since alkenes contain less than the maximum number of hydrogen atoms, they are referred to as **unsaturated hydrocarbons.**

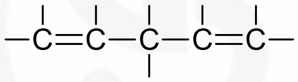
Alkenes are often found as plant products and in petroleum. Many alkenes are biologically active compounds. For example, ethene is a plant hormone that induces ripening of fruits.

Alkenes can be classified on the basis of the number of double bonds present in the molecule. Hydrocarbons containing one carbon-carbon double bond are called monoenes. The monoenes have the general formula C_nH_{2n}.

Hydrocarbons containing two double bonds are called diolefins or alkadienes or dienes. They have the general formula C_nH_{2n-2} and are isomeric with alkynes. Trienes have three double bonds and tetraenes have four double bonds. The term polyene is used for hydrocarbons containing more than four double bonds.

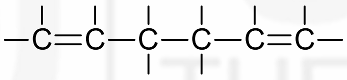
Dienes are divided into three main classes depending on the relative positions of the two double bonds in the molecule: i) isolated or non-conjugated dienes ii) conjugated dienes and iii) cumulated dienes.

In isolated dienes, the two double bonds are separated by at least two single bonds for which two typical skeletons are given below:



$-C=C-C-C=C-$

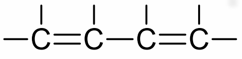
isolated diene
(two single bonds between
two double bonds)



$-C=C-C-C-C=C-$

isolated diene
(three single bonds between
two double bonds)

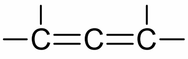
In conjugated dienes, the two double bonds are separated by a single bond. A typical conjugated diene skeleton is given below:



$-C=C-C=C-$

conjugated diene

In cumulated dienes, two double bonds are present on the same carbon atom; a typical skeleton is given below:



$-C=C=C-$

cumulated diene (allene)

Compounds that contain cumulated double bonds are known, but are very uncommon. The conjugated dienes are the most important among the dienes. They show certain reactions that are not shown by monoenes or other dienes. Thus, in these two units (Unit 16 and Unit 17), we shall concentrate our attention on monoenes and conjugated dienes.

Structure of Monoenes and Dienes

The carbon-carbon double bond is both an important structural unit and an importantfunctional group in organic chemistry. The shape of the organic molecule is influenced by thepresence of the double bond which is also the site of most of the chemical reactions thatalkenes undergo. Therefore, it is necessary to understand the structure of these molecules.

Carbon-carbon double bond is the distinguishing feature of the monoenes and dienes. You havealready studied about the bonding of monoenes in your earlier classes. As we know the carbon atoms involved in double bond formation are sp^2 hybridised. The bond angle around the sp^2 hybridised carbon atoms is 120° (Fig. 16.1). Bonding in dienes with isolated double bonds is similar to that of monoenes. Thus here we shall discuss structure of conjugate and cumulated systems.

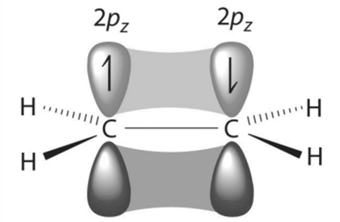


Fig. 16.1: Orbital structure of ethene

Now, let us consider 1, 3-butadiene as an example of a conjugated diene,

$$H_2C{=}CHCH{=}CH_2$$

1,3-butadiene

Each of the four carbon atoms of butadiene contains an unhybridised *p* orbital. The sideways overlap of unhybridised orbitals gives rise to two localised π bonds, i.e., the bonds between C_l and C_2 and C_3 and C_4 (Fig. 16.2). The four carbon atoms and the six hydrogen atoms of butadiene lie in the same plane so that there is a certain amount of overlapping between the electrons clouds o f the *p* orbitals of C_1 and C_3. This give rise to completely deldcalised π orbitals spread over all thefour carbon atoms. It is this delocalisation of π electrons which imparts stability to 1,3-butadiene.

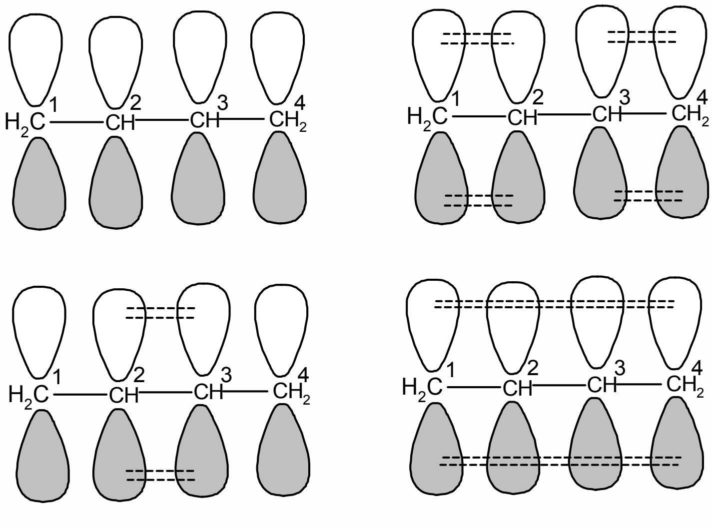


Fig. 16.2 :Orbital structure of 1,3-butadiene

SAQ 1

Fill in the blanks given below:

a) Dienes are isomeric with ………………………

b) Polyenes contain more than …………………….. double bonds.

c) Double bonds that alternate with single bonds are called…………. .

16.3 PHYSICAL PROPERTIES

In general, the physical properties of alkenes are similar to those of the corresponding alkanes. Like alkanes, the boiling points of a homologous series of alkenes increase by 20-30 K per CH_2 group except for the very small homologues. Like alkanes, branching in an alkene also lowers the boiling point. Lower alkenes, from ethene to butene, are colourless gases but the higher ones, from C_5–C_{15}, are liquids and the rest are solids at room temperature.

Like alkanes, alkenes are highly flammable and non polar compounds. Alkenes are slightly more soluble in water than the corresponding alkanes because the π-electrons are attracted to the partially positive hydrogen atoms of the water molecules.

SAQ 2

State which of the following statements aretrue/false? Write (T) for true and (F) for false in the boxes against the statements:

a) Physical properties of alkenes are similar to alkyl halides. ☐

b) Pentene is a liquid hydrocarbon. ☐

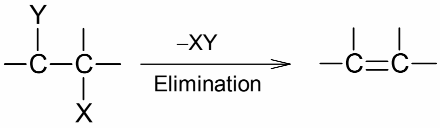
c) Boiling point of hexene is higher than octene. ☐

d) Octene is more soluble in water than octane. ☐

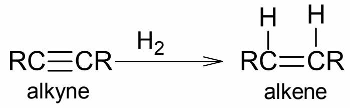
e) 2-Methyl-1-propene has lower boiling point than 1-butene ☐

16.4 PREPARTION OF ALKENES AND DIENES

Alkenes are prepared by introducing a double bond in saturated hydrocarbons through elimination of atoms or groups from two adjacent carbon atoms. The result is the formation of a double bond between these two carbon atoms.



Alkenes can also be prepared by partial hydrogenation of alkyne (addition of two hydrogen atoms to an alkyne) i.e.

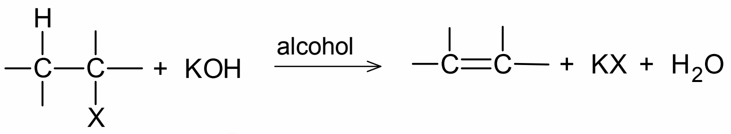

$$RC\equiv CR \xrightarrow{H_2} RHC=CHR$$

Alkenes can be prepared from number of starting materials but here we will discuss only few of them i.e. dehydrohalogenation of alkyl halides, dehydration of alcohols.Alkenes can also be prepared by Wittig reaction. We will discuss few methods of preparation of dienes, like ratro Diels-Alder reaction, dehydration of diol and by cracking process these methods are summarised in Table 16.1.

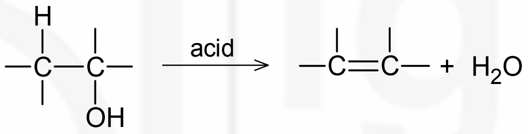
Table 16.1: Preparation of alkenes and dienes

A) Preparation of Alkenes

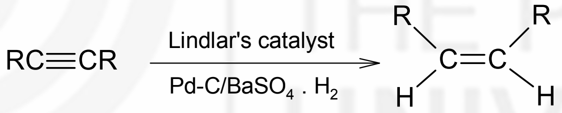
i) Dehydrohalogenation of Alkyl Halides


$$-\overset{H}{\underset{|}{C}}-\underset{X}{C}- + KOH \xrightarrow{alcohol} -C=C- + KX + H_2O$$

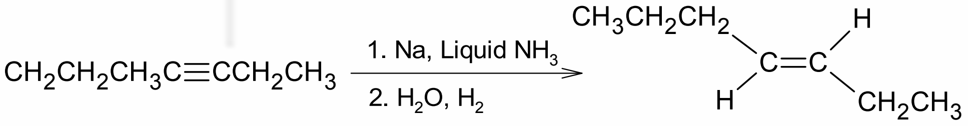
ii) Dehydration of Alcohols


$$-\overset{H}{\underset{|}{C}}-\underset{OH}{C}- \xrightarrow{acid} -C=C- + H_2O$$

iii) Hydrogenation of Alkynes



iv) Birch Reduction

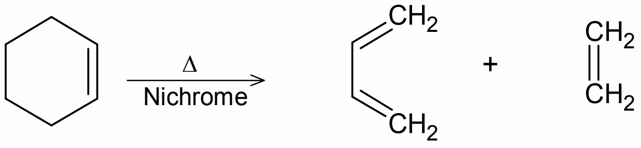


v) Wittig Reaction

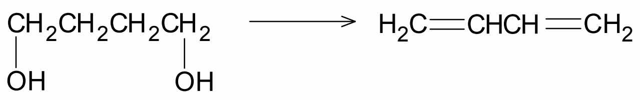

$$-\overset{|}{C}=O \xrightarrow{\text{Wittig reaction}} -\overset{|}{C}=\overset{|}{C}-$$

B) Preparation of Dienes

i) Retro Diels-Alder Reaction

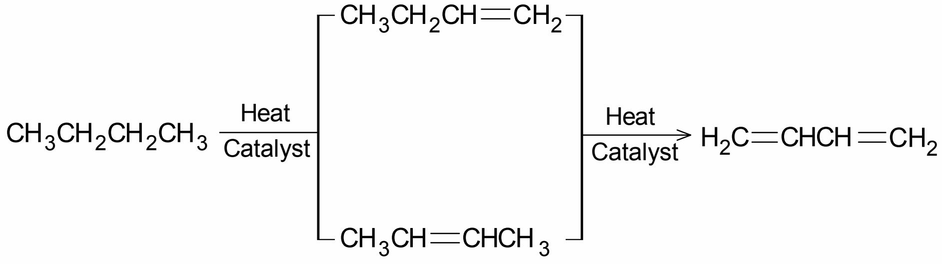


ii) From 1,4-dihydroxybutane



$$\underset{OH}{CH_2}CH_2CH_2\underset{OH}{CH_2} \longrightarrow H_2C{=}CHCH{=}CH_2$$

iii) Cracking Process



16.4.1 Dehydrohalogenation of Alkyl Halides

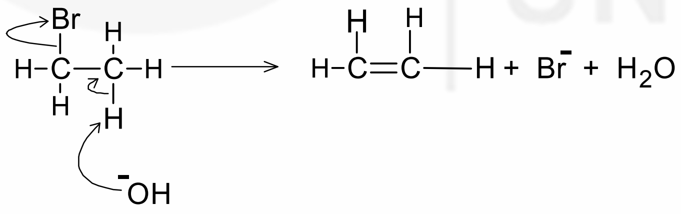
Alkyl halides are converted into alkenes by dehydrohalogenation. Dehydrohalogenation involves elimination of the halogen atom together with a hydrogen atom from an adjacent carbon atom. The elimination is brought about by treating the alkyl halide with a strong base. Thus, bromoethane yields ethene when treated with potassium hydroxide in alcoholic solution.

$$CH_3CH_2Br \xrightarrow[C_2H_5OH]{KOH\ (alc)} H_2C{=}CH_2 + HBr + H_2O$$

bromoethane ethene

Mechanism

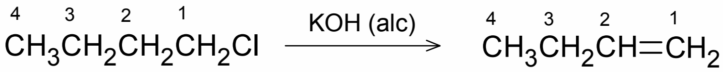
The function of hydroxide ion is to abstract hydrogen from the carbon atom next to the halogen bearing carbon. The carbon halogen bond then cleaves resulting in double bond formation. This reaction follows E2 mechanism.



The ease of dehydrohalogenation of alkyl halides is as follows:

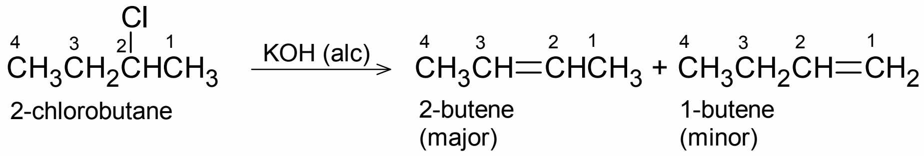
tert > *sec* > *primary*

The alkyl halides, in which halogen is attached to a terminal carbon, yield a single alkene but alkyl halides in which the halogen atom is attached to a non terminal carbon atom and both adjacent positions have hydrogen atoms, yield a mixture of alkenes.



$$\overset{4}{CH_3}\overset{3}{CH_2}\overset{2}{CH_2}\overset{1}{CH_2}Cl \xrightarrow{KOH\ (alc)} \overset{4}{CH_3}\overset{3}{CH_2}\overset{2}{CH}{=}\overset{1}{CH_2}$$

1-chlorobutane 1-butene

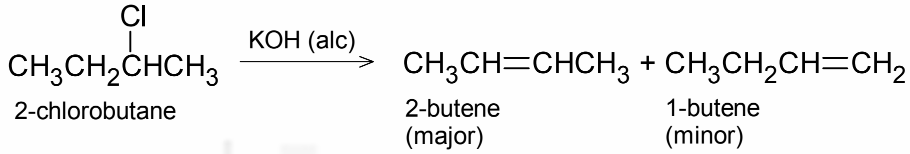


$$\overset{4}{C}H_3\overset{3}{C}H_2\overset{\overset{Cl}{|}}{\overset{2}{C}}H\overset{1}{C}H_3 \xrightarrow{\text{KOH (alc)}} \overset{4}{C}H_3\overset{3}{C}H{=}\overset{2}{C}H\overset{1}{C}H_3 + \overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H{=}\overset{1}{C}H_2$$

In the first reaction, chlorobutane can lose hydrogen only from C_2; therefore, it gives only one product, i.e., 1-butene. However, in the second case, 2-chlorobutane can lose hydrogen from any of the two β-carbon atoms i.e. either from C1 or C3 and. Hence, it gives a mixture of 2-butene(major, 80%) and 1-butene (minor, 20%). This reaction follows Saytzeff rule.

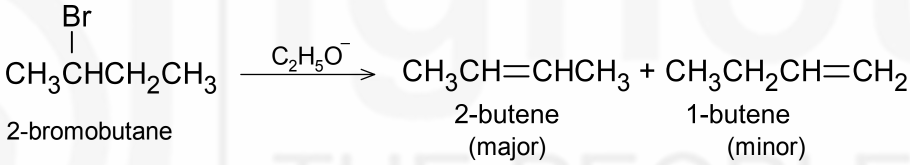
Saytzeff Rule

Saytzeff rule governs the direction of orientation in elimination reactions involving neutral substrates. **Saytzeff rule states that in an elimination reaction more substituted alkene will be formed in major amount.** Thus, in the elimination reaction of 2-chlorobutane, 2-butene will be the major product, i.e.

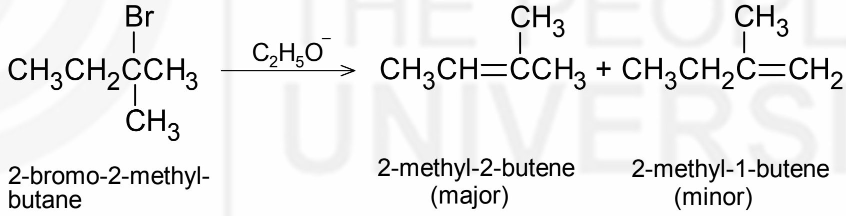


$$CH_3CH_2\overset{\overset{Cl}{|}}{C}HCH_3 \xrightarrow{\text{KOH (alc)}} CH_3CH{=}CHCH_3 + CH_3CH_2CH{=}CH_2$$

Similar products are obtained in dehydrohalogenation of 2-bromobutane and 2-bromo-2-methylbutane.



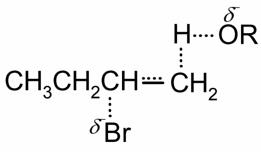
$$CH_3\overset{\overset{Br}{|}}{C}HCH_2CH_3 \xrightarrow{C_2H_5\bar{O}} CH_3CH{=}CHCH_3 + CH_3CH_2CH{=}CH_2$$



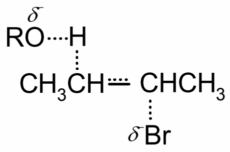
$$CH_3CH_2\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}}CH_3 \xrightarrow{C_2H_5\bar{O}} CH_3CH{=}\overset{\overset{CH_3}{|}}{C}CH_3 + CH_3CH_2\overset{\overset{CH_3}{|}}{C}{=}CH_2$$

The formation of a major and a minor product can be explained as follows.

Let us consider the transition states (TS) for the formation of the two alkenes i.e. less substituted and more substituted alkenes from an alkyl halide. Both the transition states for the elimination reaction have partial double bond character as shown below:



TS of less substituted alkene



TS of more substituted alkene

Since, both the transition states have double bond character, the transition state leading to more stable alkene is itself more stabilised and is of lower energy (Fig. 16.3)

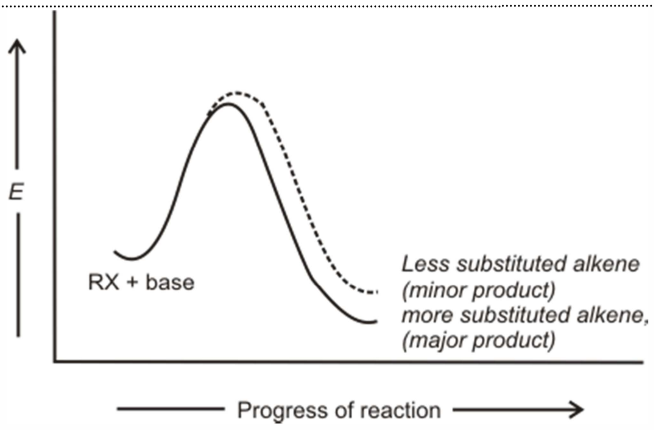
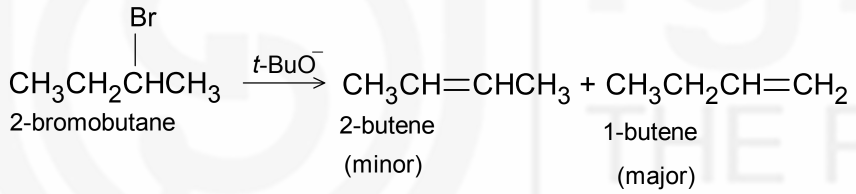


Fig. 16.3: Energy diagrams showing why the more substituted alkene predominates.

Therefore, the more stable alkene is formed as a major product. The more the number of alkyl substituents on either side of the double bond, the greater the stability of the resulting alkene. Thus, **another way of stating Saytzeff rule is to say that the more stable of the possible alkenes is formed in major amount.**

There is possibility of getting less substituted alkene as a major product from an alkylhalide. Dehydrohalogenation of alkyl halide using a bulky base leads to the formation of terminal alkene i.e. less substituted alkene, as a major product. This exception is due to steric effect of bulky base. An example of this type of elimination is:



$$CH_3CH_2\overset{Br}{C}HCH_3 \xrightarrow{t\text{-}BuO^-} CH_3CH{=}CHCH_3 + CH_3CH_2CH{=}CH_2$$

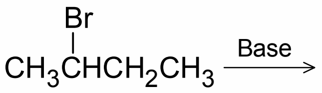
2-bromobutane; 2-butene (minor); 1-butene (major)

SAQ 3

State Saytzeff rule. Give the major products of the following reactions.

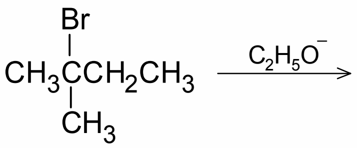
i) $CH_3CH_2CH(Br)CH_3 \xrightarrow{t\text{-}BuO^-}$ ......

ii)



$CH_3\overset{Br}{C}HCH_2CH_3 \xrightarrow{Base}$

iii)



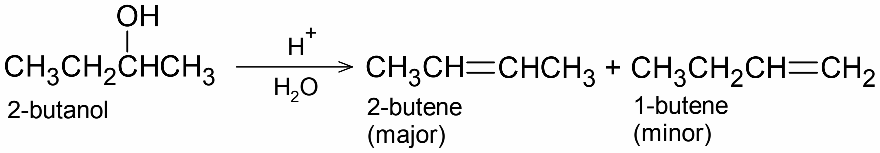
$CH_3\overset{Br}{\underset{CH_3}{C}}CH_2CH_3 \xrightarrow{C_2H_5O^-}$

16.4.2 Dehydration of Alcohols

An alcohol is converted into an alkene by dehydration, i.e., elimination of a molecule of water. Dehydration requires the presence of an acid and the application of heat. The alcohol is heated with sulphuric or phosphoric acid to a temperature as high as 475K. Dehydration is also brought about by passing the alcohol vapor over alumina (Al_2O_3) at 625-675 K, e.g.,

$$\underset{\text{ethanol}}{CH_3CH_2OH} \xrightarrow[\text{475 K}]{\text{95\% } H_2SO_4} \underset{\text{ethene}}{H_2C{=}CH_2}$$

In the case of secondary alcohols other than 2-propanol and tertiary alcohols, there exists the possibility of the formation of more than one alkene. For example, in 2-butanol, hydrogen elimination can occur either from C_1 or C_2. The direction and the rate of reaction again follow the Saytzeff rule and hence,2-butene, the more substituted alkene, is the major product and 1-butene is the minor product.



$$\underset{\text{2-butanol}}{CH_3CH_2\overset{\overset{OH}{|}}{C}HCH_3} \xrightarrow[H_2O]{H^+} \underset{\substack{\text{2-butene}\\ \text{(major)}}}{CH_3CH{=}CHCH_3} + \underset{\substack{\text{1-butene}\\ \text{(minor)}}}{CH_3CH_2CH{=}CH_2}$$

The ease of dehydration of various alcohols has been found to follow the order:

tert > sec > primary

SAQ 4

Fill in the following blanks:

a) Dehydration of *tert* alcohol is …… than that of primary alcohol.

b) An alcohol is converted into an alkene by ……………

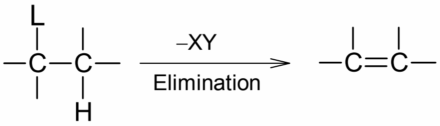
c) Dehydration requires the presence of an……………

d) In the case of ………….. alcohols, there is a possibility of formation of more than one alkene.

Since elimination reactions are the main method for preparation of alkene, here we will give only brief idea about elimination reactions (E1 and E2). In Unit 13 of 2nd level course you will study elimination reactions in detail.

Elimination Reactions

There are many types of elimination reactions i.e. 1,1-elimination, 1,2-elimination and 1,3-elimination etc. Formation of alkene involves 1,2-elimination.

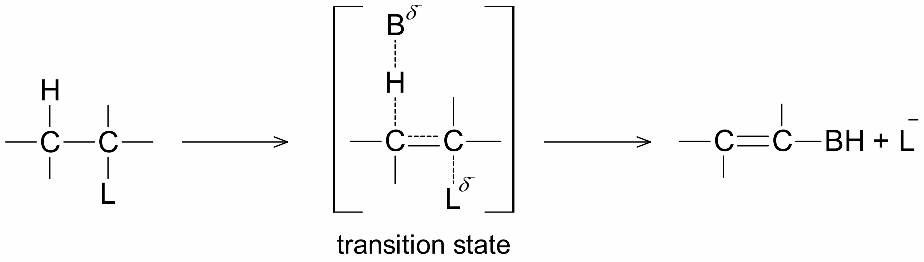


$$-\overset{\overset{L}{|}}{\underset{|}{C}}-\overset{|}{\underset{\underset{H}{|}}{C}}- \xrightarrow[\text{Elimination}]{-XY} -\overset{|}{C}{=}\overset{|}{C}-$$

Elimination reactions take place through one of the two mechanisms, i.e. unimolecular elimination (E1) or bimolecular elimination (E2). E1 and E2 mechanisms are different from each other in the timing of the breaking of C–H and C–L bonds and consequently in their kinetics. Before discussing the different methods for preparation of alkenes or dienes let us discuss general mechanism of elimination reactions (E1 and E2)

E2 Mechanism

E2 mechanism involves breaking of C–L and C–H bonds simultaneously. The base pulls away hydrogen, as a proton, from carbon atom; simultaneously the leaving group departs and a double bond is formed. The leaving group takes its electrons pair with it and hydrogen leaves its electrons pair behind to form the double bond. The is a one step mechanism involving a transition state with a partial double bond character.



Since it is a one step reaction, both reactants are involved in the transition state and rate of overall reaction depends on the concentration of the substrate as well as concentration of the base, i.e.

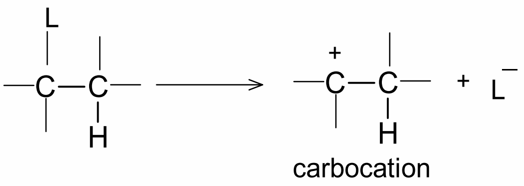
Rate $\propto$ [substrate] [base]

This reaction is known as bimolecular elimination or E2 reaction. Reaction kinetics is typically second order: first order in base and first order in the substrate.

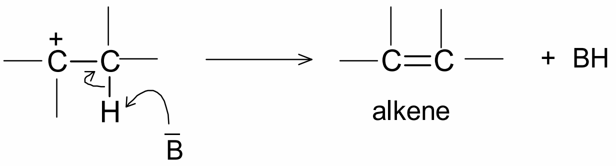
E1 Mechanism

E1 mechanism involves first the breaking of C-L bond which is then followed by breaking of C-H bond and formation of a new π bond between the two carbon atoms. In this mechanism, the bond broken and bond-made is the same as in E2 mechanism: however, bond breaking and bond making here are taking place not simultaneously, but one after the other. So, whereas, E2 is a one step process and E1 is a two-step process.

In the first step substrate undergoes heterolysis to form carbocation.



In the second step, the carbocation rapidly loses a β-proton to the base, which is generally the solvent itself, and forms the alkene.



The first step of E1 mechanism is slow and therefore, is the rate determining. Step (RDS). As shown above, only the substrate is involved in the rate determining step that means the rate of reaction is dependent only on the concentration of the substrate and is independent of the concentration of base.

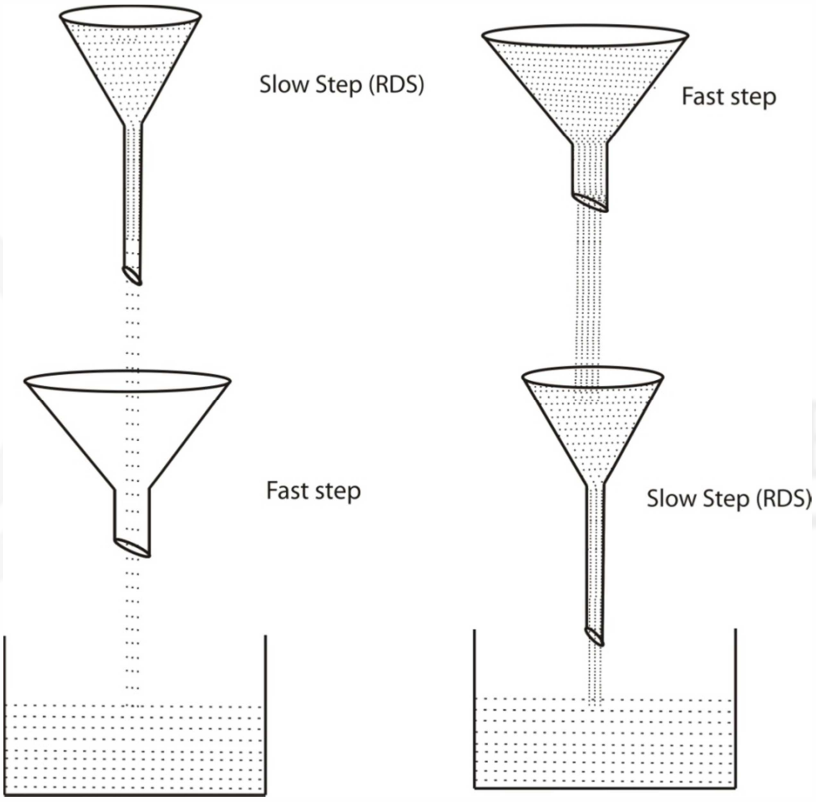
Rate $\propto$ [substrate]

Therefore, it is known as unimolecular elimination or E1 elimination and the reaction kinetic is of first order.

You can ask why the slow step is the rate determining step (RDS). Let us try to understand this by performing a very simple activity.

Activity

Suppose you want to transfer some amount of water from one container to another container. Take two funnels of different sizes. In the first instance place the smaller funnel above the bigger one and pour water from the top as shown in (Fig.16.4)



(a) (b)

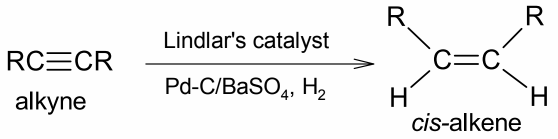
Fig. 16.4: Explanation of rate determining steps

You will observe that the time taken for the transfer of water from one container to the other is dependent on the speed with water is drained through the smaller funnel (Fig 16.4 a) Now reverse the placement of two funnels. i.e. the bigger one above the smaller one as shown in Fig.16.4b. Here again you would observe that it is the smaller funnel which will determine the transfer of water from one container to the other container. The above activity proves that the rate is determined by the slower step, whether it is first step or second step.

16.4.3 Hydrogenation of Alkynes

Like alkenes, alkynes undergo catalytic hydrogenation. The addition of hydrogen to an alkyne takes place in two steps. First addition results in the formation of an alkene; since an alkene can also undergo catalytic hydrogenation, the second addition give an alkane. By using a calculated amount of hydrogen and a poisoned catalyst, hydrogenation can be stopped at the alkene stage. These catalysts **selectively** block the hydrogenation of alkenes.

A catalyst mixed with a selective inhibiting agent is called a poisoned catalyst.



This is stereoselective addition reaction giving predominantly *cis*-alkenes. In the absence of a poison, catalytic hydrogenation of an alkyne gives the alkanes.

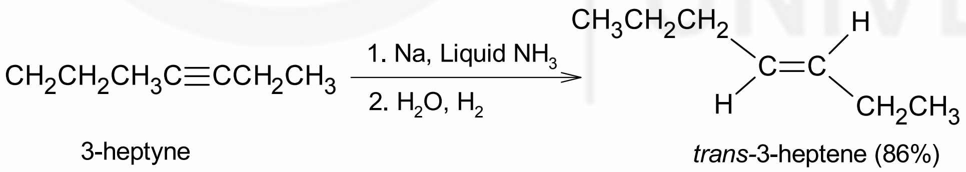
Stereoselective reaction is a reaction which yields predominantly one isomer.

$$\underset{\text{alkyne}}{RC{\equiv}CR} \xrightarrow[\text{No poison}]{H_2,\ Pd/C} \underset{\substack{\text{alkane}\\ \text{95\% yield}}}{RCH_2CH_2R}$$

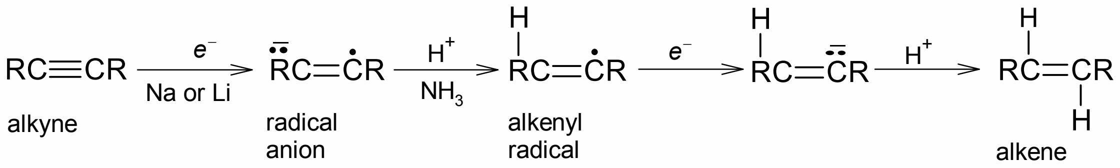
16.4.4 Birch Reduction

Now you can ask: can we modify the reduction of alkynes so as to get only *trans*-alkenes? The answer is yes; we can get only *trans*-products, but with a different reducing agent and through a different mechanism.

If we carry out the reduction of an alkyne with sodium metal or lithium metal in liquid ammonia, *trans*-alkene is almost an exclusive product. This reduction is known as **Birch Reduction**. For example, 3-heptyne is reduced to *trans*-3-heptene in the following way:

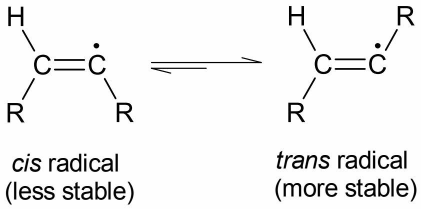


In the first step of this mechanism, the alkyne accepts one electron to give a radical anion. The radical anion is protonated by ammonia solvent to give an alkenyl radical; which gets further reduced by accepting another electron to give an alkenyl anion. This species is again protonated to give the alkene.

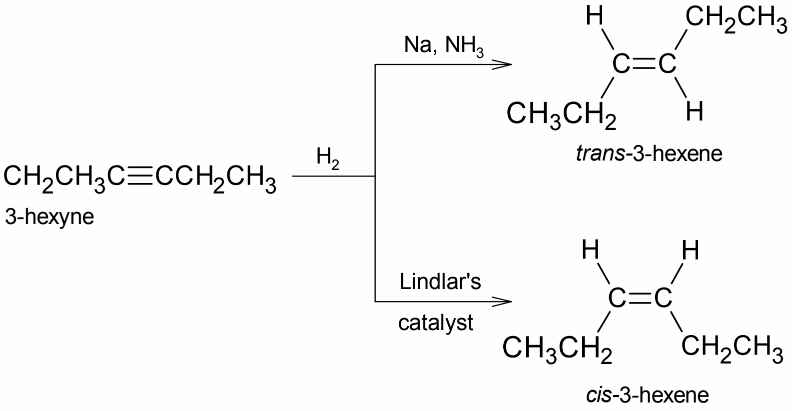


$$\underset{\text{alkyne}}{RC{\equiv}CR} \xrightarrow[\text{Na or Li}]{e^-} \underset{\substack{\text{radical}\\ \text{anion}}}{\overset{\bullet\bullet}{\bar{R}}C{=}\dot{C}R} \xrightarrow[NH_3]{H^+} \underset{\substack{\text{alkenyl}\\ \text{radical}}}{R\overset{H}{C}{=}\dot{C}R} \xrightarrow{e^-} R\overset{H}{C}{=}\overset{\bullet\bullet}{\bar{C}}R \xrightarrow{H^+} \underset{\text{alkene}}{R\overset{H}{C}{=}\underset{H}{C}R}$$

Formation of the *trans* alkenes is due to the rapid equilibration of the intermediate alkenyl radical between the *cis*- and *trans*- forms. The equilibrium lies on the side of the more stable *trans* species.



In other words, we can say reduction of alkyne to double bond can yield either *cis*-alkene or *trans*-alkene, depending upon the choice of the reducing agent.



SAQ 5

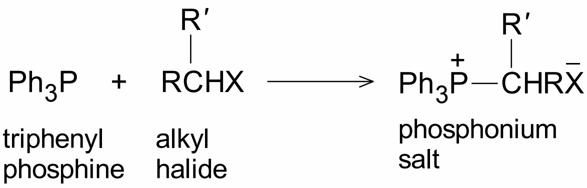
How do you prepare *cis*-and *trans*-alkenes from an alkyne?

16.4.5 Wittig Reaction

In 1954, George Wittig reported a method of synthesising alkenes from carbonyl compounds. This reaction is applicable to aldehyde and ketones and leads to replacement of carbonyl oxygen by the group=CRR' (where R and R' are hydrogen or alkyl group).

$$-\overset{|}{C}{=}O \xrightarrow{\text{Wittig reaction}} -\overset{|}{C}{=}\overset{|}{C}-$$

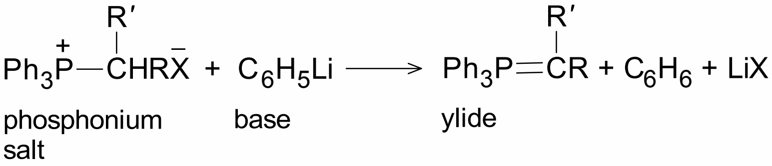
There are two main steps in Wittig reaction. In the first step, the nucleophilic reagent triphenylphosphine reacts with primary or secondary alkyl halide to give phosphonium salt.



$$Ph_3P + R\overset{R'}{\overset{|}{C}}HX \longrightarrow Ph_3\overset{+}{P}-\overset{R'}{\overset{|}{C}}HR\overset{-}{X}$$

triphenyl phosphine, alkyl halide, phosphonium salt

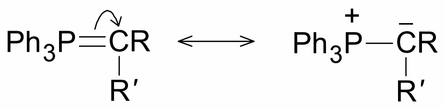
This phosphonium salt further reacts with a strong base, which abstracts a weakly acidic α-hydrogen to give alkylidenetriphenylphosphorane (the phosphorous **ylide**) commonly known as the **Wittig reagent**.



$$Ph_3\overset{+}{P}-\overset{R'}{\overset{|}{C}}HR\overset{-}{X} + C_6H_5Li \longrightarrow Ph_3P{=}\overset{R'}{\overset{|}{C}}R + C_6H_6 + LiX$$

phosphonium salt, base, ylide

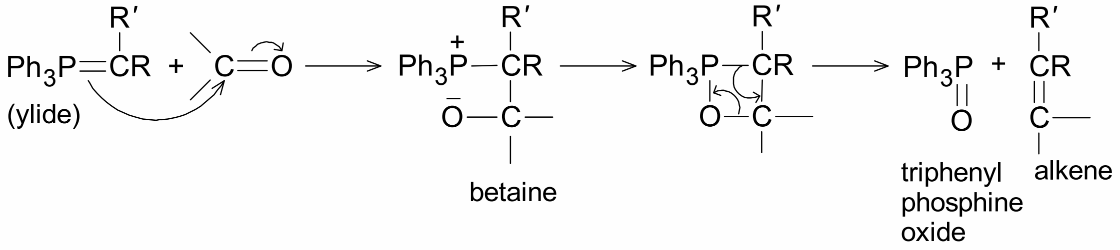
The phosphorous ylide has a hybrid structure and it is the negative charge on carbon that is responsible for their characteristic reactions.



$$Ph_3P{=}\underset{R'}{CR} \longleftrightarrow Ph_3\overset{+}{P}{-}\overset{-}{\underset{R'}{C}}R$$

The resulting phosphorous ylide attacks the carbonyl carbon to form **betaine** which often undergoes elimination spontaneously to give alkene.

The mechanism of the Wittig reaction has been the subject of much discussion, but evidence is now strongly in favour of formation of an intermediate betaine followed by ring closure and then fission.



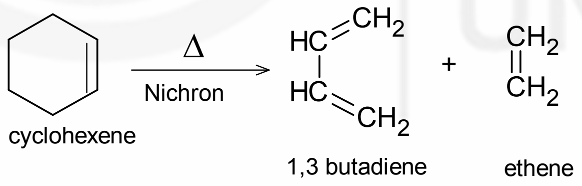
SAQ 6

What is role of phosphonium salt in Wittig reaction?

16.4.6 Preparation of Dienes

i) Retro Diels-Alder Reaction

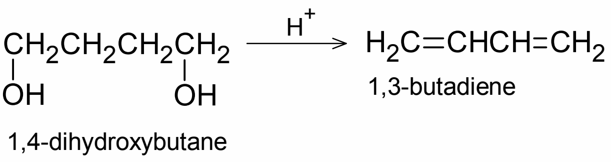
Dienes are usually prepared by the adaptation of the methods used to make simple alkenes. However, 1,3-butadiene is prepared by passing vapours of cyclohexene over heated nichrome (Ni-Cr-Fe) alloy.



This reaction is also known as the Retro Diels-Alder reaction as it is the reverse of the Diels-Alder reaction.

ii) Dienes from 1,4-dihydroxybutane

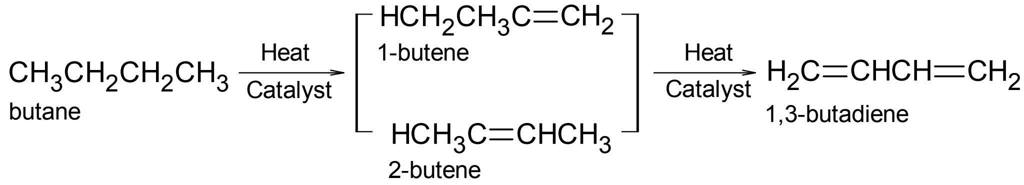
As stated above, dienes are usually prepared by adaptation of the method used to make simple alkenes. For example, 1,4-dihydroxybutane on treatment with sulphuric acid gives 1,3-butadiene.



$$\underset{OH}{CH_2}CH_2CH_2\underset{OH}{CH_2} \xrightarrow{H^+} H_2C{=}CHCH{=}CH_2$$

iii) Cracking Process

1,3-Butadiene can also be prepared from butane by the cracking process using Cr_2O_3, as illustrated below:



$$\underset{\text{butane}}{CH_3CH_2CH_2CH_3} \xrightarrow[\text{Catalyst}]{\text{Heat}} \begin{bmatrix} \underset{\text{1-butene}}{HCH_2CH_3C{=}CH_2} \\ \\ \underset{\text{2-butene}}{HCH_3C{=}CHCH_3} \end{bmatrix} \xrightarrow[\text{Catalyst}]{\text{Heat}} \underset{\text{1,3-butadiene}}{H_2C{=}CHCH{=}CH_2}$$

SAQ 7

How would you prepare 1, 3-butadiene from the following ?

a) 1-butene

b) 1, 4-dihydroxybutane

c) cyclohexene

16.5 SUMMARY

In this unit, you have learnt that:

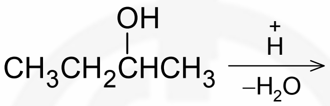
- hydrocarbons containing one carbon-carbon double bond are known as monoenes or olefins.
- hydrocarbons containing two double bonds are known as alkadienes or dienes. They have the general formula C_nH_{2n-2} and are isomeric with alkynes.
- trienes have three double bonds tetraenes have four double bonds.
- the term polyene is used for hydrocarbons containing more than four double bonds.
- dienes are divided into three classes, i.e., conjugated dienes, isolated dienes and cumulated dienes.
- in general, the physical properties of alkenes are similar to the corresponding alkanes.
- like alkanes, the boiling points of a homologous series of alkenes increase 20-30 K per CH_2 group except for the very small homologues.
- alkenes are highly flammable and non polar compounds.
- alkenes are generally prepared by the elimination of atoms or groups from the adjacent carbon atoms. Two such reactions are dehydrohalogenation of alkyl halides and dehydration of alcohols.
- formation of alkene involves 1,2-elimination.

- elimination reactions take place through one of the two mechanisms, i.e. unimolecular elimination (E1) or bimolecular elimination (E2).
- the ease of dehydrohalogenation of alkyl halides and dehydration of alcohol is: *tert* > *sec* >*primary.*
- *cis* alkenes can also be prepared by partial hydrogenation of alkynes.
- *trans*alkenescan be prepared from alkyne by Birch reduction.
- 1,3-butadiene is prepared by passing vapours of cyclohexene over heated nichrome (Ni-Cr-Fe) alloy. This reaction is also known as the Retro Diels-Alder reaction.
- dienes are prepared by adaptation of the methods used to make simple alkenes. e.g.1,3-butadiene can also be prepared from 1,4-dihydroxybutane on treatment with sulphuric acid.
- 1,3-butdiene can also be prepared from butane by the cracking process using Cr_2O_3.

16.6 TERMINAL QUESTIONS

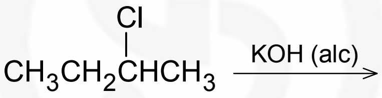
1. Predict the product of the following reactions:

a)



$CH_3CH_2\overset{\overset{OH}{|}}{C}HCH_3 \xrightarrow[-H_2O]{\overset{+}{H}}$

b)



$CH_3CH_2\overset{\overset{Cl}{|}}{C}HCH_3 \xrightarrow{KOH\ (alc)}$

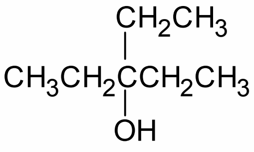
c) $CH_3CH_2CH_2Cl \xrightarrow{KOH\ (alc)}$

2. Elimination reaction of a normal alkyl halide gives more substituted alkene as a major product Explain.

3. How will you prepare alkene from a) alkyl halide and b) alcohol? Write one equation for each.

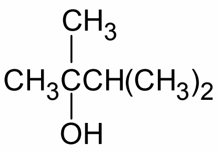
4. Identify the alkene obtained on dehydration/dehydrohalogenation of each of the following compounds:

a)



$CH_3CH_2\overset{\overset{CH_2CH_3}{|}}{\underset{\underset{OH}{|}}{C}}CH_2CH_3$

b)



$CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}CH(CH_3)_2$

5. State Saytzeff's rule giving suitable example.

16.7 ANSWERS

Self-Assessment Questions

1. a) alkynes

   b) four

   c) conjugated

2. a) T

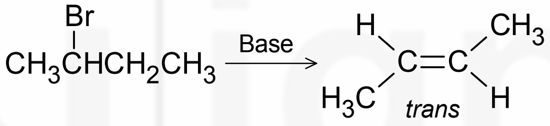
   b) T

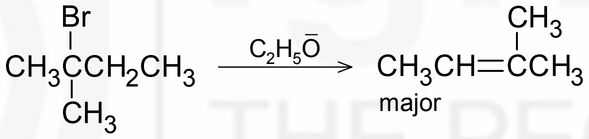
   c) F

   d) T

   e) T

3. i) $$CH_3CH_2CH(Br)CH_3 \xrightarrow{t\text{-Bu}\bar{O}} \underset{\substack{\text{2-butene}\\ \text{(minor)}}}{CH_3CH{=}CHCH_3} + \underset{\substack{\text{1-butene}\\ \text{(major)}}}{CH_3CH_2CH{=}CH_2}$$

   ii) 

   iii) 

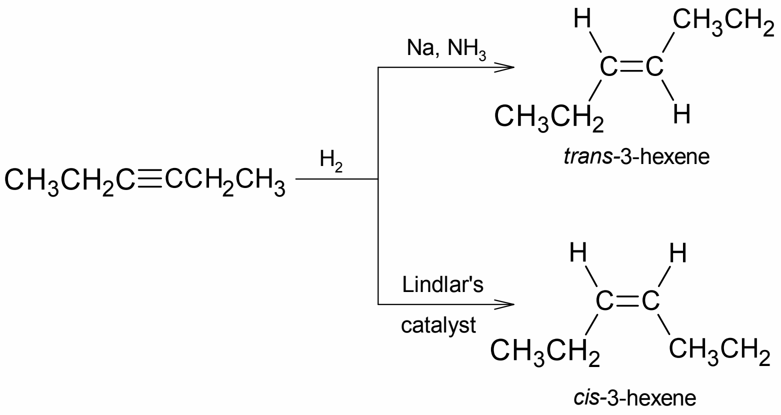
$$CH_3\overset{\displaystyle Br}{\underset{\displaystyle CH_3}{C}}CH_2CH_3 \xrightarrow{C_2H_5\bar{O}} \underset{\text{major}}{CH_3CH{=}\overset{\displaystyle CH_3}{C}CH_3}$$

4. a) easier

   b) dehydration

   c) acid

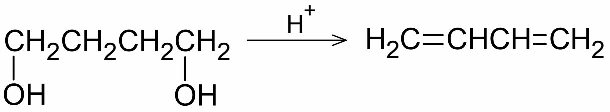
   d) secondary alcohols other than 2-propanol or tertiary

5. 

6. This phosphonium salt further reacts with a strong base, which abstracts a weakly acidic α-hydrogen to give alkylidenetriphenylphosphorane (the phosphorous ylide) commonly known as the **Wittig reagent**.

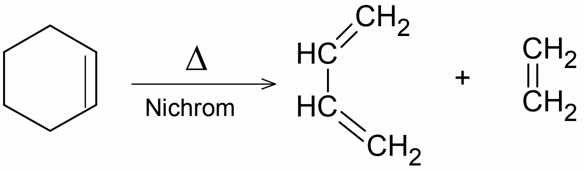
7. a) $CH_3CH_2CH{=}CH_2 \xrightarrow[\text{Catalyst}]{\text{Heat}} H_2C{=}CHCH{=}CH_2$

b)



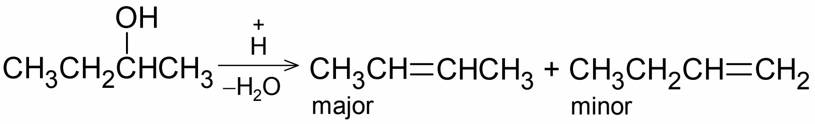
$$\underset{\text{OH}}{\underset{|}{C}}H_2CH_2CH_2\underset{\text{OH}}{\underset{|}{C}}H_2 \xrightarrow{H^+} H_2C{=}CHCH{=}CH_2$$

c)



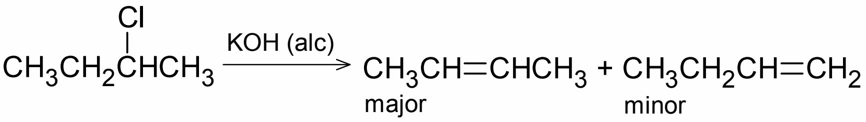
Terminal Questions

1. a)



$$CH_3CH_2\overset{\text{OH}}{\overset{|}{C}}HCH_3 \xrightarrow[-H_2O]{\overset{+}{H}} \underset{\text{major}}{CH_3CH{=}CHCH_3} + \underset{\text{minor}}{CH_3CH_2CH{=}CH_2}$$

b)



$$CH_3CH_2\overset{\text{Cl}}{\overset{|}{C}}HCH_3 \xrightarrow{\text{KOH (alc)}} \underset{\text{major}}{CH_3CH{=}CHCH_3} + \underset{\text{minor}}{CH_3CH_2CH{=}CH_2}$$

c) $CH_3CH_2CH_2CH_2Cl \xrightarrow{\text{KOH (alc)}} CH_3CH_2CH{=}CH_2$

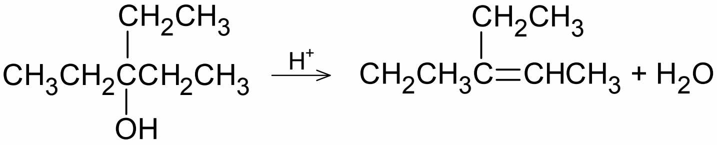
2. Let us consider the transition states (TS) for the formation of the two alkenes i.e. less substituted and more substituted alkenes from an alkyl halide. Both the transition states for the elimination reaction have partial double bond character.

Since, both the transition states have double bond character, the transition state leading to more stable alkene is itself more stabilised and is of lower energy. Therefore, the more stable alkene is formed as a major product. (Ref.16.4.2)

3. a) $CH_3CH_2OH \xrightarrow[475\text{ K}]{95\%\ H_2SO_4} H_2C{=}CH_2$

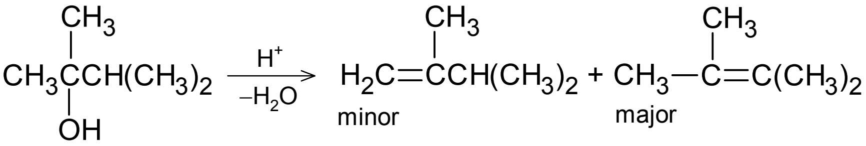
b) $CH_3CH_2Br \xrightarrow[C_2H_5OH]{\text{KOH (alc)}} H_2C{=}CH_2 + HBr + H_2O$

4. a)



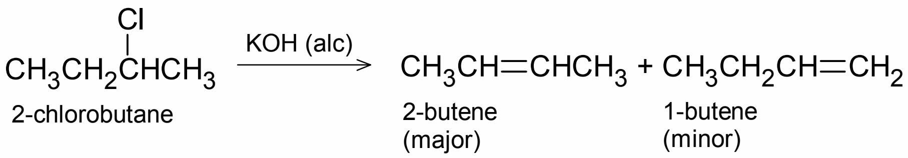
$$CH_3CH_2\underset{\text{OH}}{\underset{|}{\overset{CH_2CH_3}{\overset{|}{C}}}}CH_2CH_3 \xrightarrow{H^+} CH_2CH_3\overset{CH_2CH_3}{\overset{|}{C}}{=}CHCH_3 + H_2O$$

b)



$$CH_3\underset{\text{OH}}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH(CH_3)_2 \xrightarrow[-H_2O]{H^+} \underset{\text{minor}}{H_2C{=}\overset{CH_3}{\overset{|}{C}}CH(CH_3)_2} + \underset{\text{major}}{CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}C(CH_3)_2}$$

5. Saytzeff rule states that in an elimination reaction more substituted alkene will be formed in major amount. Thus, in the elimination reaction of 2-chlorobutane, 2-butene will be the major product, i.e.



$$\underset{\text{2-chlorobutane}}{CH_3CH_2\overset{\overset{Cl}{|}}{C}HCH_3} \xrightarrow{\text{KOH (alc)}} \underset{\substack{\text{2-butene}\\\text{(major)}}}{CH_3CH{=}CHCH_3} + \underset{\substack{\text{1-butene}\\\text{(minor)}}}{CH_3CH_2CH{=}CH_2}$$

UNIT 17

ALKENES – II

Structure

17.1 INTRODUCTION

In the last unit, you have studied about the alkenes and their methods of preparations. This unit deals with the important reactions of alkenes with different reagents. Alkenes are unsaturated hydrocarbons and their functional group is carbon-carbon double bond. The characteristics reactions of alkenes are electrophilic addition reactions to the unsaturated carbon-carbon double bonds.

In this unit, first we will study electrophilic addition reactions of alkenes, which include halogenation, hydrohalogenation and hydration. Then, we will discuss concerted addition reactions in which we will take some examples of hydroboration, ozonolysis and hydroxylation only. In the next unit, you will study about the chemistry of **alkynes**.

Expected Learning Outcomes

After studying this unit, you should be able to:

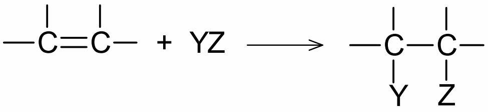
- explain the electrophilic addition reactions of alkenes;
- write the mechanism of electrophilic addition reaction of alkenes;
- explain halogenation and hydrohalogenation of alkenes;
- explain hydration and oxymercuration-demercuration of alkenes;

- explain peroxide effect;
- discuss hydroboration and its importance; and
- describe ozonolysis and its importance in structure determination of alkenes.

17.2 REACTIONS OF ALKENES

The characteristic reactions of alkenes are electrophilic addition reactions to the unsaturated carbon-carbon double bond. In addition to electrophilic addition reaction, some concerted reactions of alkenes are also very important. In this unit we will concentrate on these two types of reactions

The carbon-carbon double bond of alkenes consists of a strong σ bond and a weak π bond. Most of the reactions of alkenes would involve the breaking of this weaker π bond.



$$-\overset{|}{C}=\overset{|}{C}- + YZ \longrightarrow -\overset{|}{\underset{Y}{C}}-\overset{|}{\underset{Z}{C}}-$$

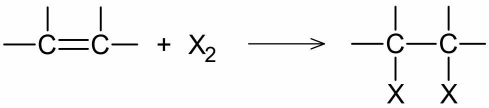
In the addition reactions of alkenes, the π-bond is broken and the electron pair comprising it is used in the formation of two new σ bonds. Thus, two sp^2 hybridised carbon are rehybridised to sp^3 hybridisedcarbon atoms. Compounds containing π bonds are usually of higher energy than those having σ bonds. Consequently, these addition reactions are usually exothermic processes.

If we consider the structure of an alkene in the region of the double bond, there is a cloud of electron density above and below the plane of bonded atoms. The π electrons are loosely held by the nuclei and are thus easily available to electron-seeking reagents. Such reagents are called electrophilic reagents or electrophilies and the typical reactions of alkenes are the electrophilic addition reactions.

In contrast to electrophilic addition reactions, there are a group of reagents which attack the double bond from the same face of the double bond. These do not involve highly charged intermediates like carbocation. These are known as concerted addition reactions. Some important reactions of alkenes are given in Table 17.1.

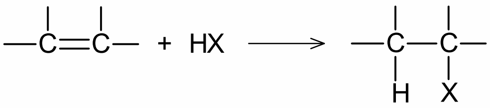
Table 17.1: Reactions of alkenes

i) Halogenation



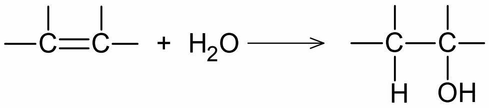
$$-\overset{|}{C}=\overset{|}{C}- + X_2 \longrightarrow -\overset{|}{\underset{X}{C}}-\overset{|}{\underset{X}{C}}-$$

ii) Hydrohalogenation

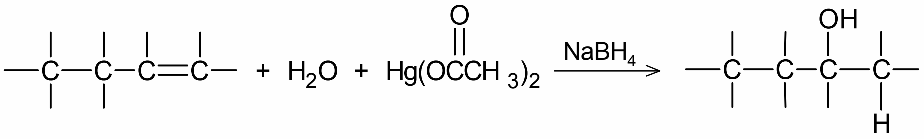


$$-\overset{|}{C}=\overset{|}{C}- + HX \longrightarrow -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{X}{C}}-$$

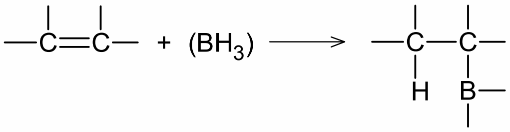
iii) Hydration



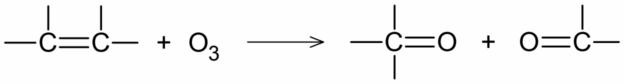
iv) Oxymercuration-demercuration Reaction



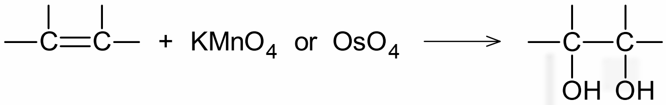
v) Hydroboration



vi) Ozonolysis



vii) Hydroxylation



Let us discuss these reactions in detail.

SAQ 1

Fill in the following blanks:

i) The characteristic reactions of alkenes are …….addition reactions.

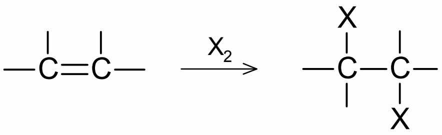
ii) Most of the reactions of alkenes would involve the breaking of this ……….bond.

iii) Compounds containing π bonds are usually of …….energy than those having σ bonds.

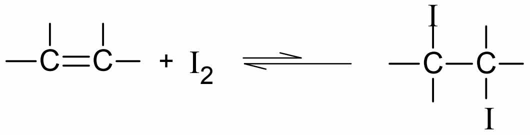
iv) The reactions in which the reagent attacks the double bond from the same face of the double bond are known as……….addition reactions.

17.2.1 Halogenation

Alkenes are quite reactive towards halogens. Treatment of alkenes with halogens gives 1,2-dihalogenated alkanes.



Bromine and chlorine are particularly effective electrophilic reagents. Fluorine tends to be too reactive and its reaction with alkene is difficult to control for most laboratory procedures and therefore, requires special techniques. Iodine does not react with alkenes. Addition of iodine to alkene is a reversible reaction i.e., 1,2-diiodo product is unstable and loses I_2 to reform the alkene.

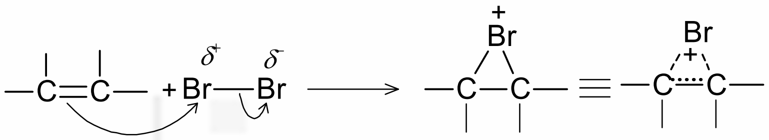


$$-\overset{|}{\underset{}{C}}=\overset{|}{C}- + I_2 \rightleftharpoons -\overset{I}{\underset{|}{C}}-\overset{|}{\underset{I}{C}}-$$

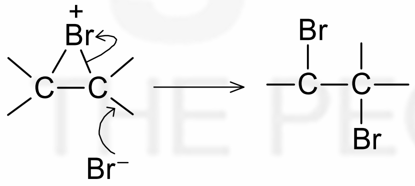
These reactions are generally carried out in an inert solvent (e.g. CCl_4). Since, at high temperature substitution products may be formed, these reactions are carried out at room temperature.

Mechanism

Although bromine is non-polar, it is nevertheless highly polarisable in the vicinity of the nucleophilic double bond. Hence, a partial positive charge (δ^+) develops on one bromine atom and a partial negative charge (δ^-)develops on the other bromine atom. The π electrons of alkene attack the positive end of the polarised bromine molecule, displacing bromide ion and forming a cyclic bromonium ion.



The cyclic structure of the intermediate shields one side of the molecule and, for this reason, bromide attacks from the opposite side to give *trans* product. This process is known as *trans* addition.



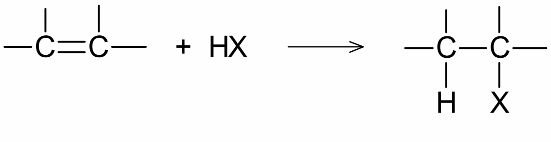
Addition of bromine is extremely useful for detection of carbon-carbon double bond. Rapid decolourisation of bromine solution serves as a test for the presence of the carbon-carbon double bond in a compound.

SAQ 2

Addition of Br_2 to alkene gives *trans* product. Explain.

17.2.2 Hydrohalogenation

The reaction of hydrogen halides (halogen acids)with an alkene gives the corresponding alkyl halides. Such reactions are called **hydrohalogenation reactions.**

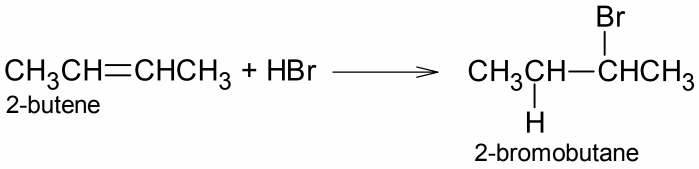


$$-\overset{|}{C}=\overset{|}{C}- + HX \longrightarrow -\underset{H}{\overset{|}{C}}-\underset{X}{\overset{|}{C}}-$$

The order of reactivity of HX towards alkene is:

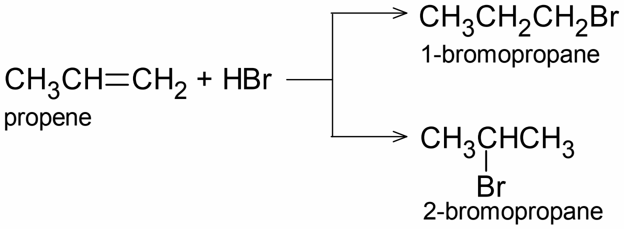
HI > HB r > HCl > HF

As long as the alkene is symmetrical, we get only one product. In case of unsymmetrical alkenes, the position of attachment of nucleophile (halide ion) is governed by the nature of substituents. Addition of HBr to 2-butene (symmetrical alkene) gives only one product, i.e. 2-bromobutane, For example,



$$\underset{\text{2-butene}}{CH_3CH{=}CHCH_3} + HBr \longrightarrow \underset{\text{2-bromobutane}}{CH_3\underset{\substack{| \\ H}}{C}H-\overset{\substack{Br \\ |}}{C}HCH_3}$$

While addition of HBr to unsymmetrical alkenes, say propene, should give two products, i.e.,1-bromopropane and 2-bromopropane.i.e.



However, only one product, 2-bromopropane, is formed. Such reactions are called **regiospecific** reactions. To explain the exclusive formation of only one product, the Russian chemist Markownikoff formulated a rule know after him as Markownikoff's rule,

Regiospecific: Only one of the two directions of addition is observed.

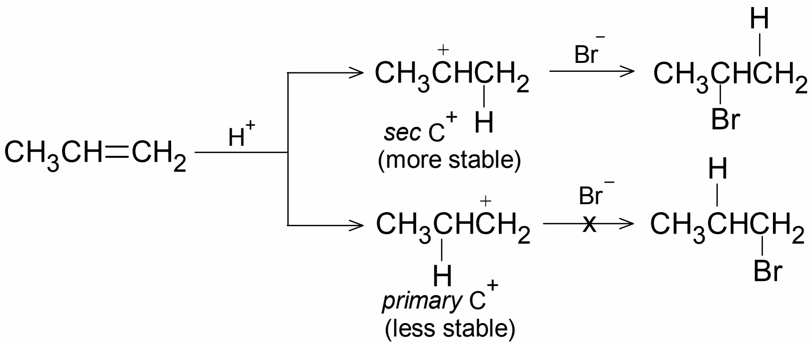
Markownikoff's Rule

Markownikoff's rule states that **addition of a hydrogen halide to an unsymmetrical alkene takes place in such a way that the positive part of the reagent goes to that carbon atom of the alkene which carries the more number of hydrogen atoms**.

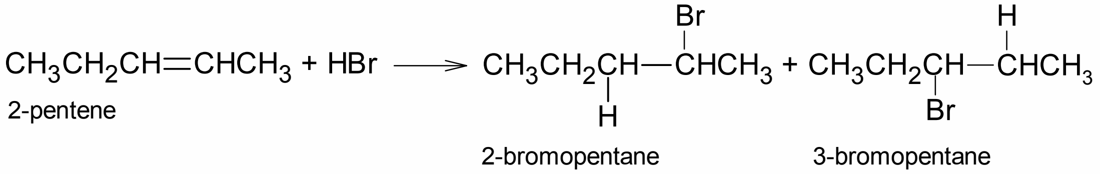
Markownikoff's rule can be explained on the basis of the relative stabilities of carbocations which are in the order of*:*

tertiary> secondary > primary.

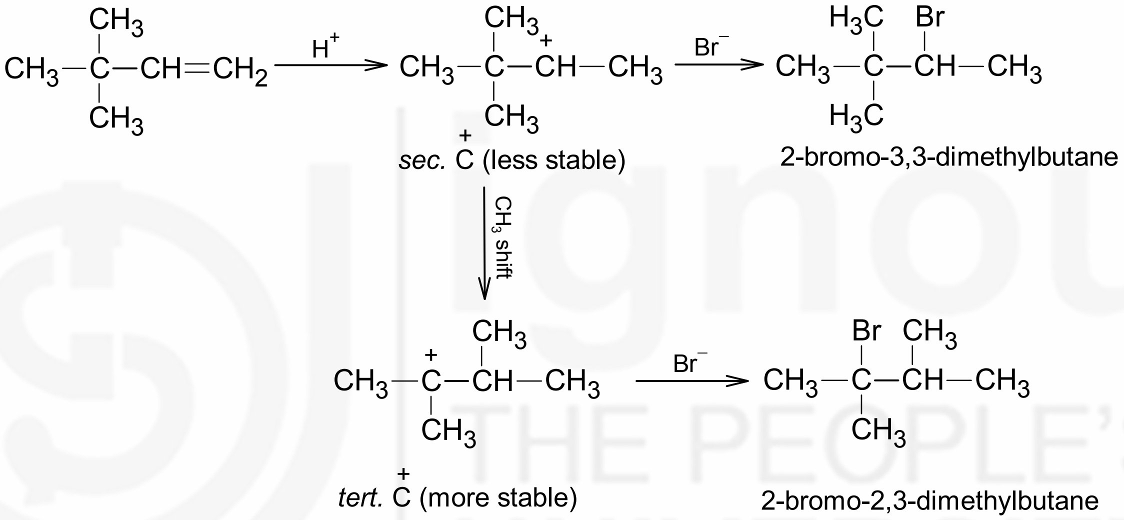
Accordingly, the more substituted carbocation is formed as an intermediate in preference to the less substituted one. For example, in the addition of H^+ to propene, there is possibility of the formation of either a primary or a secondary carbocation. Since, the secondary carbocation is more stable than the primary carbocation, addition of H^+ to propene gives more stable secondary carbocation which gives exclusively 2-bromopropane.



However, there may be cases, when both carbon atoms forming the double bond have the same number of hydrogen atoms in an unsymmetrical alkenethen a mixture of products results. For example, when 2-pentene reacts with hydrogen bromide, it gives a mixture of 2-bromopentane and 3-bromopentane.

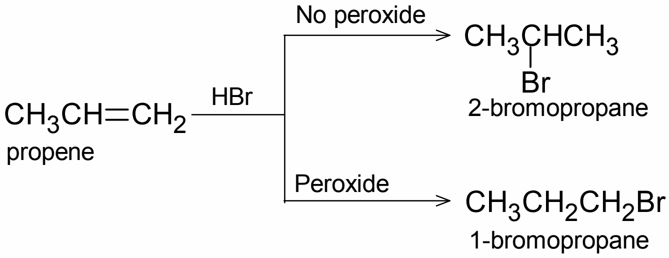


Rearrangement: Rearrangement is one of the characteristic reactions of a carbocation. A carbocation formed, in an addition reaction of a hydrogen halide to an unsymmetrical alkene, often undergoes rearrangement (alkyl shift) to give a more stable carbocation. For example, addition of HBr to 3,3-dimethyl-1-butene gives two products, 2-bromo-3,3-dimethylbutane (normal product) and 2-bromo- 2,3-dimethylbutane (rearranged product) as shown in following scheme:



Peroxide effect

You must be under the impression that addition of hydrogen halide to alkene always gives Markwonikoff's product. But it is not so. After an extensive study of the mechanism of addition of HBr to alkenes, Kharasch and Mayo found that in the presence of peroxide, the product obtained was not the one predicted by Markownikoff's rule but it was contrary to the Markwonikoff's rule. Such additions are referred to as *anti*-Markownikoff additions. Since, the reversal of the addition reaction is brought about in the presence of peroxides, it is known as the **peroxide effect**. For example, the addition of hydrogen bromide to propene in presence of peroxides gives 1-bromopropane rather than 2-bromopropane.

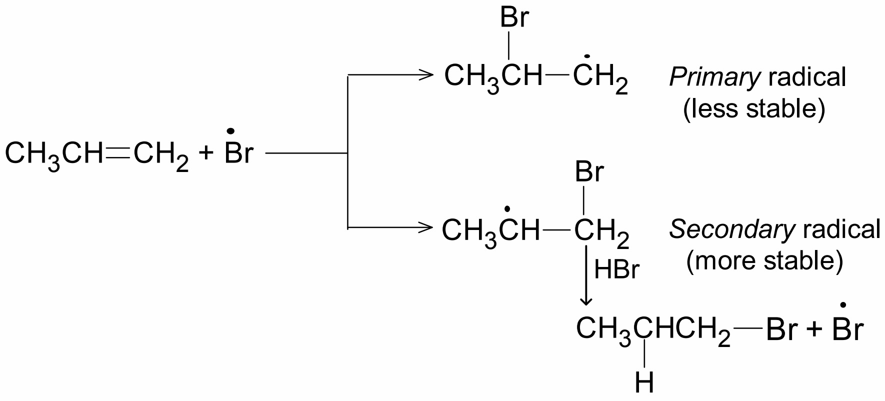


The reaction intermediate in such additions is a free radical rather than a carbocation. The function of peroxide is to generate the free radical.

$$(RCO_2)_2 \longrightarrow 2RC\dot{O}_2 \longrightarrow 2\dot{R} + 2CO_2$$

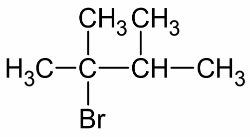
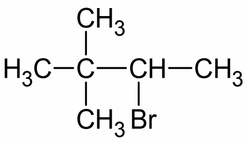
$$\dot{R} + HBr \longrightarrow RH + \dot{Br}$$

Bromine radical can add to either of the two carbon atoms producing either a primary or a secondary free radical.



The bromine radical prefers to react at the terminal carbon to give a secondary radical because, the secondary radical is more stable than a primary radical. The orientation of addition product is based on the principle that it takes place in a manner such that the more stable radical, of the possible alternatives, is generated. Consequently, the final product of reaction of HBr with alkene is (in presence of peroxide) generally the one with bromine attached to the less substituted carbon atom. The products formed from the addition of HBr to some substituted alkene are given in Table 17.2.

Table 17.2: Orientation pattern on addition of HBr to substituted alkenes

Alkene	Product
1. $CH_3CH{=}CH_2$	$CH_3CH(Br)CH_3$
2. $(CH_3)_2C{=}CH_2$	$(CH_3)_2C(Br)CH_3$
3. $(CH_3)_3CCH{=}CH_2$	 $H_3C-\underset{Br}{\overset{CH_3}{C}}-\overset{CH_3}{CH}-CH_3$ and/or  $H_3C-\underset{CH_3}{\overset{CH_3}{C}}-\underset{Br}{CH}-CH_3$
4. $C_6H_5CH{=}CH_2$	$C_6H_5CH(Br)CH_3$

SAQ 3

Reaction of HBr with 3,3-dimethyl-1-butene gives 2-bromo-2,3-dimethylbutane as a major product. Explain.

SAQ 4

Fill in the following blanks:

a) Addition of bromine is useful for detection of............. bond.

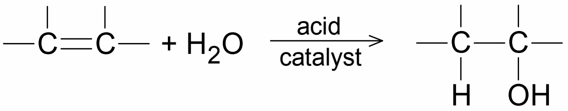
b) ……………does not react with alkenes.

c) Addition of HBr to unsymmetrical alkenes gives……….products,

d) Reaction of propene with HBr in presence of peroxide gives …………………………product.

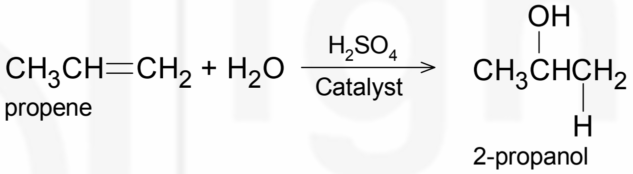
17.2.3 Hydration

Addition of H_2O to alkenes is known as hydration. This reaction occurs when H_2O adds to an alkene in the presence of an acid catalyst to yield an alcohol.

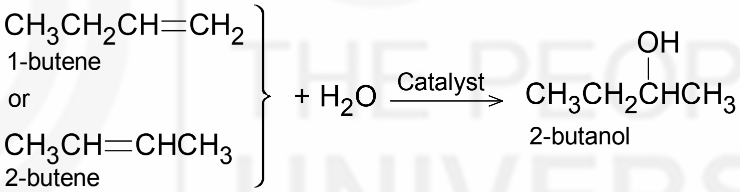


$$-\overset{|}{C}=\overset{|}{C}- + H_2O \xrightarrow[\text{catalyst}]{\text{acid}} -\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}-$$

Like hydrohalogenation, addition of H_2O to an unsymmetrical alkene follows Markownikoff's rule.



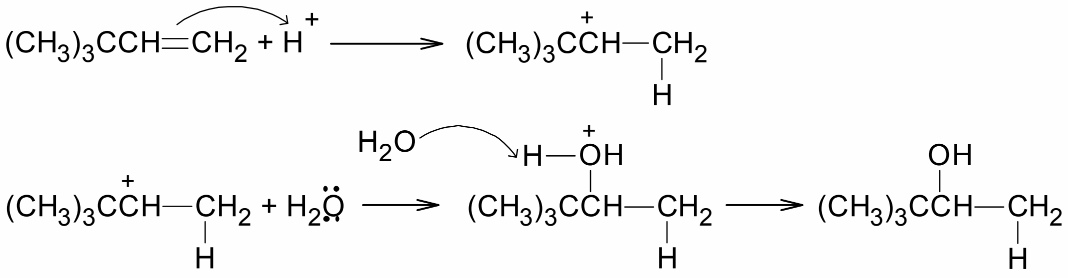
$$\underset{\text{propene}}{CH_3CH=CH_2} + H_2O \xrightarrow[\text{Catalyst}]{H_2SO_4} \underset{\text{2-propanol}}{CH_3\overset{OH}{C}H\underset{H}{C}H_2}$$



$$\left.\begin{array}{l} \underset{\text{1-butene}}{CH_3CH_2CH=CH_2} \\ \text{or} \\ \underset{\text{2-butene}}{CH_3CH=CHCH_3} \end{array}\right\} + H_2O \xrightarrow{\text{Catalyst}} \underset{\text{2-butanol}}{CH_3CH_2\overset{OH}{C}HCH_3}$$

Mechanism

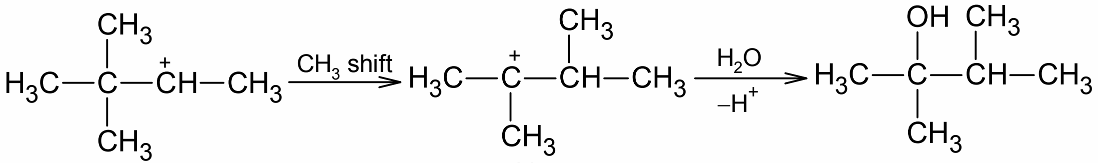
This reaction also follows Markownikoff's rule, a pattern with which we are now familiar. As expected, the reaction occurs in two steps. The alkene is first protonated to give a carbocation. Attack of the nucleophile (H_2O) on the carbocation, in the second step, and loss of a proton from the resulting adduct completes the reaction.



$$(CH_3)_3CCH=CH_2 + H^+ \longrightarrow (CH_3)_3C\overset{+}{C}H-\underset{H}{C}H_2$$

$$(CH_3)_3C\overset{+}{C}H-\underset{H}{C}H_2 + H_2\ddot{O} \longrightarrow (CH_3)_3C\overset{H-\overset{+}{O}H}{C}H-\underset{H}{C}H_2 \longrightarrow (CH_3)_3C\overset{OH}{C}H-\underset{H}{C}H_2$$

Because a carbocation is involved, rearrangement is possible. Carbocation can undergo a 1,2-shift of CH_3 group to yield the more stable carbocation, e.g.



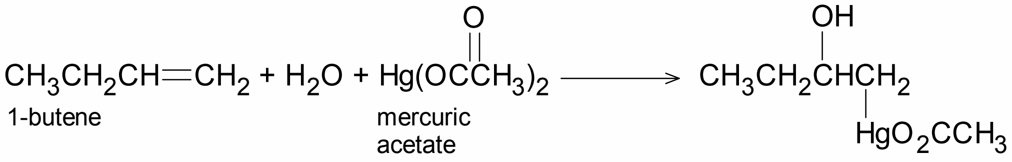
less stable (*sec.* C^+)

more stable (*tert.* C^+)

2,3-dimethyl-2-butanol

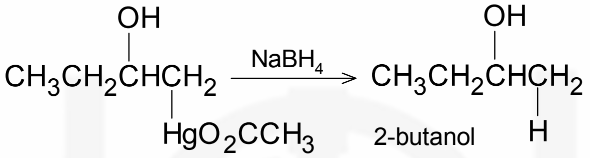
17.2.4 Oxymercuration-demercuration Reaction

Another method used to accomplish Markownikoff's hydration of an alkene is **oxymercuration-demercuration.** The alkene reacts with mercuric acetate in presence of water to give hydroxyl-mercurial compound which on reduction leads to demercuration and produces an alcohol. The products of oxymercuration-demercuration reaction usually give better yield of alcohol than the addition of water with H_2SO_4..



1-butene

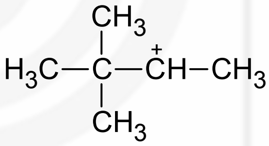
mercuric acetate



2-butanol

SAQ 5

Write the rearranged carbocation of the following:



SAQ 6

Which of the following statements is true/false? Write 'T' for true and 'F' for false in the box given.

a) Addition of H_2O to alkenes in the presence of an acid catalyst gives an alcohol. ☐

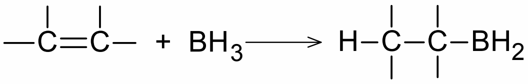
b) Addition of H_2O to unsymmetrical alkene follows Markownikoff's rule. ☐

c) Addition of HBr to 3,3-dimethyl-1-butene gives rearranged product i.e. 2-bromo- 2,3-dimethylbutane. ☐

d) Oxymercuration-demercuration does not follow Markownikoff's rule. ☐

17.2.5 Hydroboration

When an alkene reacts with borane, addition to the carbon-carbon double bond takes place to yield an organoborane– a compound with a carbon-boron bond. The reaction is known as **hydroboration.**



$$-\overset{|}{C}=\overset{|}{C}- + BH_3 \longrightarrow H-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-BH_2$$

This reaction is very facile and requires only few seconds for completion at 273K and gives organoboranes in a very high yield.

The addition takes place in a stepwise fashion via successive addition of each boron hydrogen to the alkene.

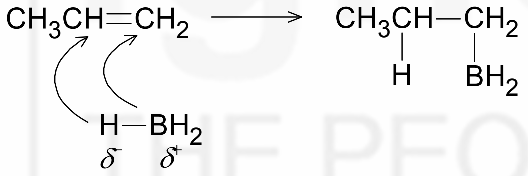
Step 1 $H_2C{=}CH_2 + (BH_3)_2 \longrightarrow CH_3CH_2{-}BH_2$

Since BH_3 has three hydrogen atoms, addition occurs three times to produce trialkylborane product e.g.

Step 2 $H_2C{=}CH_2 + CH_3CH_2{-}BH_2 \longrightarrow (CH_3CH_2)_2{-}BH$

Step 3 $H_2C{=}CH_2 + (CH_3CH_2)_2{-}BH \longrightarrow (CH_3CH_2)_3{-}B$

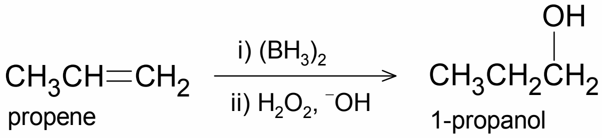
Hydroboration reaction is described as *anti*-Markownikoff's addition. But this is not true. Hydrogen is the electronegative portion of the molecule instead of the electropositive portion.



As shown above, the hydrogen (as a hydride ion, H^-) goes to the more substituted carbon. The result appears to be *anti*-Markownikoff's addition because mostly in other addition reaction hydrogen participates as H^+.

Organoboranes are generally not isolated but are instead used directly as reactive intermediates for further synthetic reactions. Some important reactions of organoboranes are given below:

i) One of the most important reactions of organoboranes is H_2O_2 oxidation. Oxidation of an organoboranes by alkaline H_2O_2 gives the corresponding alcohol. It appears as if water had been added to the double bond in an *anti*-Markownikoff's manner.

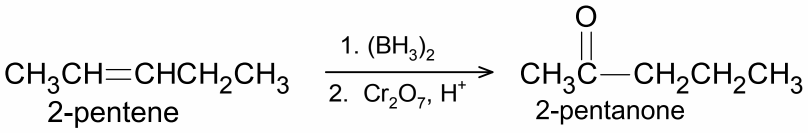


$$\underset{\text{propene}}{CH_3CH{=}CH_2} \xrightarrow[\text{ii) } H_2O_2,\ ^{-}OH]{\text{i) } (BH_3)_2} \underset{\text{1-propanol}}{CH_3CH_2\overset{OH}{\overset{|}{C}}H_2}$$

ii) Treatment of organoboranes with a carboxylic acid leads to an alkane. The acid-hydrolysis of organoboranes provides a useful method for carrying out hydrogenation of alkenes.

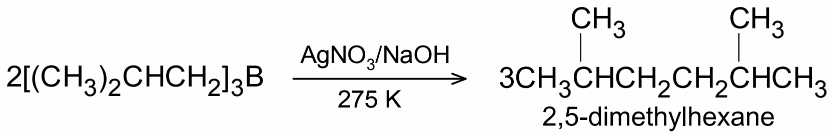
$$\underset{\text{1-propene}}{CH_3CH{=}CH_2} \xrightarrow[CH_3COOH]{(BH_3)_2} \underset{\text{propane}}{CH_3CH_2CH_3}$$

iii) Oxidation of organoboranes with chromic acid yields carbonyl compounds.



$$\underset{\text{2-pentene}}{CH_3CH{=}CHCH_2CH_3} \xrightarrow[2.\ Cr_2O_7,\ H^+]{1.\ (BH_3)_2} \underset{\text{2-pentanone}}{CH_3\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2CH_2CH_3}$$

iv) Reaction of trialkylboranes with alkaline silver nitrate solution induces a coupling reaction and hence provides a method for the synthesis of higher alkanes.



$$2[(CH_3)_2CHCH_2]_3B \xrightarrow[275\ K]{AgNO_3/NaOH} \underset{\text{2,5-dimethylhexane}}{3CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_3}$$

SAQ 7

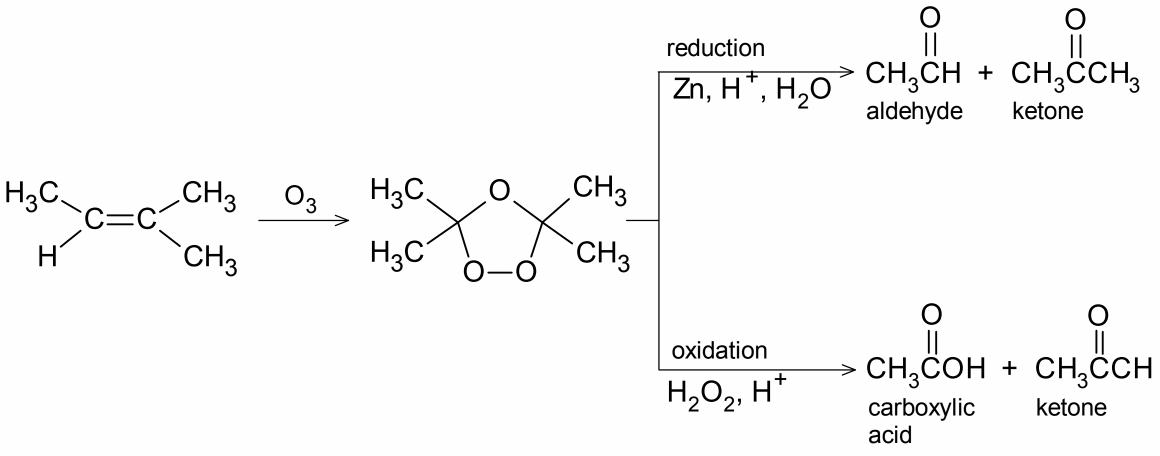
Hydroboration reaction appears as *anti*-Markownikoff's addition. Explain.

17.2.6 Ozonolysis

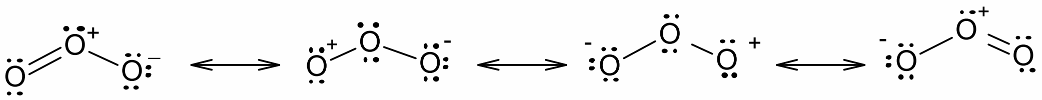
In all the reactions of alkenes studied so far, the carbon skeleton of the starting material has been left intact. We have seen the conversion of the carbon-carbon double bond into new functional groups (halide, alcohol, etc.) by addition different reagents, but the carbon skeleton has not been broken. Ozonolysis is a cleavage reaction, in which the double bond is completely altered or broken and the alkene molecule is converted into two smaller molecules.

$$>C{=}C< \ + \ O_3 \longrightarrow \ >C{=}O \ + \ O{=}C<$$

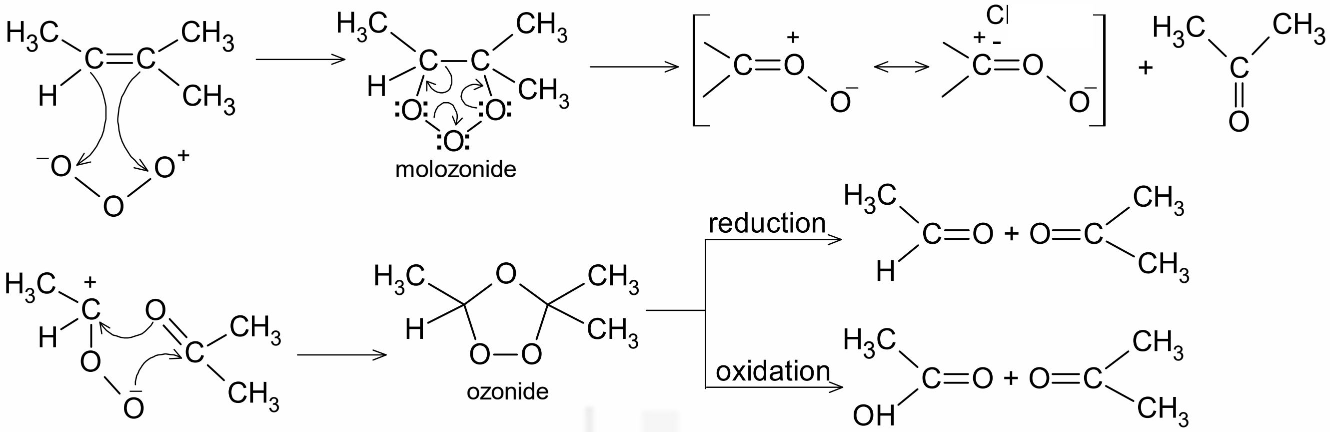
Ozonolysis consists of two separate reactions, first is the oxidation of the alkene or alkyne by ozone to give an ozonide; and the second is either oxidation or reduction of the ozonide to yield the cleavage products. For example reductive ozonolysis of 2-methyl-2-butene yields an aldehyde and a ketone, while oxidative ozonolysis give a carboxylic acid and a ketone.



Mechanism: Ozone can be represented as resonance hybrid of the following contributing structure:

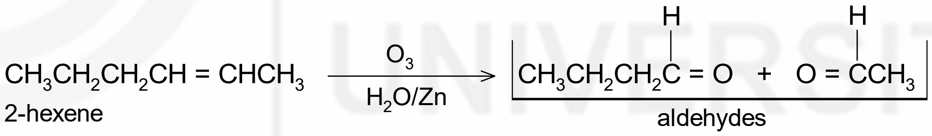


The first step consists of a 1,3-dipolar addition of ozone to the double bond forum, forming a molozonide. The molozonide, being unstable, subsequently decomposes into fragments. Recombination of these fragments in an alternative way yields an ozonide.

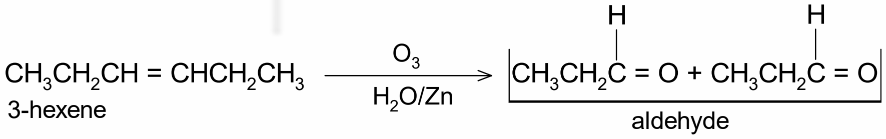


Low molecular-weight ozonides are highly explosive and are, therefore, not isolated. Instead, ozonides are usually further treated with either a reducing agent such as zinc metal in ethanoic acid or an oxidising agent, such as hydrogen peroxide to yield cleaved products. The overall reaction is known as ozonolysis. Knowing the number and arrangement of carbon atoms in those cleaved products, one can locate the position of the double bond in the original alkene.

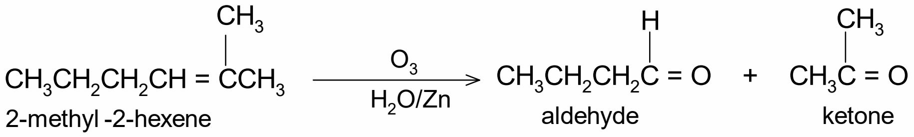
Some examples of ozonolysis are given below:



$$\underset{\text{2-hexene}}{CH_3CH_2CH_2CH = CHCH_3} \xrightarrow[H_2O/Zn]{O_3} \underbrace{CH_3CH_2CH_2\overset{H}{\overset{|}{C}} = O \;+\; O = \overset{H}{\overset{|}{C}}CH_3}_{\text{aldehydes}}$$



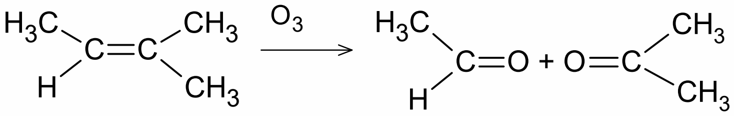
$$\underset{\text{3-hexene}}{CH_3CH_2CH = CHCH_2CH_3} \xrightarrow[H_2O/Zn]{O_3} \underbrace{CH_3CH_2\overset{H}{\overset{|}{C}} = O + CH_3CH_2\overset{H}{\overset{|}{C}} = O}_{\text{aldehyde}}$$



$$\underset{\text{2-methyl -2-hexene}}{CH_3CH_2CH_2CH = \overset{CH_3}{\overset{|}{C}}CH_3} \xrightarrow[H_2O/Zn]{O_3} \underset{\text{aldehyde}}{CH_3CH_2CH_2\overset{H}{\overset{|}{C}} = O} \;+\; \underset{\text{ketone}}{CH_3\overset{CH_3}{\overset{|}{C}} = O}$$

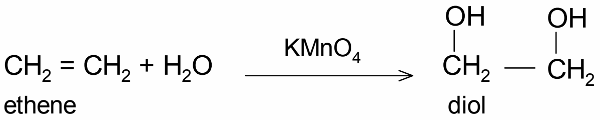
SAQ 8

Give the mechanism of the following reaction:

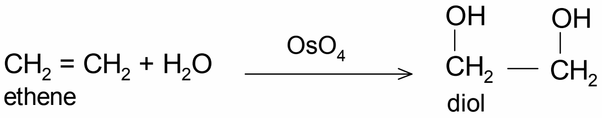


17.2.7 Hydroxylation

Alkenes are readily hydroxylated (addition of hydroxyl groups) to form a dihydroxy compound (diol) known as glycol. The most popular reagent used to convert an alkene to diol is cold alkaline aqueous solution of potassium permanganate or osmium tetraoxide. The yield with $KMnO_4$is quite low as compared to OsO_4, but the use of OsO_4 is limited because it is quite expensive and toxic.



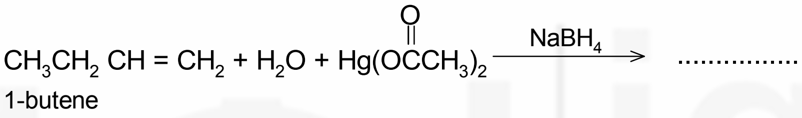
$$\underset{\text{ethene}}{CH_2 = CH_2 + H_2O} \xrightarrow{KMnO_4} \underset{\text{diol}}{\overset{OH}{\overset{|}{CH_2}} - \overset{OH}{\overset{|}{CH_2}}}$$



$$\underset{\text{ethene}}{CH_2 = CH_2 + H_2O} \xrightarrow{OsO_4} \underset{\text{diol}}{\overset{OH}{\overset{|}{CH_2}} - \overset{OH}{\overset{|}{CH_2}}}$$

SAQ 9

Predict the products of the following reactions:

a) 

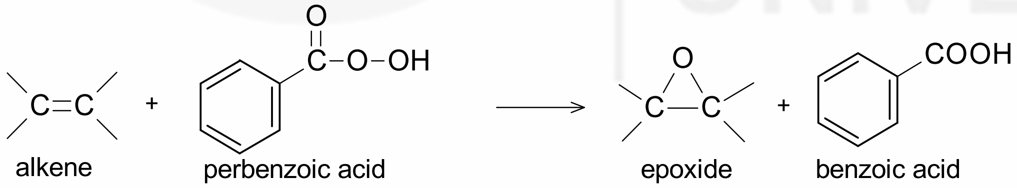
$$\underset{\text{1-butene}}{CH_3CH_2\,CH = CH_2} + H_2O + Hg(O\overset{O}{\overset{\|}{C}}CH_3)_2 \xrightarrow{NaBH_4} \ldots\ldots\ldots\ldots\ldots\ldots$$

b) $CH_2 = CH_2 + H_2O \xrightarrow{KMnO_4}$ ....

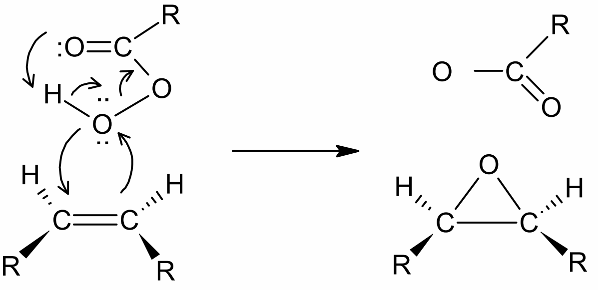
ethene

17.2.8 Expoxidation

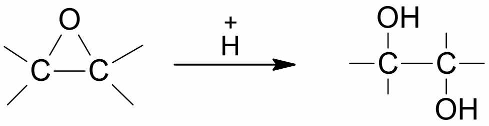
Oxidation of alkenes also gives epoxide. The double bond in alkene is converted into epoxide in presence of peracids. Epoxide is also known as oxirane. The peracids are perbenzoic acid ($C_6H_5COO_2H$), monoperphathalic *meta*-chloroperbenzoic acid (*m*-$ClC_6H_4CO_3H$, MCPBA), etc.



Mechanism



Expoxide easily converted into diol (glycols) in presence of an acid. In this reaction the diol formed is always a *trans* diol. That means the –OH group are introduced from the opposite site of the double bond.



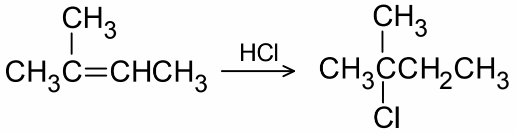
17.3 SUMMARY

In this Unit you have learnt that:

- the main reactions of alkenes are electrophilic addition reactions.
- these reactions include addition of halogen, alkyl halide and water.
- addition of hydrogen halide/water to unsymmetrical alkene follows Markownikoff's rule.
- Markownikoff's rule states that addition of a hydrogen halide to an unsymmetrical alkene takes place in such a way that the positive part of the reagent goes to that carbon atom of the alkene which carries the more number of hydrogen atoms.
- addition of HBr to alkenes in the presence of peroxide gives *anti*-Markownikoff's product.
- alkenes can be oxidised by ozone, giving an aldehyde or a ketone or a mixture of both.
- reaction of alkenes with permanganate and osmium tetraoxide gives dihydroxy compounds.
- borane adds to an alkene to give organoboranes, which undergo a variety of chemical reactions

17.4 TERMINAL QUESTIONS

1. Give the oxidation product of organoborane by alkaline H_2O_2.
2. Give the structural formula for the carbocation intermediate that leads to the principle product in the following reactions:



$$CH_3\overset{CH_3}{\overset{|}{C}}{=}CHCH_3 \xrightarrow{HCl} CH_3\underset{Cl}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_2CH_3$$

3. Give the products formed when HBr reacts with 2-methyl-2-butene in the presence of peroxide and in the absence of peroxide.
4. Complete the following reactions:

a) $CH_3CH_2{=}CH_2 + H_2O \xrightarrow[273\ K]{KMnO_4}$

b) $CH_3CH_2CH{=}CHCH_3 + HBr \longrightarrow$

c) $\underset{\text{1-propene}}{CH_3CH{=}CH_2} \xrightarrow[CH_3COOH]{(BH_3)_2}$

5. A, B and C are isomeric heptanes. On ozonolysis A gives ethanal and pentanal, B gives propanone and butanone and C gives ethanal and penta-3-one. Predict the structural formulae of A, B and C.

6. Iodine does not react with alkenes. Explain.

17.5 ANSWERS

Self-Assessment Questions

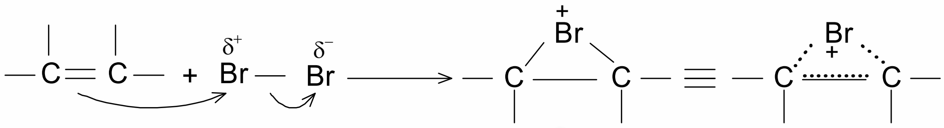
1. i) electrophilic

   ii) π

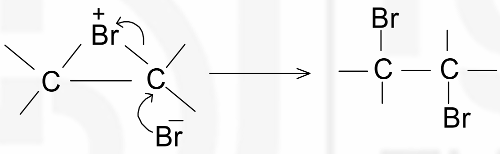
   iii) higher

   iv) concerted

2. Let us see the steps involved in the reaction.



The cyclic intermediate shields one side of the molecule and, hence, bromide attacks from the opposite side of the double bond to give *trans* product. This process is known as *trans* addition.



Addition of bromine is extremely useful for detection of carbon-carbon double bond. Rapid decolourisation of bromine solution serves as a test for the presence of the carbon-carbon double bond in a compound.

3. A carbocation formed, in an addition reaction of a hydrogen halide to an unsymmetrical alkene, often undergoes rearrangement (alkyl shift) to give a more stable carbocation. For example, addition of HBr to 3,3-dimethyl-1-butene gives two products, 2-bromo-3,3-dimethylbutane (normal product) and 2-bromo- 2,3-dimethylbutane (rearranged product).

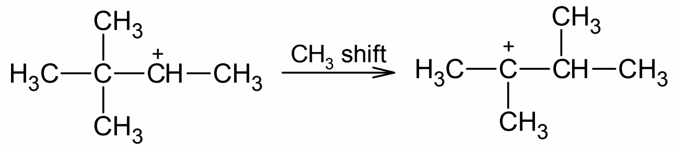
4. a) double

   b) iodine

   c) two

   d) *anti*-Markownikoff's

5.



$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-\overset{+}{C}H-CH_3 \xrightarrow{CH_3\ \text{shift}} H_3C-\underset{CH_3}{\overset{+}{C}}-\overset{CH_3}{C}H-CH_3$$

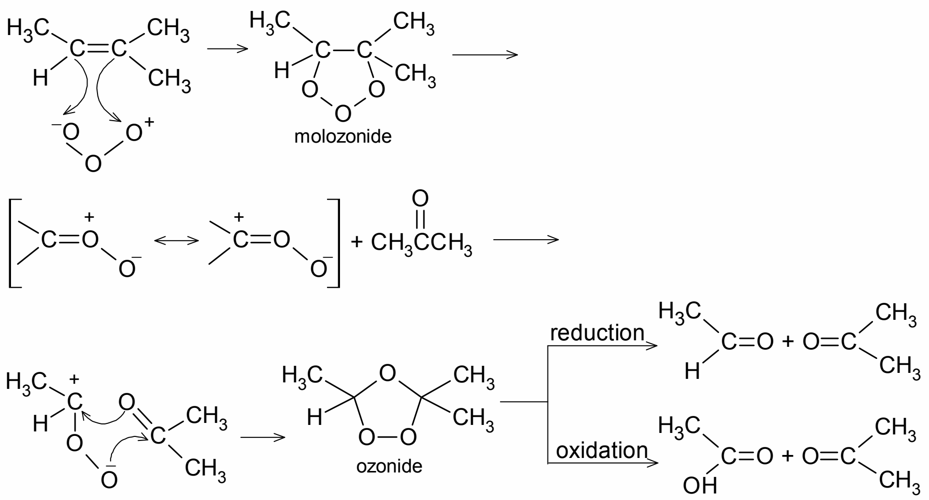
less stable (*sec.* C^+) more stable (*tert.* C^+)

6. a) T c) T

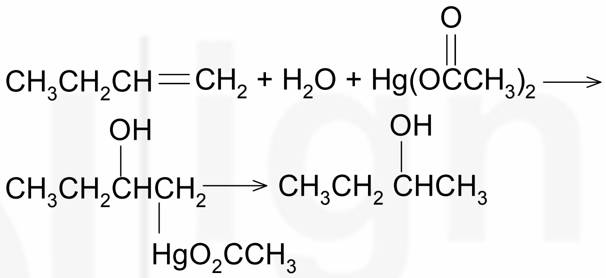
   b) T d) F

7. This is true only in literal sense, because hydrogen mostly acts as an electrophile, but in hydroboration hydrogen is the electronegative portion of the molecule instead of the electropositive portion.

8.



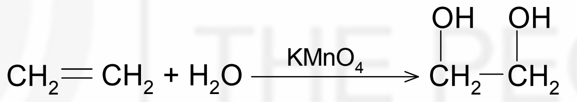
9. a)



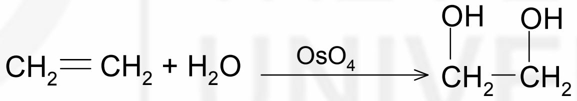
$$CH_3CH_2CH{=}CH_2 + H_2O + Hg(O\overset{\overset{O}{\|}}{C}CH_3)_2 \longrightarrow$$

$$CH_3CH_2\overset{\overset{OH}{|}}{C}H\underset{\underset{HgO_2CCH_3}{|}}{C}H_2 \longrightarrow CH_3CH_2\overset{\overset{OH}{|}}{C}HCH_3$$

b)



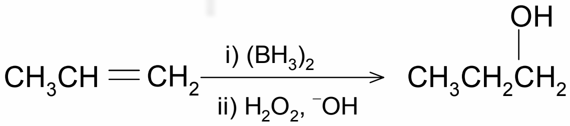
$$CH_2{=}CH_2 + H_2O \xrightarrow{KMnO_4} \overset{\overset{OH}{|}}{C}H_2{-}\overset{\overset{OH}{|}}{C}H_2$$



$$CH_2{=}CH_2 + H_2O \xrightarrow{OsO_4} \overset{\overset{OH}{|}}{C}H_2{-}\overset{\overset{OH}{|}}{C}H_2$$

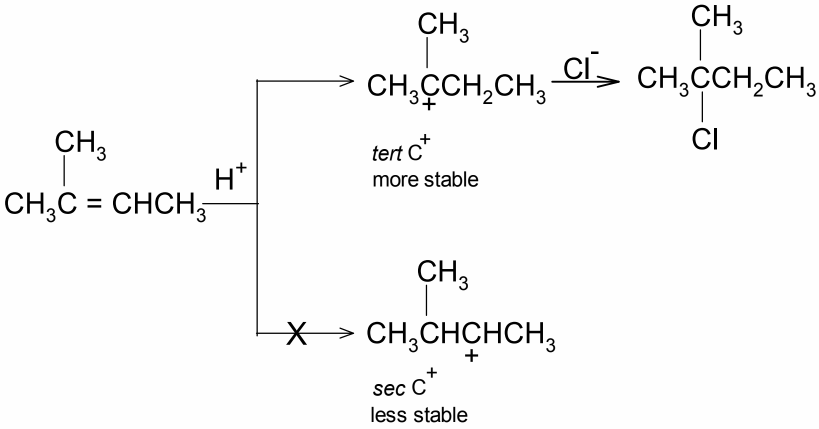
Terminal Questions

1.

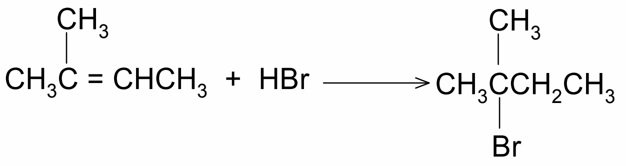


$$CH_3CH{=}CH_2 \xrightarrow[\text{ii) } H_2O_2,\ ^{-}OH]{\text{i) } (BH_3)_2} CH_3CH_2\overset{\overset{OH}{|}}{C}H_2$$

2.

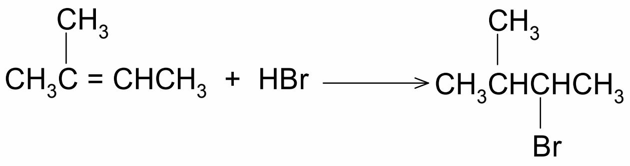


3. The addition of HBr in the absence of peroxide gives Markownikoff's product.



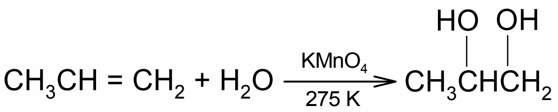
$$CH_3\overset{CH_3}{\overset{|}{C}} = CHCH_3 + HBr \longrightarrow CH_3\overset{CH_3}{\underset{Br}{C}}CH_2CH_3$$

The addition of HBr in the presence of peroxide gives Markownikoff's product.



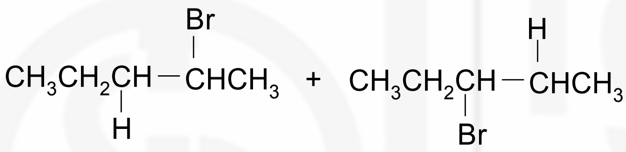
$$CH_3\overset{CH_3}{\overset{|}{C}} = CHCH_3 + HBr \longrightarrow CH_3\overset{CH_3}{CH}\underset{Br}{CH}CH_3$$

4. a)



$$CH_3CH = CH_2 + H_2O \xrightarrow[275\ K]{KMnO_4} CH_3\overset{HO}{CH}\overset{OH}{CH_2}$$

b) $CH_3CH_2CH = CHCH_3 + HBr \longrightarrow$

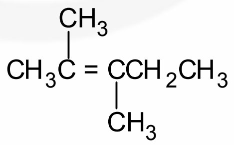


$$CH_3CH_2\underset{H}{CH}-\overset{Br}{C}HCH_3 + CH_3CH_2\underset{Br}{CH}-\overset{H}{C}HCH_3$$

c) $CH_3CH = CH_2 \xrightarrow[CH_3COOH]{(BH_3)_2} CH_3CH_2CH_3$

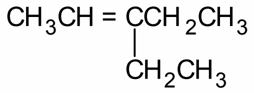
5. Compound A = $CH_3 = CHCH_2CH_2CH_2CH_3$

Compound B =



$$CH_3\overset{CH_3}{C} = \underset{CH_3}{C}CH_2CH_3$$

Compound C =



$$CH_3CH = \underset{CH_2CH_3}{C}CH_2CH_3$$

6. Addition of iodine to an alkene is a reversible reaction i.e., 1,2-diiodo product is unstable and loses I_2 to reform the alkene.

UNIT 18

ALKYNES

Structure

18.1 INTRODUCTION

In the preceding three units, you have studied the chemistry of alkanes and alkenes. We shall now study another kind of hydrocarbons known as alkynes which contain carbon-carbon triple bond(s).

First we will discuss the types of alkynes, their physical properties as well as uses. In the next part of this unit, we will learn the different methods of preparation of alkynes. Then you will study in this unit that the carbon-carbon triple bond reacts with many of the regents that react with alkenes. You will also study about the chemistry of alkynes.

Expected Learning Outcomes

After studying this unit, you should be able to:

- describe the various kinds of alkynes;
- list the physical properties of alkynes;
- discuss various methods for the preparation of alkynes; and
- explain the chemical reactions of alkynes.

18.2 ALKYNES AND THEIR TYPES

Alkynes, also known as acetylenes, constitute the homologous series of open chain unsaturated hydrocarbons that contain one or more carbon-carbon triple bond. The general formula of alkyneshaving one triple bond is C_nH_{2n-2}, e.g.

$HC\equiv CH$,	$HC\equiv C-CH_3C$,	$CH_3C\equiv CCH_3$, etc.
ethyne (acetylene)	1-propyne	2-butyne

Alkynes are of two types: terminal and internal. In the terminal alkynes, the triple bond lies at the end of the carbon chain and in the internal alkynes, the triple bond lies anywhere except at the terminal position.

$CH_3C\equiv CH$	$CH_2CH_3C\equiv CCH_2CH_3$
1-propyne (terminal alkyne)	3-hexyne (internal alkyne)

18.3 PHYSICAL PROPERTIES AND USES

The physical properties of alkynes are similar to those of corresponding alkenes. They are all colourless and odourless (except ethyne). The first three members, i.e. ethyne, propyne and 1-butyne, are gases at room temperature; the next eight members are liquids and the higher members are solids. Their physical constants like melting points, boiling points and densities increase gradually with the increase in the molecular weight. Alkynes have slightly higher boiling points than the corresponding alkenes and alkanes. Terminal alkynes have lower boiling points than the isomeric internal alkynes and hence, can be separated by careful fractional distillation. Alkynes share with alkanes and alkenes the properties of low density and low water solubility. They are nonpolar and dissolve readily in typical organic solvents, such as diethyl ether, chlorinated hydrocarbons, etc.

Ethyne, the simplest alkyne, was burnt in the miners' lamps before electric lamps were developed. It is used in oxyacetylene torches for cutting and welding metals. It is extensively used as a fuel gas. In industry, it is the starting material for preparation of many important chemicals, e.g., ethanoic acid, chloroethene (vinyl chloride), propanone, ethanol, butanol, etc.

A large number of naturally occurring compounds containing triple bonds have been isolated from plant kingdom. For example, a triyne from safflower has considerable activity against nematodes and evidently forms part of the plant's chemical **defense against infestation.**

SAQ 1

State which of the following statements are true/false. Write (T) for true and (F) for false in the boxes against the statements:

i) Ethyne is a colourless and odourless gas. ☐

ii) 1-Butyne is liquid at room temperature. ☐

iii) Alkynes have slightly higher boiling points than the corresponding alkenes and alkanes. ☐

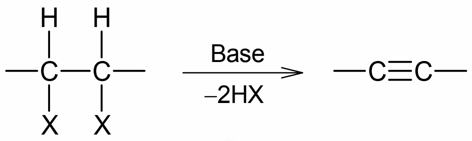
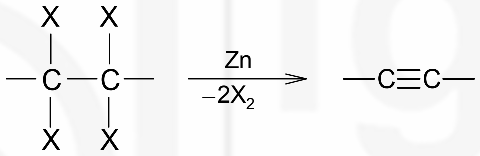
iv) Propyne is nonpolar and does not dissolve readily in diethyl ether, and chlorinated hydrocarbons. ☐

v) Alkyne has higher density than alkene and is highly soluble in water. ☐

18.4 PREPARTION OF ALKYNES

Organic synthesis makes use of two major reaction types: one is functional group transformation and the other is carbon-carbon bond forming reactions. Both these strategies are applied for preparation of alkynes. In this unit, we shall discuss how alkynes are prepared by elimination reactions and by adding alkyl group(s) to the smaller ethyne unit. Some important methods of preparation of alkynes are outlined in Table 18.1.

Table 18.1: Methods preparation of alkynes

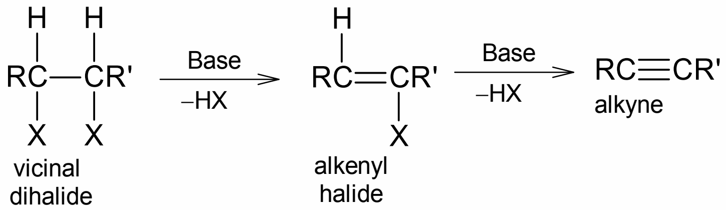
i)	**Dehydrohalogenation of dihalides** 
ii)	**Dehydrohalogenation of tetra halides** 
iii)	**Alkylation of terminal ethyne** $—C\equiv CH \xrightarrow{NaNH_2} —C\equiv \overset{-}{C}{:}\ \overset{+}{Na} \xrightarrow{RX} —C\equiv CR$

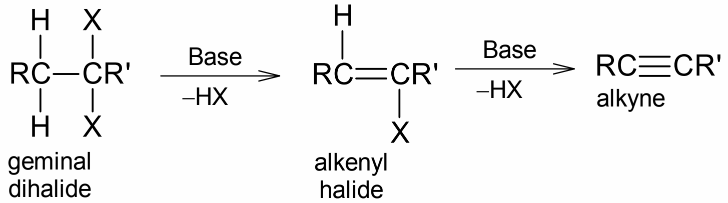
18.4.1 Dehydrohalogenation of Dihalides

You have already seen in Unit 17 that an alkene can be prepared by the elimination of HX from an alkyl halide. Similarly, an alkyne can be prepared by the elimination of two molecules of HX from a dihalide. The dihalide may be of the vicinal orgerminal type.

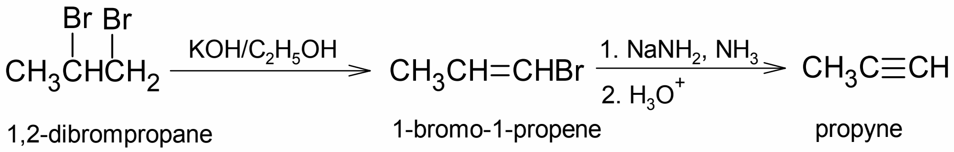
Vicinal dihalide: One in which halogen atoms are present on adjacent carbon atoms.

Geminal dihalide: One in which both the halogen atoms are present on the same carbon atom.



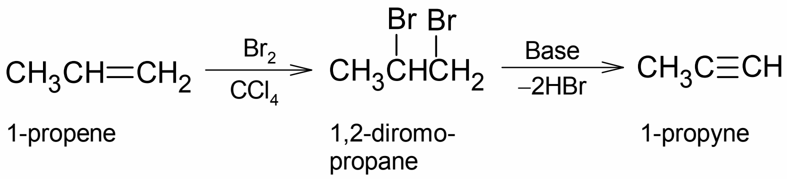


Since, an alkyne contains a triple bond, two molecules of HX must be eliminated from dihalide to get an alkyne. Therefore, stronger conditions are required to remove the second HX molecule. For example, when 1,2-dibromopropane reacts with a strong base, a two-fold elimination occurs and as a result propyne is produced.



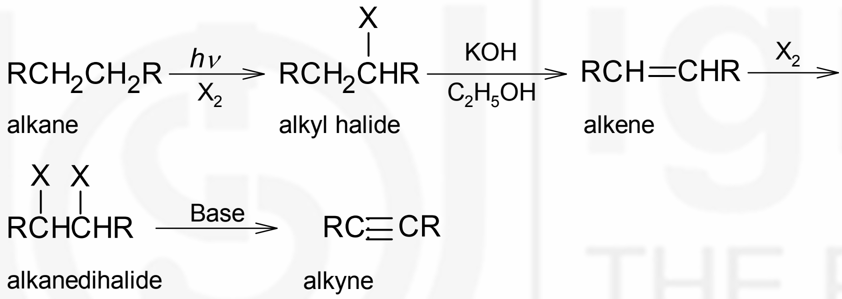
$$CH_3\overset{Br}{\overset{|}{C}}H\overset{Br}{\overset{|}{C}}H_2 \xrightarrow{KOH/C_2H_5OH} CH_3CH{=}CHBr \xrightarrow[2.\ H_3O^+]{1.\ NaNH_2,\ NH_3} CH_3C{\equiv}CH$$

You have studied in Unit 17 that dihalides are prepared by the addition of halogens to an alkene which leads to the formation of alkyne, e.g.



$$CH_3CH{=}CH_2 \xrightarrow[CCl_4]{Br_2} CH_3\overset{Br}{\overset{|}{C}}H\overset{Br}{\overset{|}{C}}H_2 \xrightarrow[-2HBr]{Base} CH_3C{\equiv}CH$$

You may recall that alkenes can be prepared by elimination reactions of alkyl halides, which again can be obtained from alkanes. Thus, we can say that alkanes can serve as a starting material for the preparation of alkynes.



$$RCH_2CH_2R \xrightarrow[X_2]{h\nu} RCH_2\overset{X}{\overset{|}{C}}HR \xrightarrow[C_2H_5OH]{KOH} RCH{=}CHR \xrightarrow{X_2}$$

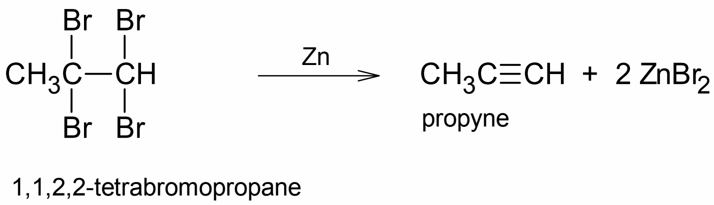
$$R\overset{X}{\overset{|}{C}}H\overset{X}{\overset{|}{C}}HR \xrightarrow{Base} RC{\equiv}CR$$

Different bases can be used for dehydrohalogenation; sodium amide is preferred, since it usually gives a higher yield.

The two-fold dehydrohalogenation follows the same mechanism as the dehydrohalogenation of alkyl halides to give alkenes, as mentioned in Unit 16.

18.4.2 Dehalogenation of Tetrahalides

Alkynes can also be prepared by dehalogenation of tetrahalides. For example, propyne is formed when the vapours of 1,1,2,2-tetrabromopropane are passed over heated zinc.



$$CH_3\underset{Br}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-\underset{Br}{\underset{|}{\overset{Br}{\overset{|}{C}}}}H \xrightarrow{Zn} CH_3C{\equiv}CH + 2\,ZnBr_2$$

This reaction does not have any synthetic importance, since the tetrahalides themselves are usually prepared from alkynes. However, it provides a method for the purification of alkynes.

18.4.3 Alkylation of Ethyne

One of the major differences between the chemistry of alkynes and that of alkenes or alkanes is that the hydrogen bonded to a triple bonded carbon atom of a terminal alkyne is quite acidic. It can be removed by a strong base, such as sodium amide, $NaNH_2$, to ethynide anion or acetylide anion. Ethyne is less acidic than water but 10^{13} times more acidic than ammonia and 10^{18} times more acidic than ethene or ethane.

As you have studied in your earlier classes, the acidic character of hydrogen bonded to triple bond is due to high electronegativity of triply bonded carbon (*sp* hybrid).

Reactions that lead to the attachment of an alkyl group to a molecular fragment are called alkylation.

In this sub-section, we shall see how alkynes are prepared by combining smaller units to build larger carbon chains. One of these structural units is ethyne itself. By attaching alkyl group to ethyne, larger chain alkyne can be prepared. For example,

$$HC{\equiv}CH \xrightarrow{Na/NH_3} \underset{\text{sodium ethynide}}{HC{\equiv}\overset{-}{C}{:}\overset{+}{Na}}$$

$$HC{\equiv}\overset{-}{C}{:}\overset{+}{Na} + \underset{\text{1-iodobutane}}{ICH_2CH_2CH_2CH_3} \longrightarrow \underset{\substack{\text{1-hexyne}\\ \text{(86\% yield)}}}{HC{\equiv}C(CH_2)_3CH_3} + NaI$$

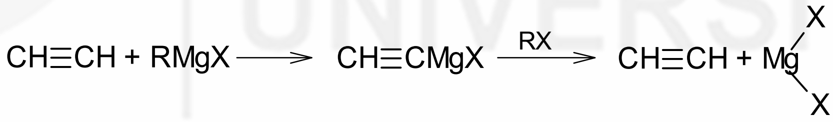
Alkylation is a two-step process. In the first step, ethyne reacts with sodium amide to give ethynide ion, the conjugated base of ethyne.

In the second step, sodium ethynide attacks the C-1 carbon atom of 1-iodobutane and pushes out the iodide ion, yielding the terminal alkyne,. 1-hexyne, giving an overall 86% yield. Again, 1-hexyne can itself be converted into an alkynide anion and can be alkylated a second time to yield an internal alkyne. A different alkyl halide can be used this time.

$$\underset{\text{1-hexyne}}{CH_3(CH_2)_3C{\equiv}CH} \xrightarrow[\text{2. } CH_3CH_2Br]{\text{1. } NaNH_2} \underset{\text{3-octyne}}{CH_3(CH_2)_3C{\equiv}CCH_2CH_3}$$

This reaction gives good yields of alkyne only with primary alkyl bromides and iodides.

Alkylation can also be carried out by reacting ethyne and Grignard reagent, followed by the action of an alkyl halide,



$$CH{\equiv}CH + RMgX \longrightarrow CH{\equiv}CMgX \xrightarrow{RX} CH{\equiv}CH + Mg\begin{smallmatrix}X\\X\end{smallmatrix}$$

SAQ 2

Suggest a method for preparation of the following alkynes starting with ethyne. Use any alkyl halide needed.

a) 2-Heptyne

b) 3-Heptyne

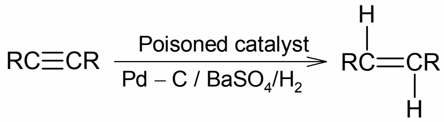
18.5 REACTIONS OF ALKYNES

The simplest alkyne that is ethyne is useful in many industries. It is a source of number of compounds which are used to make polymers. Due to the presence of loosely held π electrons, alkynes undergo reactions similar to those of alkenes. You will see in this unit that some of the chemical characteristics of alkynes are similar to those of alkenes. The characteristic reactions of alkynes include i) hydrogenation, ii) halogenation, iii) hydrohalogenation, iv) hydration, v) ozonolysis and vi) hydroboration. These actions of alkynes are summarised in Table 18.2.

Table 18.2: Reactions of Alkynes

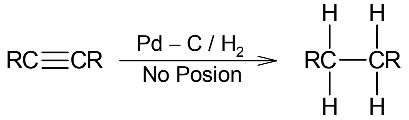
i) Hydrogenation

a)



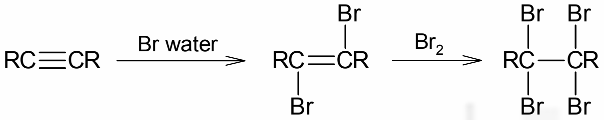
$RC\equiv CR \xrightarrow[\text{Pd – C / BaSO}_4\text{/H}_2]{\text{Poisoned catalyst}} \overset{H}{\overset{|}{RC}}=\underset{H}{\underset{|}{CR}}$

b)



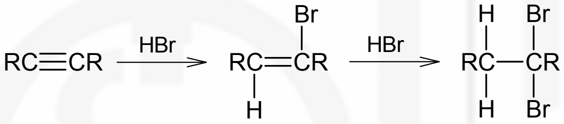
$RC\equiv CR \xrightarrow[\text{No Posion}]{\text{Pd – C / H}_2} \underset{H}{\underset{|}{\overset{H}{\overset{|}{RC}}}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{CR}}}}$

ii) Halogenation



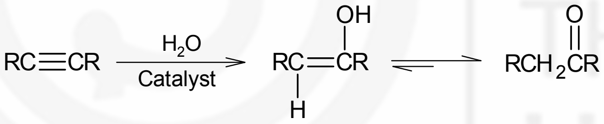
$RC\equiv CR \xrightarrow{\text{Br water}} \underset{Br}{\underset{|}{RC}}=\overset{Br}{\overset{|}{CR}} \xrightarrow{Br_2} \underset{Br}{\underset{|}{\overset{Br}{\overset{|}{RC}}}}-\underset{Br}{\underset{|}{\overset{Br}{\overset{|}{CR}}}}$

iii) Hydrohalogenation



$RC\equiv CR \xrightarrow{HBr} \underset{H}{\underset{|}{RC}}=\overset{Br}{\overset{|}{CR}} \xrightarrow{HBr} \underset{H}{\underset{|}{\overset{H}{\overset{|}{RC}}}}-\underset{Br}{\underset{|}{\overset{Br}{\overset{|}{CR}}}}$

iv) Hydration

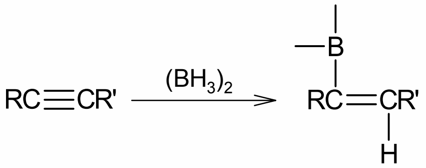


$RC\equiv CR \xrightarrow[\text{Catalyst}]{H_2O} \underset{H}{\underset{|}{RC}}=\overset{OH}{\overset{|}{CR}} \rightleftharpoons RCH_2\overset{O}{\overset{\|}{C}}R$

v) Ozonolysis

$RC\equiv CR \xrightarrow{O_3} RCOOH + HOOCR$

vi) Hydroboration



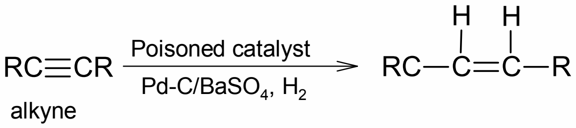
$RC\equiv CR' \xrightarrow{(BH_3)_2} \overset{-\overset{|}{B}}{\overset{|}{RC}}=\underset{H}{\underset{|}{CR'}}$

18.5.1 Hydrogenation

Like alkenes, alkynes undergo catalytic hydrogenation. Hydrogenation of an alkyne in presence of Pd, Pt or Ni catalyst yields an alkane. The addition of hydrogen to an alkyne takes place in two steps. The first addition results in the formation of an alkene; since an alkene can also undergo catalytic hydrogenation, the second addition of hydrogen gives an alkane. By using a

A catalyst mixed with a selective inhibiting agent is called a poisoned catalyst.

calculated amount of hydrogen and a poisoned catalyst, hydrogenation can be stopped at the alkene stage. These catalysts **selectively** block the hydrogenation of alkenes.



$$\underset{\text{alkyne}}{RC\equiv CR} \xrightarrow[\text{Pd-C/BaSO}_4,\ H_2]{\text{Poisoned catalyst}} RC-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-R$$

This is stereoselective addition reaction giving predominantly the *cis* alkenes. In the absence of a poison, the catalytic hydrogenation of an alkyne gives the alkane.

Stereoselective reaction is a reaction which yields predominantly one isomer.

$$RC\equiv CR \xrightarrow[\text{No poisoned catalyst}]{H_2,\ Pd/C} \underset{\text{alkane (95\% yield)}}{RCH_2CH_2R}$$

If we carry out the reduction of an alkyne with sodium metal or lithium metal in liquid ammonia, *trans*-alkene is almost an exclusive product. This reaction is known as **Birch reduction** which you have studied in sub-section 16.4.4 of Unit 16.

SAQ 3

Suggest a method for the synthesis of the following compounds from 2-hexyne:

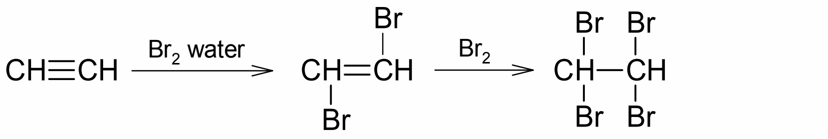
a) *trans*-2-hexene

b) *cis*-2-hexene

c) hexane

18.5.2 Halogenation

Alkynes react with chlorine and bromine to yield tetrahaloalkanes. Two molecules of halogen add to the triple bond. A dihaloalkene is an intermediate and can be isolated using proper reaction conditions. Ethyne, on treatment with bromine water gives only 1,2-dibromoethene whereas with bromine alone, it forms 1,1,2,2-tetrabromoethane.



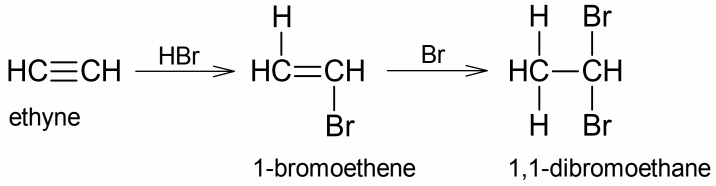
$$CH\equiv CH \xrightarrow{Br_2\text{ water}} \underset{\underset{Br}{|}}{CH}=\overset{\overset{Br}{|}}{CH} \xrightarrow{Br_2} \overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{CH}}-\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{CH}}$$

1,2-dibromoethene 1,1,2,2-tetrabromoethane

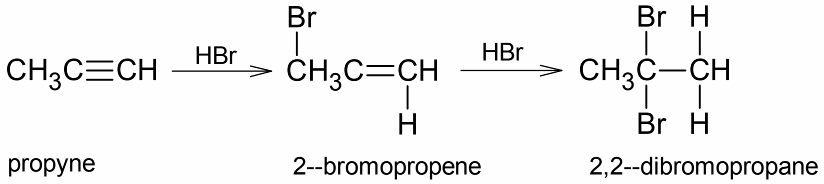
The addition of halogens to ethyne is stereoselective; the predominant product is the *trans* isomer.

18.5.3 Hydrohalogenation

Halogen acid (HX) can add on the alkyne giving haloalkene or haloalkane. This reaction is known as **hydrohalogenation**. Like alkenes, the addition is in accordance with Markownikoff's rule. In case of symmetrical alkynes, it gives one product. For example, ethyne combines with hydrogen bromide to form first 1-bromoethene and then the addition of second hydrogen bromide molecule gives 1,1-dibromoethane.

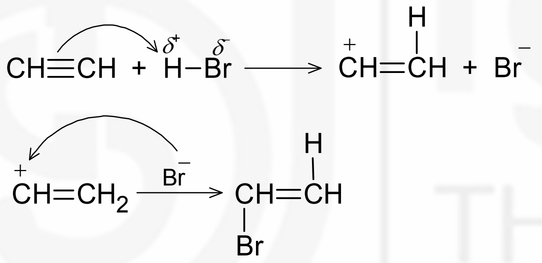


But in case of unsymmetrical alkynes there is a possibility of forming two products. For example, addition of HBr to 1-propyne will give 2, 2-dibromopropane not 1,1-dibromopropane as it follows Markownikoff's addition.

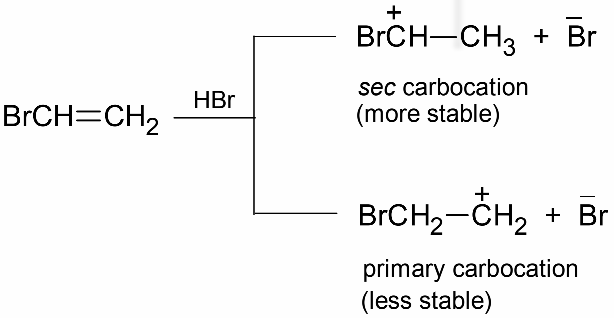


Mechanism

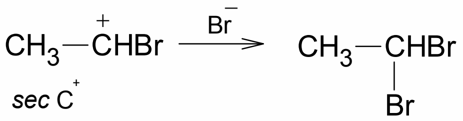
The mechanism of these reactions is the same as in the hydrohalogenation of alkenes, i.e.,



Addition of another molecule of hydrogen bromide could give either a secondary carbocation or a primary carbocation.

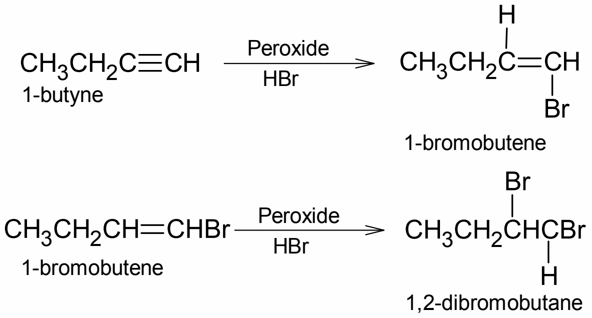


Since, the secondary carbocation is more stable than the primary carbocation, the reaction proceeds via the secondary carbocation to form 1,1-dibromoethane. Thus,



Because of the electron-withdrawing nature of bromine atom, the availability of π electrons in 1-bromoethene is less than that of ethene. Hence, the electrophilic addition of HBr to 1-bromoethene is much slower than that to ethene.

In the presence of free radical initiators such as peroxides, *anti*-Markownikoff's addition of HBr is observed as with alkenes. For example, addition of HBr in the presence of peroxides to 1-butyne gives 1,2-dibromobutane, as shown below:



$$\underset{\text{1-butyne}}{CH_3CH_2C\equiv CH} \xrightarrow[\text{HBr}]{\text{Peroxide}} \underset{\text{1-bromobutene}}{CH_3CH_2\overset{H}{C}=\underset{Br}{CH}}$$

$$\underset{\text{1-bromobutene}}{CH_3CH_2CH=CHBr} \xrightarrow[\text{HBr}]{\text{Peroxide}} \underset{\text{1,2-dibromobutane}}{CH_3CH_2\overset{Br}{C}H\underset{H}{C}Br}$$

SAQ 4

Write chemical equation for the reaction of propyne with each of the following reagents:

a) HCl

b) Cl_2

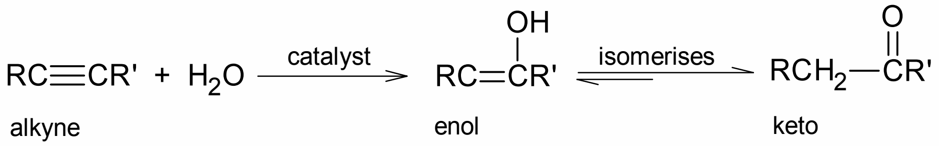
c) HBr (in presence of peroxide)

SAQ 5

Addition of HBr to ethene is much faster than that to 1-bromoethene. Explain.

18.5.4 Hydration

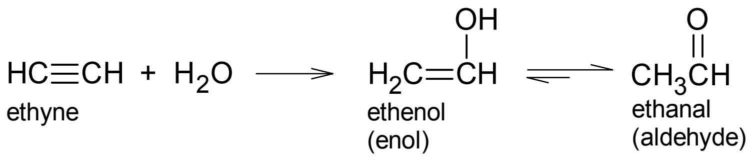
You have seen in Unit17that addition of a water molecule to an alkene gives an alcohol. Similarly, addition of a water molecule to an alkyne gives an enol. An enol has the –OH group attached to a carbon-carbon double bond.



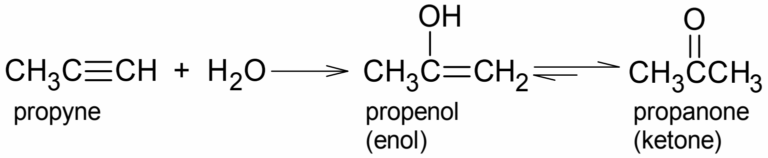
$$\underset{\text{alkyne}}{RC\equiv CR'} + H_2O \xrightarrow{\text{catalyst}} \underset{\text{enol}}{RC=\overset{OH}{C}R'} \underset{}{\overset{\text{isomerises}}{\rightleftharpoons}} \underset{\text{keto}}{RCH_2-\overset{O}{\overset{\|}{C}}R'}$$

The arrow is longer towards aldehyde or ketone side showing the direction in which the equilibrium is favoured.

In fact, enols are very unstable and they isomerise (or tautomerise) to give aldehyde or ketones. The process by which enols are converted into aldehydes or ketones is called keto-enol isomerism or keto-enol tautomerism. For example, when ethyne undergoes hydration, it gives an aldehyde, i.e., ethanal; while, propyne gives a ketone, i.e. propanone.



$$\underset{\text{ethyne}}{HC\equiv CH} + H_2O \longrightarrow \underset{\text{ethenol (enol)}}{H_2C=\overset{OH}{C}H} \rightleftharpoons \underset{\text{ethanal (aldehyde)}}{CH_3\overset{O}{\overset{\|}{C}}H}$$

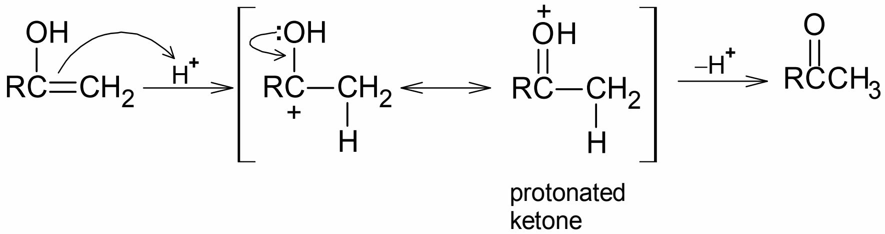


$$CH_3C{\equiv}CH + H_2O \longrightarrow CH_3\overset{OH}{\overset{|}{C}}{=}CH_2 \rightleftharpoons CH_3\overset{O}{\overset{||}{C}}CH_3$$

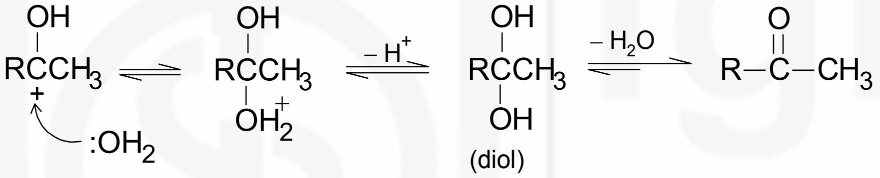
In case of unsymmetrical alkynes, addition of water takes place in accordance with Markwonikoff's rule.

Mechanism

Enol is converted into an aldehyde or a ketone by a mechanism similar to the hydration of a double bond. The enol double-bond is protonated to give a carbocation. The carbocation, in the example below, is a protonated ketone. Instead of addition of water,this ion loses a proton to give ketone.

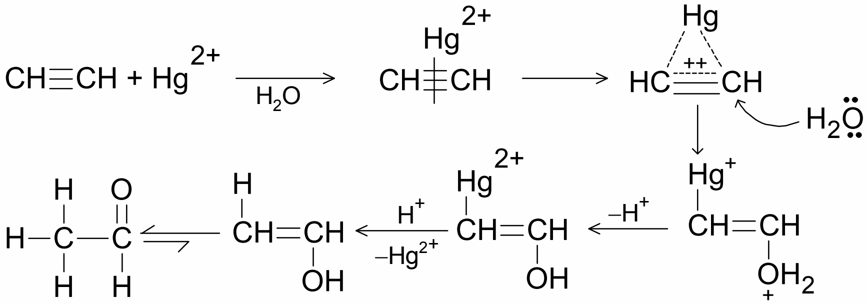


Now you may ask why carbocation is not attacked by water molecule to give a diol, i.e.,



This reaction does not occur, because it is reversible, and the equilibrium between the ketone and the corresponding diol in most cases favours formation of the ketone.

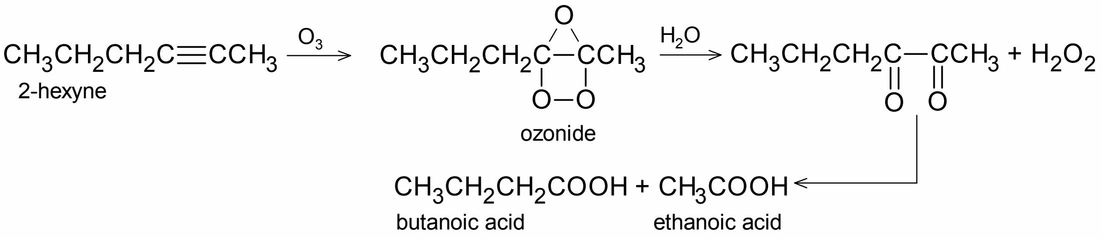
Alkynes cannot be hydrated as easily as simple alkenes, because of their lower reactivity towards electrophilic addition. However, in the presence of mercuric sulphate a catalyst, hydration occurs readily. A possible explanation of the function of the catalyst is that Hg^{2+} ion being of a large size, readily forms a bridged ion, a π complex, which then reacts as shown below:



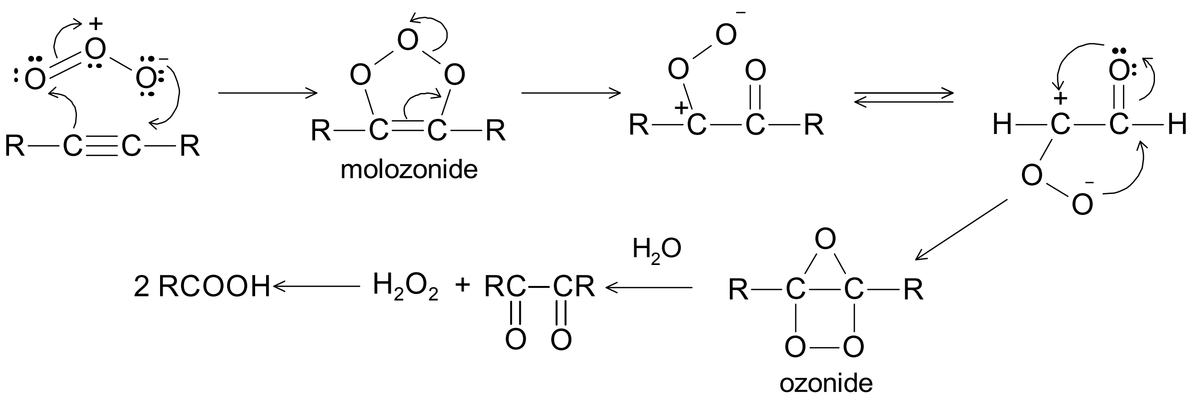
18.5.5 Ozonolysis

Reagents and reactions that lead to oxidative cleavage of alkenes also lead to cleavage of alkynes. Addition of ozone to an alkyne produces the ozonide.

The ozonide on hydrolysis gives 1,2-dicarbonyl compound, which undergo oxidative cleavage to carboxylic acids by hydrogen peroxide formed in the reaction. For example, 2-hexyne on ozonolysis gives butanoic and ethanoic acids.



Mechanism



Same products are obtained when alkynes are oxidised by alkaline permanganate and then hydrolysed using mineral acid.

$$CH_3CH_2CH_2C\equiv CCH_3 \xrightarrow[2.\ H^+]{1.\ KMnO_4,\bar{O}H} CH_3CH_2CH_2COOH + CH_3COOH$$

2-hexyne butanoic acid ethanoic acid

Oxidative cleavage reactions are used as a tool in structure determination. The carboxylic acids formed would tell us which of the carbon atoms linked through the triple bond in the original alkyne.

SAQ 6

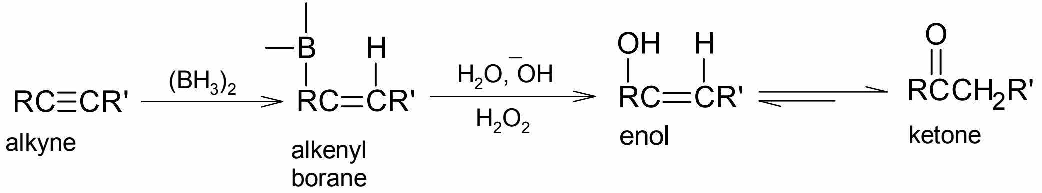
Propose structures for alkynes that give the following products on oxidative cleavage:

a) $CH_3(CH_2)_7COOH + HOOC(CH_2)_7\ COOH$

b) $CH_3CH_2COOH + CH_3CH_2COOH$

18.5.6 Hydroboration

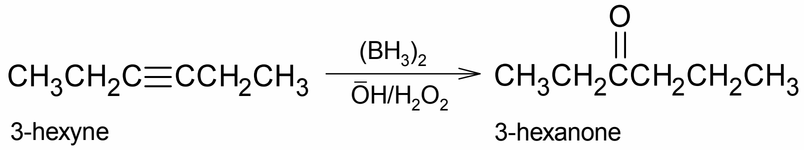
Addition of borane to alkynes gives alkenylboranes, which can be oxidised by basic hydrogen peroxide to ketones via enol.



$$RC\equiv CR' \xrightarrow{(BH_3)_2} \underset{\text{alkenyl borane}}{RC(B)=CR'(H)} \xrightarrow[H_2O_2]{H_2O,\ ^{-}OH} \underset{\text{enol}}{RC(OH)=CR'(H)} \rightleftharpoons \underset{\text{ketone}}{RC(=O)CH_2R'}$$

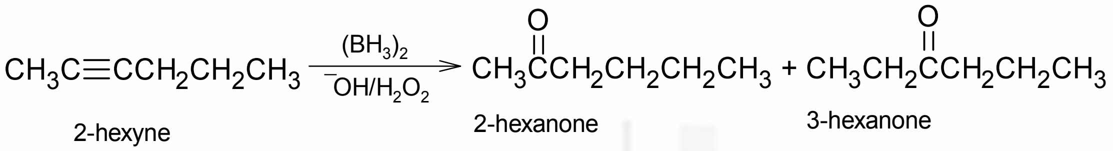
The symmetrical internal alkynes give a single product while unsymmetrical internal alkynes give a mixture of both the possible ketones. For example, 3-hexyne gives 3-hexanone while 2-hexyne gives a mixture of 2-hexanone and 3-hexanone.

Symmetrical internal alkyne



$$\underset{\text{3-hexyne}}{CH_3CH_2C\equiv CCH_2CH_3} \xrightarrow[^{-}OH/H_2O_2]{(BH_3)_2} \underset{\text{3-hexanone}}{CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3}$$

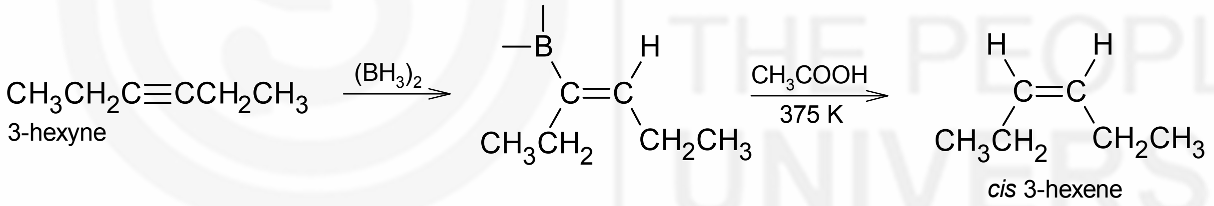
Unsymmetrical internal alkyne



$$\underset{\text{2-hexyne}}{CH_3C\equiv CCH_2CH_2CH_3} \xrightarrow[^{-}OH/H_2O_2]{(BH_3)_2} \underset{\text{2-hexanone}}{CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_3} + \underset{\text{3-hexanone}}{CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3}$$

The terminal alkynes on hydroboration give aldehydes.

Another reaction of organoboranes is **protonolysis.** That is, the alkenylboranes, formed after the addition of borane to alkynes, on treatment with ethanoic acid it gives *cis*–alkenes. This reaction sequence provides another method of converting alkynes to *cis*–alkenes.



SAQ 7

Give the equation for hydroboration of a terminal alkyne.

18.6 SUMMARY

In this unit, you have learnt that:

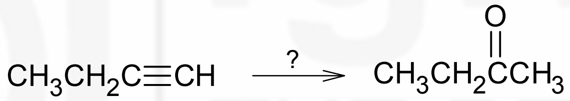
- alkynes are the hydrocarbons with one or more carbon-carbon triple bond.
- alkynesare of two types, i.e., terminal alkyne andinternal alkyne.
- physical properties of alkynes are more or less similar to alkenes.
- alkynes can also be prepared by a two-fold elimination of HX from dihalide or by dehalogenation of tetrahalides.

- higher alkynes are prepared by alkylation of terminal alkynes.
- electrophilic addition reactions (Hydrogenation, halogenation and hydrohalogenation) of alkynes follow Markownikoff's rule.
- hydration of an alkyne gives an unstable enol which tautomerises to give an aldehyde or a ketone.
- halogens add to alkynes to give tetrahaloalkanes. Using proper reaction conditions, dihaloalkene can be isolated.
- hydrogenation of an alkyne in the presence of Pd, Pt or Ni catalyst yields an alkane. By using poisoned catalyst, the intermediate *cis*-alkene can be obtained.
- reduction of an alkyne with sodium or lithium in liquid ammonia gives the *trans*-alkene.
- ozonolysis of alkynes gives carboxylic acids.
- hydroboration of alkynes may give ketones or aldehydes, depending on reaction conditions and the type of the alkyne.

18.7 TERMINAL QUESTIONS

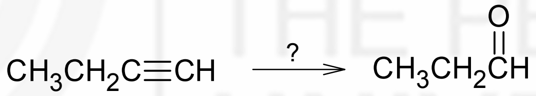
1. Write any three uses of aklynes.
2. How would you carry out the following reactions?

a)



$$CH_3CH_2C{\equiv}CH \xrightarrow{?} CH_3CH_2\overset{\overset{O}{\parallel}}{C}CH_3$$

b)

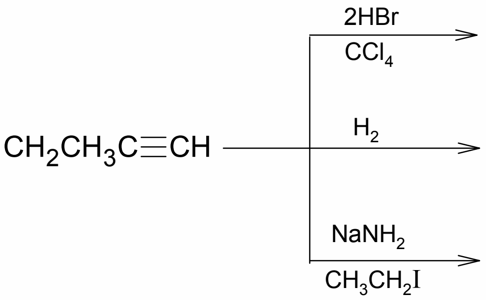


$$CH_3CH_2C{\equiv}CH \xrightarrow{?} CH_3CH_2\overset{\overset{O}{\parallel}}{C}H$$

c) $CH_3CH_2C{\equiv}CHCH_3 \xrightarrow{?} CH_3CH_2COOH + CH_3COOH$

d) $CH_3CH_2CH_2CH{=}CH_2 \xrightarrow{?} CH_3CH_2CH_2C{\equiv}CH$

3. Predict the product of the following reactions of 1-butyne:



4. How will you convert?

a) 2-bromopropane to propyne

b) 1-bromopropane to 2-hexyne.

5. Suggest steps for the followingtransformations:

   a) 2,3-dibromopentane to *trans*-2-pentene

   b) 3-methyl-1-butyne to *trans*-2-methyl-3-heptene

6. Show, by writing appropriate chemical equations, how each of the following compounds could be converted to 1-hexyne:

   a) 1,2-dibromohexane

   b) 1-hexene

   c) Hexane

18.8 ANSWERS

Self-Assessment Questions

1. i) F, ii) F, iii) T, iv) F, v) F

2. a) $HC\equiv CH \xrightarrow{NaNH_2,\ NH_3} HC\equiv\overset{-}{C}\overset{+}{Na}$

$HC\equiv\overset{-}{C}\overset{+}{Na} + CH_3(CH_2)_3Br \longrightarrow HC\equiv C(CH_2)_3CH_3$

$HC\equiv C(CH_2)_3CH_3 \xrightarrow{NaNH_2,\ NH_3} \overset{+}{Na}\overset{-}{C}\equiv C(CH_2)_3CH_3$

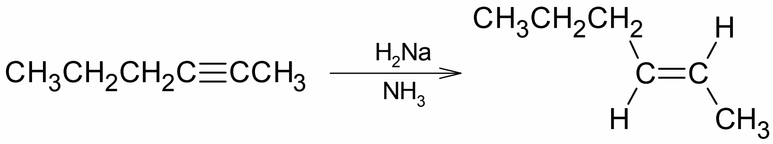
$\overset{+}{Na}\overset{-}{C}\equiv C(CH_2)_3CH_3 + CH_3Br \longrightarrow CH_3C\equiv C(CH_2)_3CH_3$

b) $HC\equiv CH \xrightarrow[2.\ CH_3(CH_2)_2Br]{1.\ NaNH_2,\ NH_3} HC\equiv C(CH_2)_2CH_3$

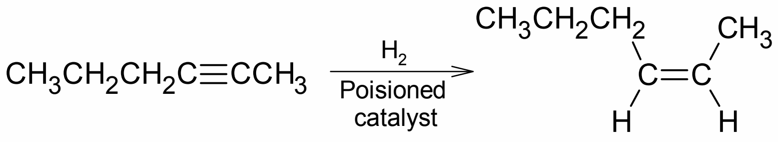
$HC\equiv C(CH_2)_2CH_3 \xrightarrow[NH_3]{NaNH_2} \overset{+}{Na}\overset{-}{C}\equiv C(CH_2)_2CH_3$

$\overset{+}{Na}\overset{-}{C}\equiv C(CH_2)_2CH_3 + CH_3CH_2Br \longrightarrow CH_3CH_2C\equiv C(CH_2)_2CH_3$

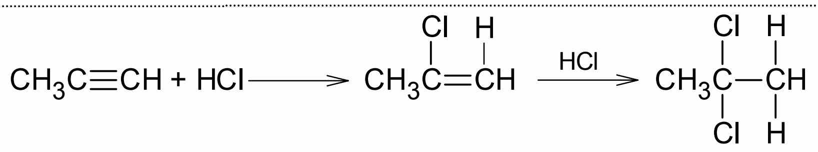
3. a)



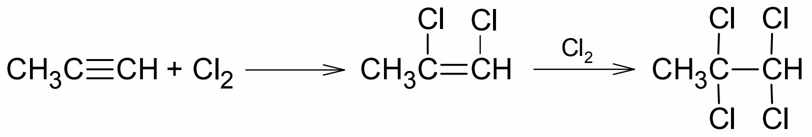
b)



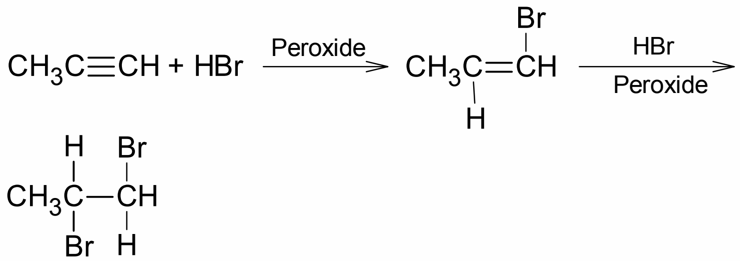
c) $CH_3CH_2CH_2C\equiv CCH_3 \xrightarrow{Pd/H_2} CH_3(CH_2)_4CH_3$

4. a) 

$$CH_3C\equiv CH + HCl \longrightarrow CH_3\overset{Cl}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}H \xrightarrow{HCl} CH_3\underset{Cl}{\overset{Cl}{C}}-\underset{H}{\overset{H}{C}}H$$

b) 

$$CH_3C\equiv CH + Cl_2 \longrightarrow CH_3\overset{Cl}{\overset{|}{C}}=\overset{Cl}{\overset{|}{C}}H \xrightarrow{Cl_2} CH_3\underset{Cl}{\overset{Cl}{C}}-\underset{Cl}{\overset{Cl}{C}}H$$

c) 

$$CH_3C\equiv CH + HBr \xrightarrow{Peroxide} CH_3\underset{H}{C}=\overset{Br}{\overset{|}{C}}H \xrightarrow[Peroxide]{HBr} CH_3\underset{Br}{\overset{H}{C}}-\underset{H}{\overset{Br}{C}}H$$

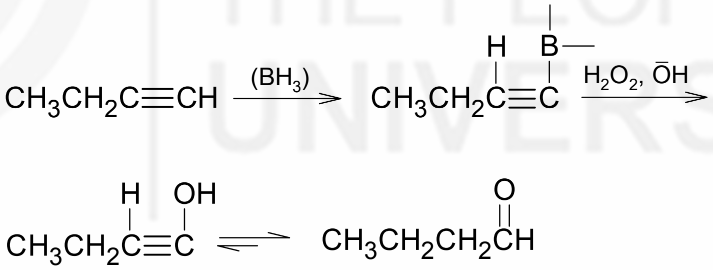
5. Because of the electron-withdrawing nature of bromine atom the availability of π electrons in 1-bromoethene is less than that of ethene. Hence, the electrophilic addition of HBr to 1-bromoethene is much slower than that to ethene.

6. a) $CH_3(CH_2)_7C\equiv C(CH_2)_7COOH \xrightarrow{O_3}$

$CH_3(CH_2)_7COOH + HOOC(CH_2)_7COOH$

b) $CH_3CH_2C\equiv CCH_2CH_3 \xrightarrow[\text{or } KMnO_4]{O_3}$

$CH_3CH_2COOH + CH_3CH_2COOH$

7. a) 

$$CH_3CH_2C\equiv CH \xrightarrow{(BH_3)} CH_3CH_2\overset{H}{\overset{|}{C}}\equiv\overset{\overset{|}{B}-}{\overset{|}{C}} \xrightarrow{H_2O_2,\ \bar{O}H}$$

$$CH_3CH_2\overset{H}{\overset{|}{C}}\equiv\overset{OH}{\overset{|}{C}} \rightleftharpoons CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}H$$

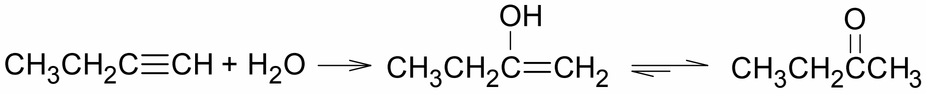
Terminal Questions

1. a) burnt in the miners lamp.

   b) used in oxyacetylene torches for cutting and welding metals.

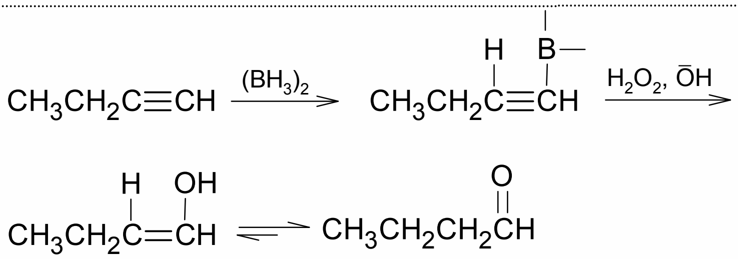
   c) extensively used as a fuel gas.

   d) In industry, it is the starting material for preparation of many important chemicals, e.g., ethanoic acid, chloroethene (vinyl chloride), propanone, ethanol, butanol, etc.

2. a) 

$$CH_3CH_2C\equiv CH + H_2O \longrightarrow CH_3CH_2\overset{OH}{\overset{|}{C}}=CH_2 \rightleftharpoons CH_3CH_2\overset{O}{\overset{\|}{C}}CH_3$$

b)

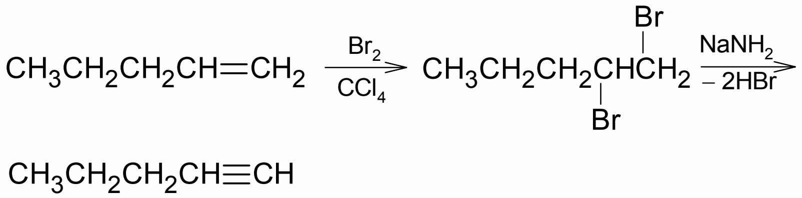


$$CH_3CH_2C\equiv CH \xrightarrow{(BH_3)_2} CH_3CH_2\overset{H}{C}\equiv\overset{B-}{C}H \xrightarrow{H_2O_2,\ \bar{O}H}$$

$$CH_3CH_2\overset{H}{C}=\overset{OH}{C}H \rightleftharpoons CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}H$$

c) $$CH_3CH_2CH_2C\equiv CCH_3 \xrightarrow[\text{or } KMnO_4]{O_3} CH_3CH_2COOH + CH_3COOH$$

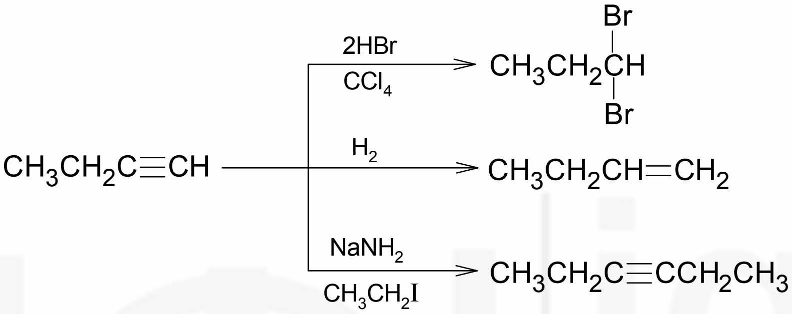
d)



$$CH_3CH_2CH_2CH=CH_2 \xrightarrow[CCl_4]{Br_2} CH_3CH_2CH_2\underset{Br}{C}H\overset{Br}{C}H_2 \xrightarrow[-\,2HBr]{NaNH_2}$$

$$CH_3CH_2CH_2CH\equiv CH$$

3.

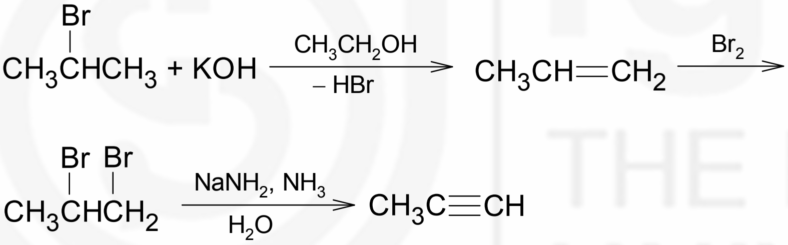


$$CH_3CH_2C\equiv CH \xrightarrow[CCl_4]{2HBr} CH_3CH_2\underset{Br}{\overset{Br}{C}}H$$

$$CH_3CH_2C\equiv CH \xrightarrow{H_2} CH_3CH_2CH=CH_2$$

$$CH_3CH_2C\equiv CH \xrightarrow[CH_3CH_2I]{NaNH_2} CH_3CH_2C\equiv CCH_2CH_3$$

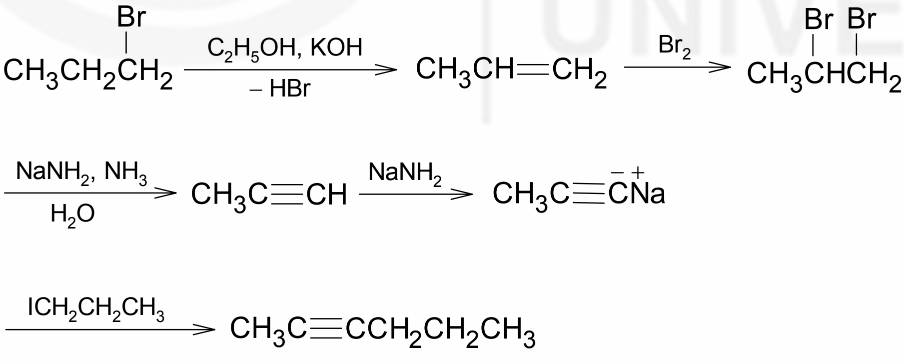
4. a)



$$CH_3\overset{Br}{C}HCH_3 + KOH \xrightarrow[-\,HBr]{CH_3CH_2OH} CH_3CH=CH_2 \xrightarrow{Br_2}$$

$$CH_3\overset{Br}{C}H\overset{Br}{C}H_2 \xrightarrow[H_2O]{NaNH_2,\ NH_3} CH_3C\equiv CH$$

b)

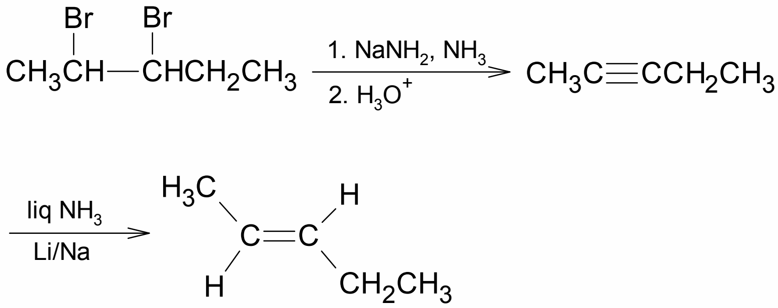


$$CH_3CH_2\overset{Br}{C}H_2 \xrightarrow[-\,HBr]{C_2H_5OH,\ KOH} CH_3CH=CH_2 \xrightarrow{Br_2} CH_3\overset{Br}{C}H\overset{Br}{C}H_2$$

$$\xrightarrow[H_2O]{NaNH_2,\ NH_3} CH_3C\equiv CH \xrightarrow{NaNH_2} CH_3C\equiv\overset{-}{C}\overset{+}{Na}$$

$$\xrightarrow{ICH_2CH_2CH_3} CH_3C\equiv CCH_2CH_2CH_3$$

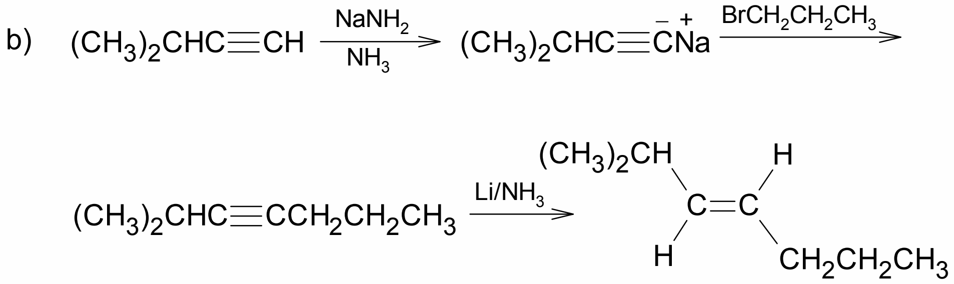
5. a)



$$CH_3\overset{Br}{C}H-\overset{Br}{C}HCH_2CH_3 \xrightarrow[2.\ H_3O^+]{1.\ NaNH_2,\ NH_3} CH_3C\equiv CCH_2CH_3$$

$$\xrightarrow[Li/Na]{liq\ NH_3}$$

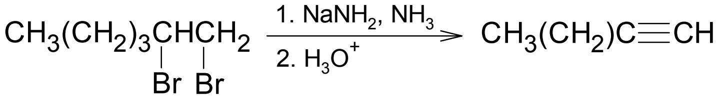
b)



$$(CH_3)_2CHC{\equiv}CH \xrightarrow[NH_3]{NaNH_2} (CH_3)_2CHC{\equiv}\overset{-\ +}{C}Na \xrightarrow{BrCH_2CH_2CH_3}$$

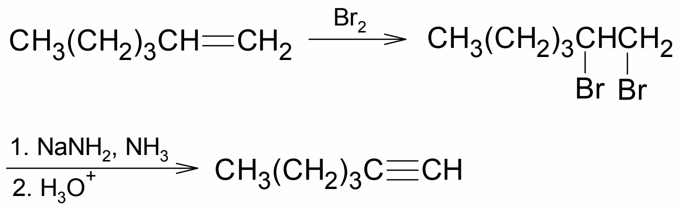
$$(CH_3)_2CHC{\equiv}CCH_2CH_2CH_3 \xrightarrow{Li/NH_3} (CH_3)_2CH(H)C{=}C(H)CH_2CH_2CH_3$$

6. a)



$$CH_3(CH_2)_3\underset{Br}{CH}\underset{Br}{CH_2} \xrightarrow[2.\ H_3O^+]{1.\ NaNH_2,\ NH_3} CH_3(CH_2)C{\equiv}CH$$

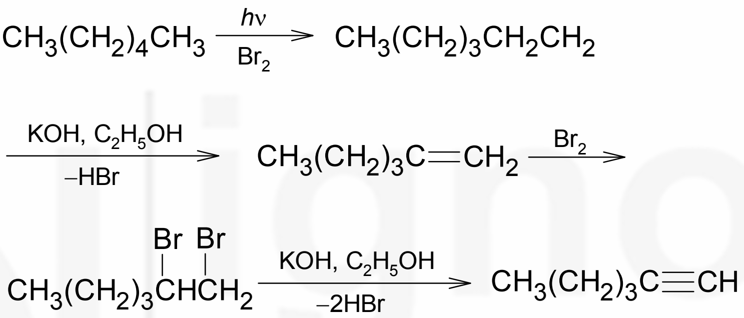
b)



$$CH_3(CH_2)_3CH{=}CH_2 \xrightarrow{Br_2} CH_3(CH_2)_3\underset{Br}{CH}\underset{Br}{CH_2}$$

$$\xrightarrow[2.\ H_3O^+]{1.\ NaNH_2,\ NH_3} CH_3(CH_2)_3C{\equiv}CH$$

c)



$$CH_3(CH_2)_4CH_3 \xrightarrow[Br_2]{h\nu} CH_3(CH_2)_3CH_2CH_2$$

$$\xrightarrow[-HBr]{KOH,\ C_2H_5OH} CH_3(CH_2)_3C{=}CH_2 \xrightarrow{Br_2}$$

$$CH_3(CH_2)_3\overset{Br}{CH}\overset{Br}{CH_2} \xrightarrow[-2HBr]{KOH,\ C_2H_5OH} CH_3(CH_2)_3C{\equiv}CH$$

UNIT 19

AROMATICITY

Structure

19.1 INTRODUCTION

In the preceding four units, we have discussed the chemistry of aliphatic hydrocarbons. Now we come to another class of compounds, namely, aromatic hydrocarbons.

Benzene, the simplest of the aromatic compounds, was isolated by Michael Faraday in 1825 from the gas obtained by pyrolysis of whale oil. Many compounds isolated from natural sources and many synthetic drugs are aromatic in nature. The local anesthetic procaine and tranquiliser diazepam (valium) are a few examples.

Keeping in view the importance of aromatic compounds, we shall study the chemistry of benzene and its derivatives in this unit. First, we will study the physical properties and nomenclature of benzene and its derivatives. Bonding of benzene plays a very important role in organic chemistry, so we will learn the structure of benzene briefly here. Then, we will learn the resonance energy and finally Hückel's rule in detail.

Expected Learning Outcomes

After studying this unit, you should be able to:

- describe the physical properties of aromatic compounds;
- give IUPAC names to the aromatic compounds;
- discuss the structure of benzene;
- explain the resonance energy of aromatic compounds;
- explain the aromaticity of aromatic compounds; and
- describe the Hückel's rule.

19.2 AROMATIC COMPOUNDS-ANINTRODUCTION

Benzene is an important organic compound with the chemical formula C_6H_6.Early in the development of organic chemistry, organic compounds were arbitrarily classified as either aliphatic or aromatic. The meaning of word "aliphatic" means fatty. The aliphatic compounds were so named because the first members of this class to be studied were the fatty acids. In addition to the aliphatic compounds, there was a large number of another type of compounds, which were also obtained from natural sources, e.g., resins, balsams, aromatic oils, etc. The structure of these compounds was unknown but they had one thing in common, a pleasant odour. Thus, these compounds were arbitrarily classified as aromatic compounds (Greek: **aroma** 'fragrant smell'). Now the word aromatic is used for benzene and related compounds. So the original meaning of the world aromatic (fragrant) has no longer any significance.

Benzene was first isolated by Michael Faraday in 1825 by pyrolysis of whale oil. Later, in 1845, Holman discovered benzene in coal tar, which contains benzene and many of its derivatives.

Large number of medicines are aromatic in nature, e.g., Aspirin, paracetamol, diclofenac sodium etc.

Benzene is carcinogenic and injurious to health. Prolonged exposure leads to bone-marrow depression. Benzene as a solvent should, therefore, be used carefully, avoiding evaporation in the open or inhaling its vapour.

19.3 PHYSICAL PROPERTIES

Benzene and many other aromatic compounds are lighter than water. They are immiscible with water but miscible with organic solvents such as alcohol and ether etc. Aromatic compounds are characterised by a sooty yellow flame. Benzene is a colorless and highly flammable liquid with a sweet smell. The boiling point of benzene is 353 K (80.1°C) and freezing point is 278.5 K (5.5°C). Its specific gravity at 293K (20°C) is 0.8788. Benzene is a non-polar compound and its dipole moment is zero. It is a useful solvent for other non-polar compounds. Benzene is an extremely poisonous substance. Inhalation of vapors or absorption through skin has a toxic effect.

SAQ 1

Which of the following statements is True or False? Write 'T' for True and 'F' for False in the box given:

a) Benzene is a colourless gas at 293 K. ☐

b) The boiling point of benzene is 253 K. ☐

c) Benzene is immiscible with alcohol. ☐

d) Dipole moment of benzene is 1 D. ☐

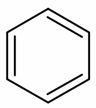
19.4 IUPAC NOMENCLATURE OF AROMATIC COMPOUNDS

In earlier days, when relatively lesser number of organic compounds were known, the names of organic compounds were based either on their origin or on their properties. As the science of organic chemistry slowly grew, the number of organic compounds increased many fold. So it became impossible to learn the names randomly assigned to the compounds. Ultimately scientists realised the need for systematic names for these compounds, which should be unambiguous, easy to pronounce, easy to spell and to remember. Apart from this, names should contain enough information so that we could generate the proper structures for them.

Since 1892, many attempts were made at international level to evolve a rational procedure for naming the organic compounds. The latest rules which are widely accepted were recommended by the Commission on Nomenclature of Organic Chemistry of the **International Union of Pure and Applied Chemistry (IUPAC)**.

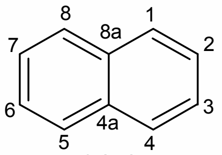
In this unit, we will discuss the IUPAC nomenclature of aromatic compounds in a little detail. The aromatic compounds can have following types of basic skeletons:

a) **Compounds containing one aromatic ring:** This class includes benzene and its derivatives. The derivatives of benzene include the compounds which can have any of the functional groups.

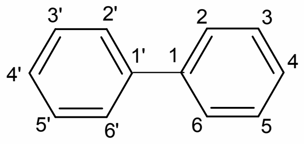


benzene

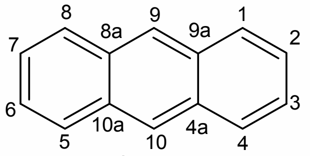
b) **Polynuclear Hydrocarbons:** Compounds containing two or more aromatic rings, examples being naphthalene, biphenyl, anthracene, and phenanthrene etc. Some polynuclear hydrocarbons are shown below:



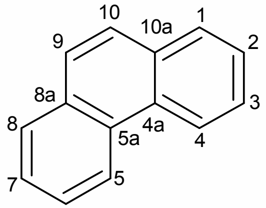
naphthalene



biphenyl

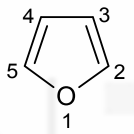


anthracene



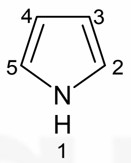
phenanthrene

c) **Heterocyclic compounds:** Aromatic compounds containing one or more hetero atoms such as O, N or S in the aromatic ring are called heterocyclic compounds. Some examples of heterocyclic compounds are given below:



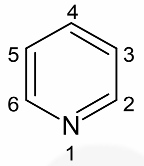
oxole(furan)

;



azole (pyrole)

;



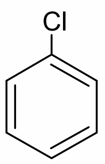
pyridine

Although numbering of carbon skeleton of polynuclear hydrocarbons and heterocyclic compounds are shown above, their nomenclature will be discussed in detail in higher courses.

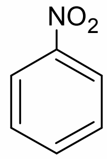
In this unit we will learn the nomenclature of benzene and its derivatives only.

19.4.1 Nomenclature of Benzene and its Derivatives

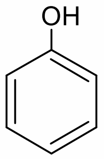
Benzene is the most important aromatic compound in organic chemistry. Most of the aromatic compounds are derivatives of benzene. A large number of aromatic compounds are known by their trivial names for a long time, hence, these names are accepted and approved by IUPAC. But, it is always better to use IUPAC names. In IUPAC system of nomenclature, benzene ring is considered as a parent hydrocarbon. When halogens or any other functional group(s) are attached to benzene, they are named as a prefix of benzene. Some examples of such compounds are given below:



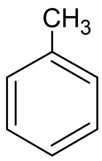
chlorobenzene



nitrobenzene

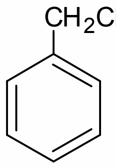


hydroxybenzene
(phenol)

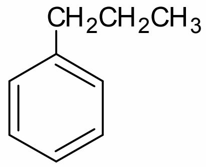


methylbenzene
(toluene)

Alkyl substituted benzenes or arenes are named in two different ways depending on the size of the carbon chain. If the carbon chain is small (less than six carbon atoms), the compounds are named as alkyl substituted benzenes. For example, ethylbenzene is the correct name not 2-phenylethane. Similarly, second one is propylbenzene not 1-phenylpropane.

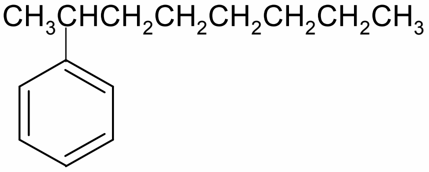


ethylbenzene

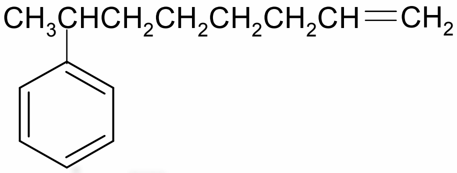


propylbenzene

If the carbon chain is large (six or more than six carbon atoms), the benzene ring is considered as substituent (called phenyl) and the compound is named as phenyl substituted alkane or alkene. For example:

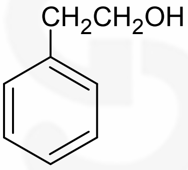


2-phenyloctane

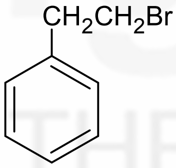


2-phenyl-1-octene

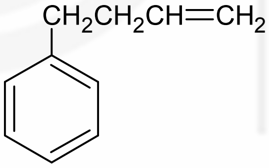
Similarly, benzene ring containing carbon chain with functional group (irrespective of the chain length) is considered as a substituent. For example,



2-phenylethanol



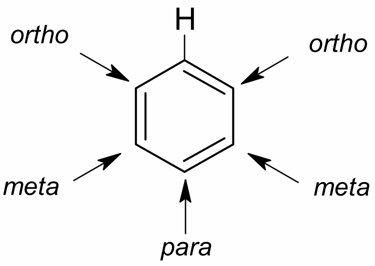
2-phenylbromoethane



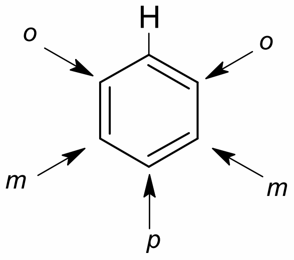
4-phenyl-1-butene

19.4.2 Disubstituted Benzenes

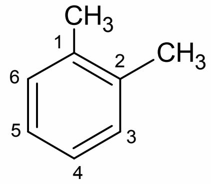
This class of the compounds is named either by using position numbers or prefixes i.e. *ortho (o), meta (m) or para (p)*.



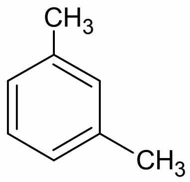
or



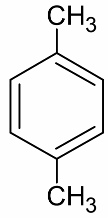
In disubstituted benzenes, if two identical groups are attached, the substituents are numbered in such a way that the second substituent gets the lowest possible number. Some examples of distributed benzene are given below:



1,2-dimethylbenzene
(*ortho*-dimethylbenzene)

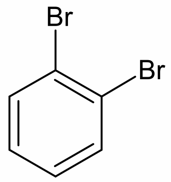


1,3-dimethylbenzene
(*meta*-dimethylbenzene)

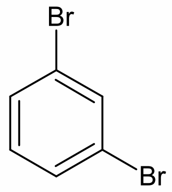


1,4-dimethylbenzene
(*para*-dimethylbenzene)

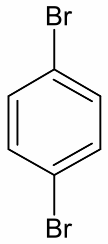
Similarly, dibromobenzenes are named as:



1,2-dibromobenzene
(*ortho*-dibromobenzene)

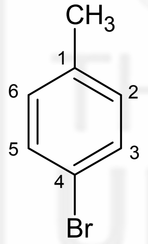


1,3-dibromobenzene
(*meta*-dibromobenzene)

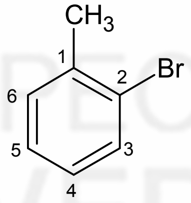


1,4-dibromobenzene
(*para*-dibromobenzene)

If an alkyl group and a halogen atom are attached to the benzene ring, then according to IUPAC nomenclature the ring carbon atomsare so numbered as to give the lowest number to the carbon atom to which halogen atom is attached. For example

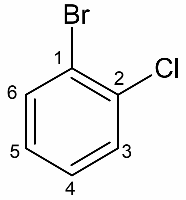


4-bromotoluene
(*para*-bromotoluene)

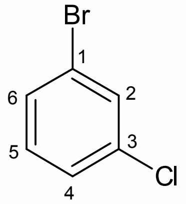


2-bromotoluene
(*ortho*-bromotoluene)

When more than one type of halogen atoms is attached in a benzene ring, their names are arranged in alphabetical orders. For example, we will name the following compound as 1-bromo-2-chlorobenzene not 2-chloro-1-bromobenzene.

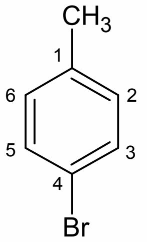


1-bromo-2-chlorobenzene
(*ortho*-bromochlorobenzene)

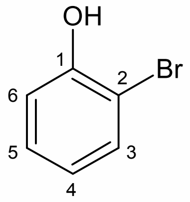


1-bromo-3-chlorobenzene
(*meta*-bromochlorobenzene)

When one of the two substituents gives a trivial name to the compound, the compound acts as a parent, and the whole compound is named as a derivative of that parent compound. For example,



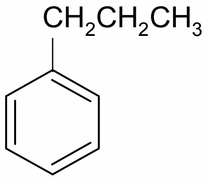
4-bromotoluene
(*para*-bromotoluene)

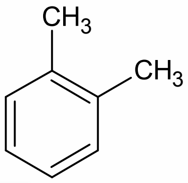


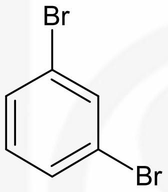
2-bromophenol
(*ortho*-bromophenol)

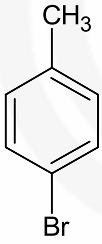
SAQ 2

Give the IUPAC names of the following aromatic compounds:

a) 

b) 

c) 

d) 

SAQ 3

Following name of aromatic compounds are wrong. Explain why.

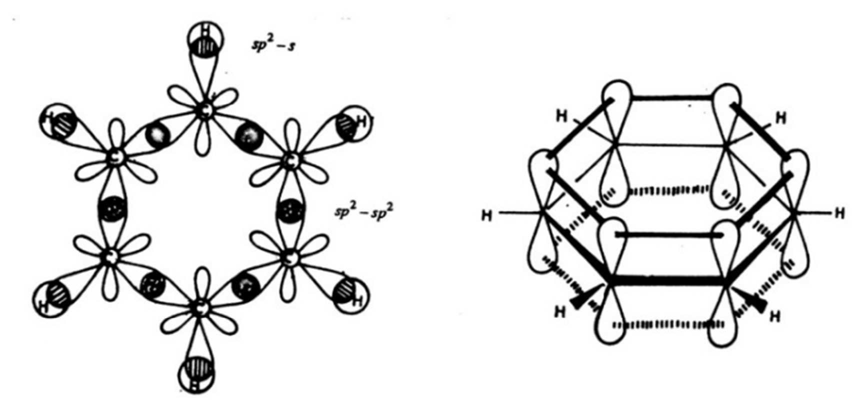
i) 1,5-dibromobenzene

ii) 2-chloro-1-bromobenzene

iii) 2-phenylethane

19.5 STRUCTURE OF BENZENE

Benzene is a conjugated triene, a cyclohexatriene that means benzene should have alternate carbon-carbon single bond and carbon-carbon double bone like 1,3-butadiene. X-ray studies show the benzene molecule is completely symmetrical hexagon (Fig. 19.1) with equal C-C bond length of 1.39 pm. Benzene is a planar flat symmetrical molecule having the shape of a regular hexagon. The C−C−C bond angle has a value of 120^0. Each carbon atom in the molecule is sp^2 hybridised. Two orbitals of the sp^2 hybridised carbon atom overlap with the two orbitals of the adjacent carbon atoms resulting in the formation of two σ bonds. The third sp^2 hybridised orbital of each carbon atom overlaps with 1*s* orbital of hydrogen atom and forms an σ bond. Thus six carbon-carbon σ bonds and six carbon-hydrogen σ bonds are formed. Each carbon atom still has a *p* orbital perpendicular to the plane of the ring. The *p* orbital has two lobes one above and the other below the plane of the ring and because all *p* orbitals are equivalent, they overlap equally well with *p* orbitals on both the neighbouring carbon atoms resulting in a delocalised π orbital cloud above and below the ring. The picture that emerges out of this discussion is given below in Fig. 19.1.



σ- skeleton π- skeleton

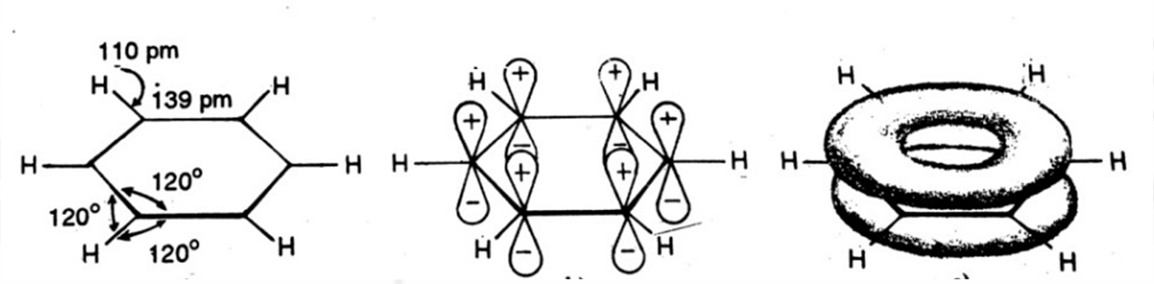


Fig 19.1: σ **and** π **skeleton of benzene**

The benzene ring is a cyclic conjugated system and is usually represented as a regular hexagon with a circle inside the ring. This gives an idea of delocalization of π-electrons as shown in Fig. 19.1.

19.5.1 Molecular Orbital Model of Benzene

In earlier orbital picture of benzene, we have mentioned that each carbon in benzene ring in sp^2hybridised and each carbon forms σ bonds with two adjacent carbons by overlap of sp^2 – sp^2 orbitals. We also stated that each carbon atoms of the benzene ring also has unhybridised 2*p* orbitals with one electron each perpendicular to the plane of the ring. We can explain this with the more accurate molecular orbital picture. As you know, according to the molecular orbital theory when atomic orbitals (AOs) combine to give molecular orbitals (MOs) the number of molecular orbitals remain equal to the original number of atomic orbitals. Thus, in the case of benzene, the combination of the six parallel 2*p* atomic orbitals gives a set of six π MOs, three bonding MOs and three *anti*-bonding MOs. Fig. 19.2 shows the six molecular orbitals and their relative energies. In ground state, all the bonding MOs are occupied by six electrons. Thus all three bonding MOs participate in bond formation. According to the MO theory, the greater stability of benzene results from the fact that three bonding MOs are much lower in energy when compared with six uncombined 2*p* atomic orbitals and even with the MOs of 1, 3, 5-hexatriene.

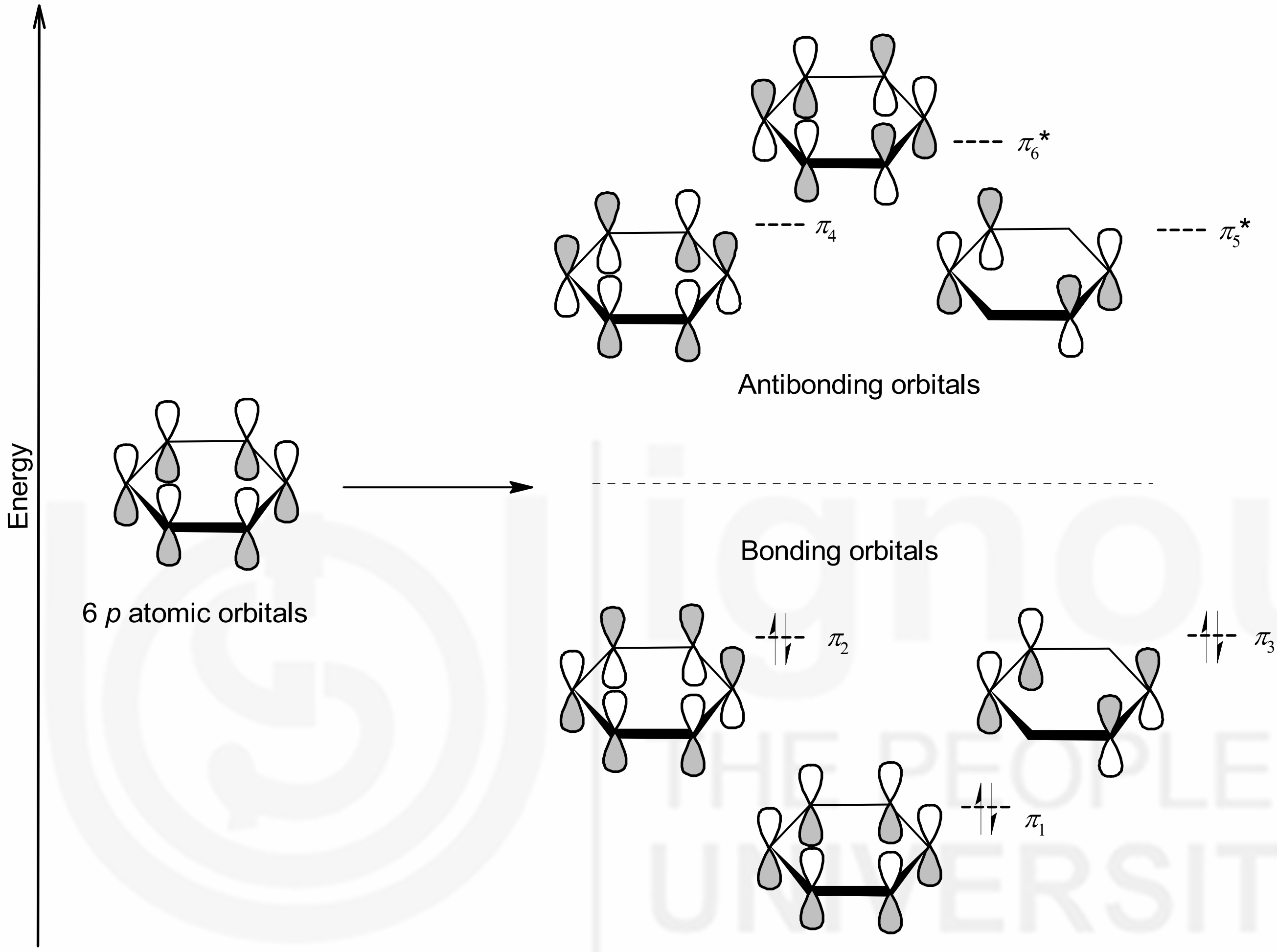


Fig. 19.2: The MO representation of the π bonding in benzene.

All the facts give the benzene ring it's thermodynamic and chemical stability i.e. the aromaticity of benzene. Bond order calculations based on MO theory also indicate that all C-C bonds are equal and have some double bond character.

SAQ 4

Fill in the following blanks:

a) The C−C−C bond angle in benzene has a value of ……………

b) Each carbon atom in the molecule is …………... hybridised.

c) Benzene is a ………… symmetrical molecule.

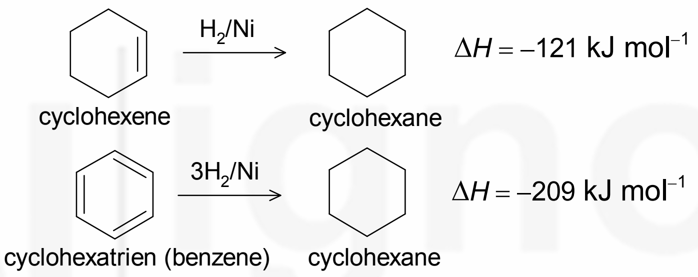
d) Benzene has …………….. σ bonds and ……………. π bonds.

19.6 RESONANCE

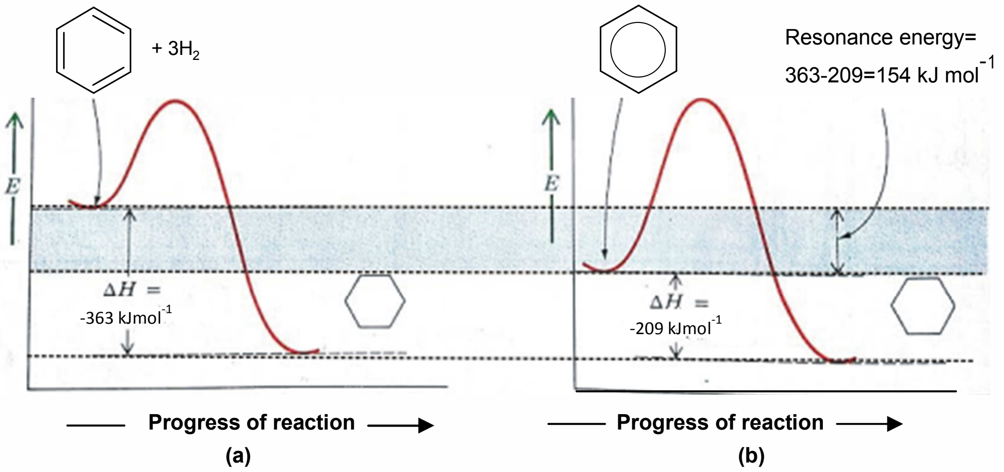
You must have studied the basic concept of resonance in your earlier classes. Here, we will discuss the resonance effect in aromatic compounds. The structures of a large number of organic compounds can be written with the help of simple bond diagrams, e.g., ethene as $CH_2=CH_2$, ethyne as $HC\equiv CH$, etc. However, there are many compounds for which simple bond diagrams do not accurately describe these compounds, one of the examples being benzene. The structure of benzene (Fig 19.1) gives the impression that it is a cyclic compound of six carbon atoms containing three single and there double bonds. If this were so, you would expect two values of carbon-carbon bondlengths, viz., one for single bonds (nearly 154 pm as in ethane) and the other for double bonds (nearly 133 pm as in ethene). Experimental evidence through X-ray diffraction studies shows that all the six carbon-carbon bonds in benzene are equal and have a length of 139 pm, which is in between 133 and 154 pm. The explanation of this is as follows:

X-ray studies give the bond lengths and bond angles.

The heats of hydrogenation of cyclohexene and benzene determined experimentally are given below:



The heat evolved when hydrogen is added to cyclohexene (having one C=C bond) is 121 kJ mol^{-1}. The expected value of the heat evolved when hydrogen is added to benzene (having three C=C bonds) should be 3×121kJ mol^{-1}=363 kJ mol^{-1} (Fig.19.3a,) but the experimental value is 209 kJ mol^{-1}. We can infer that benzene is more stable (having lower energy content) than the hypothetical molecule containing three isolated C=C bonds by 363–209=154 kJ mol^{-1} (Fig. 19.3b).This energy difference is called the resonance energy and is responsible for the stability of benzene compared to other unsaturated compounds which lack resonance stabilization (Fig.19.3).

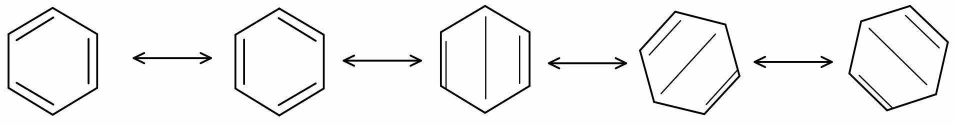


(a) (b)

Fig. 19.3: Energy diagrams for the hydrogenation of (a) cyclohexatriene (hypothetical) and (b) benzene.

19.6.1 Representation of Benzene Ring

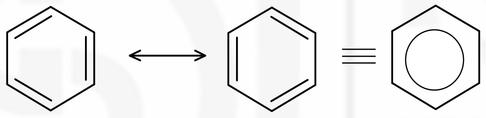
We cannot write a single structure for benzene which would encompass all its properties rather it is considered to be the resonance "hybrid" of the following hypothetical structures I-V:



I II III IV V

These structures are called resonance structures or contributors or canonical forms. The two "Kekule" forms, I and II, are of lower energy (more stable) than the three "Dewar" forms, III to V. Structures I and II could be expected to "contribute" more to the hybrid than either III, IV or V, hence, the properties of benzene would be expected to resemble more closely to either I or II than to III, IV or V. Since I and II have the same energy, each would contribute to the hybrid by the same amount. The symbol of resonance, double-headed arrow (↔), does not indicate an equilibrium. The canonical structures I-V are hypothetical and do not have any physical existence. These structures differ in their electronic arrangement and arise due to shift of π electrons within the molecule.

Structures I and II can be represented as structure VI. It shows that hydrogen atom is attached each angle of benzene ring.



I II VI

SAQ 5

State which of the following statements are true/false? Write (T) for true and (F) for false in the boxes against the statements:

i) Properties of benzene resemble more closely to II than to or V. ☐

ii) The two "Kekule" forms, of benzene, are less stable than the "Dewar" forms. ☐

iii) The canonical structures I and V are important and physical existence. ☐

iv) "Kekule" forms, differ in their electronic arrangement and arise due to shift of π electrons within the molecule. ☐

19.7 Aromaticity

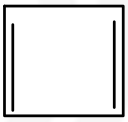
Aromaticity is the property of certain planar cyclic conjugated molecules, specially benzene and its derivatives, which exhibit unusual stability as compared to other geometric or connective arrangement of same set of atoms. Such molecules are known as aromatic. As a result of their stability, it is very difficult to break apart aromatic compounds. These compounds undergo substitution reactions rather than addition reactions. The aromaticity is associated with a conjugated system often made of alternating single and double bonds in a ring. This arrangement of bonds allows the π electrons of the molecule to delocalise around the ring increasing the stability of the molecule.

Perhaps you might have been wondering whether other cyclic compounds with π electrons might also be considered aromatic, some of these systems are indeed aromatic, but not all of them. What structural features are necessary for a molecule to be aromatic?

Hückel's Rule

A German Physicist, Erich Hückel in 1931, proposed a rule to predict whether a molecule will be aromatic or not. This rule is known as the Hückel's rule. According to this rule, an aromatic molecule must be a cyclic conjugate species having (4n+2) π-electrons where n is an integer (*n*=0, 1, 2, 3, ….). This means that only the ring with 2, 6, 10, 14,……π electrons may be aromatic but a ring with 4, 8 or 12 π electrons may not be aromatic. Hückel's rule is applicable to ionic species also. Let us look at some of the evidence supporting the Hückel's rule. Besides following the Hückel's Rule the molecule should be planner to be aromatic.

19.7.1 Cyclobutadiene



No. of π-electrons = 4

It has 4π electrons. Let us see if the molecule is aromatic or not. The Hückel's rule requires: (4n + 2) π electrons, for a compound to be aromatic.

If $n = 0$, $(4\times0 + 2)$ π electrons

$= (0 + 2)$ π electrons

$= 2$ π electrons

Or

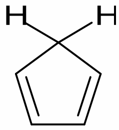
If $n = 1$, $(4\times1 + 2)$ π electrons

$= (4 + 2)$ π electrons

$= 6$ π electrons

If we apply Hückel's rule here, we find that this compound does not follow Hückel's rule. Hence, cyclobutadiene is not an aromatic compound as it has 4π-electrons and is highly unstable.

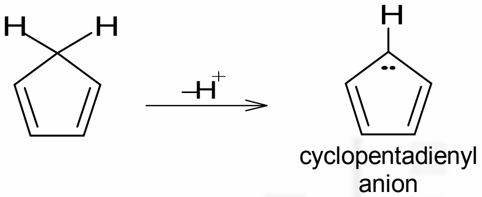
19.7.2 Cyclopentadiene



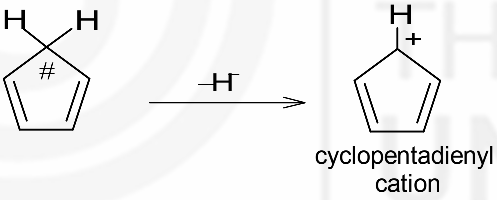
No. of π electrons = 4

Similar to cyclobutadiene, Cyclopentadieneis a conjugated diene but it has 4π electrons and does not follow Hückel's rule. Hence, it is not an aromatic compound. This can also be explained on the basis of hybridisation of its carbon atoms. CH_2carbon marked with #in the ring is *sp*^{3} hybridised and hence it is not coplanar with other atoms. Therefore cyclopentadiene is not a planar molecule and thus is not aromatic.

Removal of one H^+ from cyclopentadiene changes the hybridisation to *sp*^{2}and forms cyclopentadienyl anion.

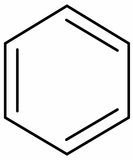


Cyclopentadienyl anion has 6 π electrons with conjugated double bonds. Hence, it is an aromatic compound. Now, we take the example of cyclopentadienyl cation, which will be formed on removal of H^- from cyclopentadiene:



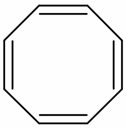
All the carbon atoms of cyclopentadienyl cation are *sp*^{2} hybridisedand it is planar and cyclic, but it has only 4π electrons. Hence, it is not an aromatic compound.

19.7.3 Benzene



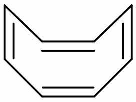
Benzene is a typical example of an aromatic compound. Here, the Hückel's rule is followed as it has 6 π-electrons which are required for a compound to be aromatic. All the carbon atoms of benzene ring are *sp*^{2} hybridised and it is a planar molecule too. It is an excellent example of an aromatic system.

19.7.4 Cyclooctatetraene



In Cyclooctatetraene as you see from its structure, the number of π-electrons is eight. Thus, it does not follow the Hückel rule. Therefore, Cyclooctatetraene is not aromatic.

Another reason why cyclooctatrene is not aromatic is that it is not even fully conjugated. It is a tub shaped molecule and the neighbouring orbitals containing the π-electrons do not have the necessary geometry for proper overlap.

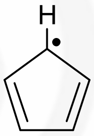


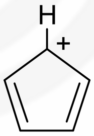
cyclooctateraene

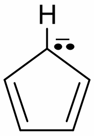
From the above example, it is clear that a flat planar geometry is required for proper overlap resulting in delocalisation of π-electrons which is a necessary condition for aromaticity.

SAQ 6

Which of the following species is/are aromatic?

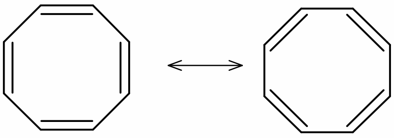
a) 

b) 

c) 

SAQ 7

Cyclooctateraene is a conjugated polyene and one can write two resonance structures of the Kekule type,



yet it is not aromatic compound. Explain.

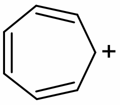
19.8 SUMMARY

In this unit, you have learnt:

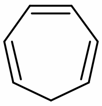
- The definition of aromatic compounds,
- the nomenclature of benzene and its derivatives,
- the physical properties of aromatic compounds,
- that the benzene ring contains six single carbon-carbon σ bonds and three alternate carbon-carbonπ bonds,
- that the benzene is a planar flat symmetrical molecule having the shape of a regular hexagon,
- the C−C−C bond angle of benzene is 120^o,
- each carbon atom in the benzene molecule is sp^2 hybridised,
- the relationship of resonance energy with the stability of aromatic compounds,
- that for aromaticity compound must be planar and follow Hückel's rule,
- according to Hückel's rule, aromatic compound must contain $(4n + 2)$ π electrons.

19.9 TERMINAL QUESTIONS

1. Show *ortho, meta* and *para* positions of nitrobenzene.
2. Draw a molecular structure of benzene.
3. Explain briefly resonance energy.
4. 1, 3, 5-cycloheptatrienyl cation is aromatic where as, 1,3,5-cycloheptatriene is not. Explain.



,



5. Draw the structure of the following compounds:

   i) 1-bromo-2-chlorobenzene

   ii) anthracene

   iii) 1,3-dibromobenzene (*meta*-dibromobenzene)

   iv) 2-phenyl-1-octane

   v) 4-phenyl-1-butene

19.10 ANSWERS

Self-Assessment Questions

1. a) F

   b) T

   c) F

   d) F

2. a) Propylbenzene

   b) *ortho*-dimethylbenzene or 1,2-dimethylbenzene

   c) *ortho*-dibromobenzene or 1,2-dibromobenzene

   d) *para*-bromotoluene or 4-bromotoluene

3. i) In disubstituted benzenes if two identical groups are attached, the substituents are numbered in such a way that the second substituent gets the lowest possible number. The correct name of the compound is 1,2-dibromobenzene not 1,5-dibromobenzene.

   ii) When more than one type of halogen atoms is attached in a benzene ring, their names are arranged in alphabetical orders. Hence the correct name of the compound is 1-bromo-2-chloro-bromobenzene not 2-chloro-1-bromobenzene.

   iii) If the carbon chain is small (less than six carbon atoms), the compounds are named as alkyl substituted benzenes. So the compound is named as ethylbenzene or propylbenzene.

4. a) 120^{o}

   b) sp^2

   c) planar

   d) 6, 3

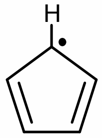
5. i) T

   ii) F

   iii) F

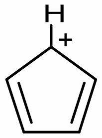
   iv) T

6.

Compound A 

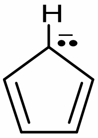
No of π-electrons= 5.

Compound A contains 5 π electrons, that means it does not follow Hückel's rule, hence it is not an aromatic compound.

Compound B 

No of π-electrons= 4.

Compound B contains 4 π electrons that mean it does not follow Hückel's rule, hence it is not an aromatic compound.

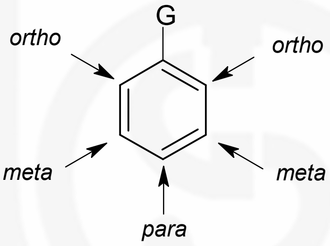
Compound C 

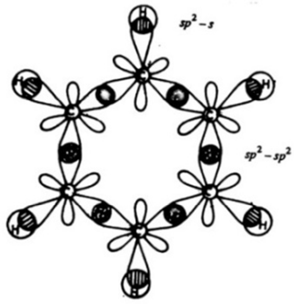
No of π-electrons= 6.

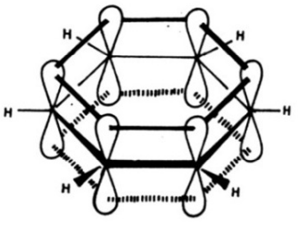
Compound C contains 6 π electrons, all the carbon atoms are and it is sp^2 hybridised and it follows Hückel's rule. Hence, it is an aromatic compound.

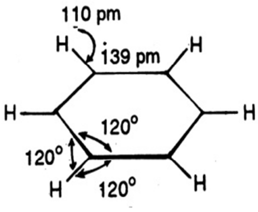
7. It is not planar molecule hence the π electrons are not completely delocalised as in benzene.

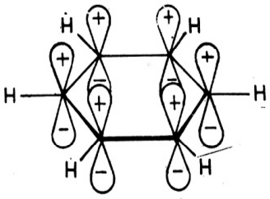
Terminal Questions

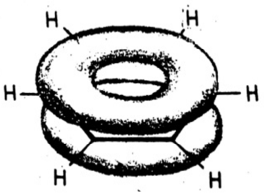
1. 

2. 







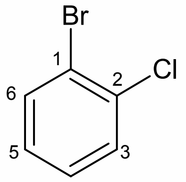


3. The heat evolved when hydrogen is added to cyclohexene (having one C=C bond) is −121 kJ mol^{-1}. The expected value of the heat evolved when hydrogen is added to benzene (having three C=C bonds) should be-3×121.kJ mol^{-1}=−363 kJ mol^{-1}, but the experimental value is −209 kJ mol^{-1}. We can infer that benzene is more stable (having lower

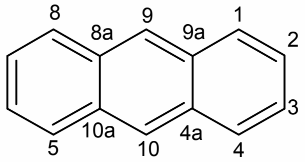
energy content) than the hypothetical molecule containing three isolated C=C bonds by−363−(−209)= −154 kJ mol^{-1}. This energy difference is called the resonance energy.

4. Cycloheptatriene has three double bonds i.e. 6π electrons but because of the presence of sp^3 carbon atoms, these π electrons cannot undergo cyclic overlapping. Generation of the cation removes the hindrance and the delocalised 6π electrons (Huckel's rule) make the cation aromatic.

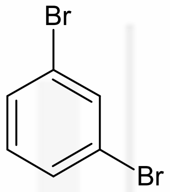
5. i)



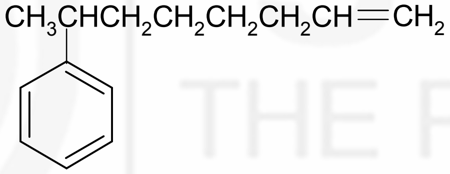
ii)



iii)

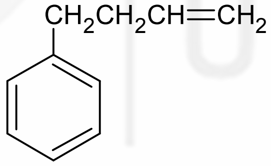


iv)



$CH_3CHCH_2CH_2CH_2CH_2CH{=}CH_2$

v)



$CH_2CH_2CH{=}CH_2$

Further Reading

1. Graham Solomons, T.W., Fryhle, C.B. & Dnyder, S.A. *Organic Chemistry,* John Wiley & Sons (2014).

2. McMurry, J.E. *Fundamentals of Organic Chemistry*, 7th Ed. Cengage Learning India Edition, 2013.

3. Sykes, P. *A Guidebook to Mechanism in Organic Chemistry,* Orient Longman, New Delhi (1988).

4. Finar, I.L. *Organic Chemistry* (Vol. I & II), E.L.B.S.

5. Morrison, R.T. & Boyd, R.N. *Organic Chemistry*, Pearson, 2010.

6 Bahl, A. & Bahl, B.S. *Advanced Organic Chemistry,* S. Chand, 2010.

INDEX