



NATIONAL OPEN UNIVERSITY OF NIGERIA

SCHOOL OF SCIENCE AND TECHNOLOGY

COURSE CODE: CHM 102

**COURSE TITLE: INTRODUCTORY ORGANIC
CHEMISTRY**

**COURSE
GUIDE****CHM 102
INTRODUCTORY ORGANIC CHEMISTRY I**

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*Published by
National Open University of Nigeria*

Printed 2009

Reprinted 2014

ISBN: 978-058-594-X

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INTRODUCTION

Chemistry is an experimental science. Indeed, experiments have played a vital role in the development of Chemistry. On the one hand, experiments have provided evidences for testing theories; on the other, their results have thrown up new questions and puzzles, which required new insights, giving rise to new theories.

THE COURSE

CHM 102 Introductory Organic Chemistry I (2 Units)

We have divided this course into four units. The first unit provides you an introduction to bonding in organic molecules, their functional groups, classification and nomenclature. In Unit 2, we acquaint you with the basic properties, methods of preparation of the group of compounds called the alkanes. In the remaining units, we discussed the chemistry of alkenes (Unit 3), and in Unit 4 we have explained the importance of the alkynes as well as their preparations and properties.

The guiding theme in the development of these materials is a brief description of the general properties, the underlying principles of the preparation and observed trends in the properties of organic compounds.

COURSE AIMS

The aim of this course is to give you a general introduction to organic chemistry, giving explanations to observed physical and chemical properties of organic compounds.

COURSE OBJECTIVES

After studying this course, you should be able to:

- *Describe the general features of a covalent bond,*
- *Define bond length, bond angle and bond energy,*
- *Explain various types of hybridization of carbon compounds,*
- *Identify the functional groups present in a molecule,*
- *Give IUPAC names of various compounds belonging to different classes, and*
- *Write the correct structure of a compound from its name.*
- *Describe the composition and fractionation of petroleum,*
- *Define octane number and cetane number,*
- *Discuss the physical properties of alkanes,*

- *List the characteristic spectral peaks of alkanes in uv, ir, nmr and mass spectra*
- *List the methods for preparation of alkanes and cycloalkanes,*
- *Discuss the important chemical reactions of alkanes and cycloalkanes.*

WORKING THROUGH THIS COURSE

This course is very important for any student intending to study Chemistry at any level, as it provides the basic ideas about the guiding principles for the preparation, classification of organic compounds.. You are, therefore, expected to put some effort in understanding this course, as some of the knowledge available in this course might not be so easy to pick up later in your study of Chemistry.

THE COURSE MATERIAL

You will be provided with the following materials:

STUDY UNITS

The following study units are contained in this course:

Module 1

Unit 1 Bonding, Functional Groups, Classification and Nomenclature of Organic Compounds

Unit 2 Alkanes

Unit 3 Alkenes

Unit 4 Alkynes

ASSESSMENT

There are two components of assessment for this course. The Tutor-Marked Assignment (TMA) and the end of course examination.

TUTOR-MARKED ASSIGNMENT

The TMA is the continuous assessment component of your course. It accounts for 30% of the total score. You will be given 4 TMA's to answer. Three of these must be answered before you are allowed to sit for the end of course examination. The TMA's would be given to you by your facilitator and returned after they have been graded.

FINAL EXAMINATION AND GRADING

This examination concludes the assessment for the course. It constitutes 70% of the whole course. You will be informed of the time for the examination. It may or may not coincide with the university semester examination.

SUMMARY

This course intends to give you an introduction to the study of organic chemistry on topics ranging from bonding to physical and chemical properties of organic compounds. At the end of this course, you will be able to answer questions of this nature.

To prepare basic organic compounds, explain observable trends in the physical and chemical properties of compounds within a given group, the relationship in properties of compounds among groups of compounds, predict the properties of organic compounds after identification.

We wish you success.

**MAIN
COURSE**

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MODULE 1

Unit 1	Bonding, Functional Groups, Classification and Nomenclature
Unit 2	Alkanes
Unit 3	Alkenes
Unit 4	Alkynes

UNIT 1 BONDING, FUNCTIONAL GROUP CLASSIFICATION AND NOMENCLATURE**CONTENTS**

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2.0	Objectives
3.0	Main Content
3.1	The Covalent Bond
3.2	Structural Formulas
3.3	Orbital Hybridization
3.3.1	sp^3 -Hybridisation
3.3.2	sp^2 -Hybridisation
3.3.3	sp -Hybridisation
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3.5	Nomenclature of Organic Compounds
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5.0	Summary
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7.0	References/Further Readings

1.0 INTRODUCTION

Organic Chemistry is a highly organized discipline. It is the study of the relationship between the structures of molecules and their reactions. We will begin our study with the type of bonding and structural aspects of the molecules. You are already familiar with the fact that compounds can be broadly divided into two classes, ionic and covalent. Ionic compounds are composed of positively and negatively charged ions which are held together by electrostatic forces. Since ions can be regarded as spheres having symmetrical distribution of charge, no particular direction can be assigned to such type of bonding. For example, in NaCl lattice, Na^+ and Cl^- ions are held together by electrostatic forces; no Na^+ ion can be regarded as bonded to a particular Cl^- ion. In other words, there is no such entity which can be called as NaCl molecule. In fact, the electrostatic forces operate between a particular ion (Na^+) and all its neighbouring ions (Cl^-) of

opposite charge. On the other hand, in covalent compounds, molecules are the structural units. In contrast to the ionic compounds, in covalent compounds, the molecules are formed by the sharing of electron pair(s) between the constituent atoms. The bonds formed by sharing of pair(s) of electrons are called covalent bonds. Since in organic compounds, the bonds formed by carbon atom are covalent in nature, we will study some features of the covalent bonding in detail. We will then explain shapes of molecules using the concept of hybridization. We shall also learn various types of functional groups present in organic compounds and classify these compounds into various classes on the basis of the functional groups. Finally, we will study, how to name the compounds belonging to various classes.

2.0 OBJECTIVES

After studying this unit, you should be able to:

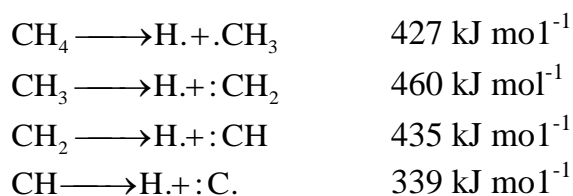
- describe the general features of a covalent bond
- define bond length, bond angle and bond energy
- explain various types of hybridization of carbon compounds
- identify the functional groups present in a molecule
- give IUPAC names of various compounds belonging to different classes
- write the correct structure of a compound from its name.

3.0 MAIN CONTENT

3.1 The Covalent Bond

The sharing of electrons to form a covalent bond leads to an increase in electron density in between the nuclei. In such an arrangement, the forces holding the atoms together are also electrostatic in nature; but this time the forces operate between the electrons of one atom and the nucleus of the other. Such a system has lower energy and is more stable as compared to the energy of isolated atoms. It is so because each electron is now attracted by two nuclei. As a result, the formation of the bond is accompanied by the release of the energy. The same amount of energy has to be supplied to break that particular bond. The amount of energy required to break a particular bond (expressed in terms of kJ mol^{-1}) is called its bond **dissociation energy**. You should not confuse **bond dissociation energy** with another term **bond energy** which is an **average** value for a particular bond. The difference in these two energies can be illustrated by taking the example of methane, CH_4 . If the C – H bonds are successively broken as shown below, then the bond dissociation energy for each step is as indicated on the right hand side.

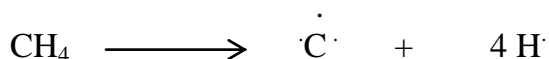
Bond Dissociation Energy



You can see from these values that the dissociation energies are different for each C-H bond breakage. On the other hand, bond energy is a single average value which can be obtained as,

$$\begin{aligned} \text{Bond energy of the C-H bond} &= \frac{427 + 460 + 435 + 339}{4} \text{ kJ mol}^{-1} \\ &= \frac{1661}{4} \text{ kJ mol}^{-1} = 415.25 \text{ kJ mol}^{-1} \end{aligned}$$

Thus, the C-H bond energy in methane is one-fourth of the energy required for the following change.



Clearly, if the molecule is diatomic, then bond dissociation energy and bond energy are the same. Generally, bond dissociation energy values are more useful.

Table 1.1: Lists the bond energies and bond dissociation energies for some bonds in kJ mol^{-1} (at 298 K and 1 atm, pressure).

Table 1.1: Bond Energy and Bond Dissociation Energy Values in kJ mol^{-1}

Bond Energy	Bond Energy	Bond Energy	Bond Energy	Bond Dissociation	Bond Dissociation	Bond	Bond
H-H	436	N-N	163	CH ₃ -H	427	Ph-OH	341
F-F	158	N=N	409	CH ₃ CH ₂ -H	418	Ph-NH ₂	381
Cl-Cl	242	N≡N	945	CH ₂ CH ₂ CH ₂ -H	410	Ph-F	485
Br-Br	193	O-H	463	(CH ₃) ₂ CH-H	395.5	Ph-Cl	406
I-I	151	O=O	497	CH ₃ -CH ₃	368	Ph-I	272

H-Cl	424.8	C-O	334.7	CH ₃ -F	451
H-Br	364	C=O	94.5	CH ₃ -Cl	349
H-I	297.1	O=C=O	803.3	CH ₃ -Br	293
C-H	414	C-N	284.5	CH ₃ -I	234
C-F	484	C=N	15.1	HO-H	498
C-Cl	338	C=N	64.1	CH ₃ O-H	427
C-Br	276	N-H	89.1	CH ₃ -OH	383
C-I	238	N-O	00.8	Ph-H	431
C-C	348	N=O	04.7	PhCH ₂ -H	356
C=C	612	S-H	347.3	Ph-CH ₃	389
C≡C	813	S-S	25.9	PhO-H	356
		S=O	97.9		

There are two more parameters associated with a covalent bond which determine the shape of a molecule and are known as bond length and bond angle. Bond length can be defined as the average distance between the nuclei of the atoms which are covalently bound together. Bond angle can be defined as the angle between the atoms, forming the bonds to the same atom. Table 1.2 gives the bond lengths for some of the bonds.

Table 1.2: Bond lengths for some of the bonds

Bond	Bond length/pm	Bond	Bond length/pm
H-H	74	C-F	142
C-H	112	C-Cl	177
C-C	154	C-Br	191
C=C	134	C-I	213
C≡C	120	C-O	143
F-F	144	C=O	120
Cl-Cl	198	N-H	103
Br-Br	228	N-N	147
I-I	266	N=N	130
C-C in C ₆ H ₆	139	C=N	130
O-H	97	C≡N	110

$$1 \text{ pm} = 1 \text{ picometer} = 10^{-12} \text{ m}$$

From these values of bond lengths, we can conclude that:

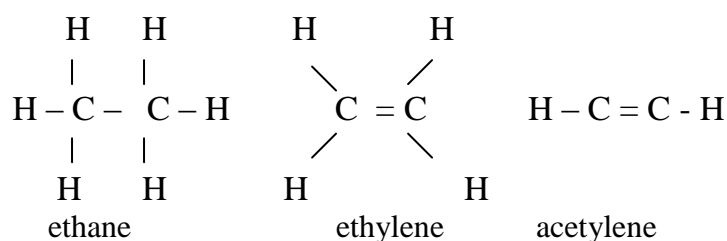
- (i) bond length decreases with the increase in multiplicity of the bond. Thus, the decreasing – order for bond lengths for carbon – carbon bonds is
 $\text{C-C} > \text{C} = \text{C} > \text{C} \equiv \text{C}$.
- (ii) bond lengths increase with the increasing size of the bonded atoms, i.e., the increasing order of bond lengths is $\text{C-H} < \text{C-F} < \text{C-Cl} < \text{C-Br} < \text{C-I}$.

We will study more about bond lengths and bond angles later in Sec. 1.4, when we discuss hybridization. You will see in the later units in this course how important these parameters of a bond are in deciding the chemical reactivity of a compound.

Before proceeding further, let us study something about how the structures for organic compounds are written.

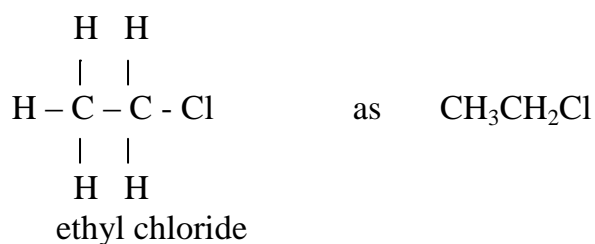
3.2 Structural Formulas

The structural formula of a compound is its Lewis structure, which shows how various atoms are connected to each other. You are already familiar with Lewis structures of some of the compounds. Some examples are:



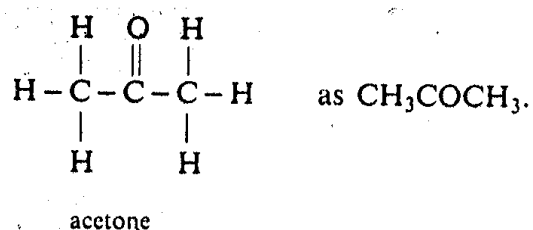
To save space and time, these structures are represented by condensed formulas which do not show the bonds. For example, the condensed formula for ethane can be written as CH_3CH_3 .

Similarly, we can write condensed structural formula for

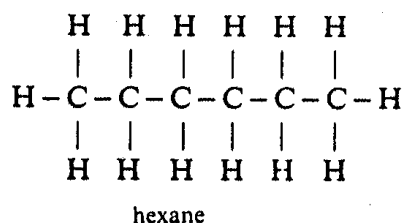


N.B. Remember that all the representations of the formulas are in two dimensions but actually molecules are three-dimensional in nature.

and for



Repeating units such as $(-\text{CH}_2-)$ in the structural formula can be enclosed in brackets and hence hexane.



can be written as $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$.

Condensed formulas for compounds having multiple bounds can be written as show below:

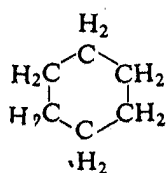
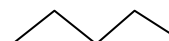


For simple compounds, it is easy to write the condensed formulas. But, when the molecules are complex, these formulas look rather awkward and can be further abbreviated. These representations are called **line** or **skeletal** structures. Here, the Hydrogens are not shown and **each end and bends** represents the carbon atoms as shown below for some cases:

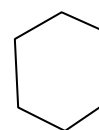
Compound**Line structure**

The skeletal structures or line structures show only the carbon-carbon bonds

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
pentane

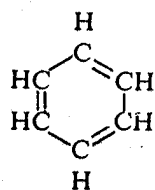
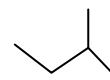


cyclohexane

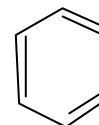


$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}_3 \end{array}$

2-methylbutane



benzene

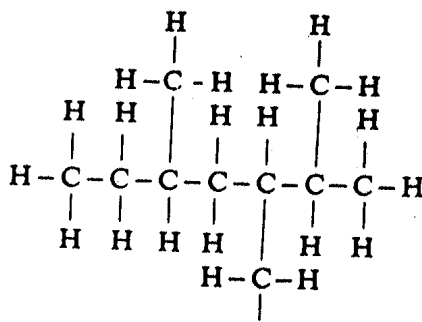


Having understood the above representations, answer the following SAQ.

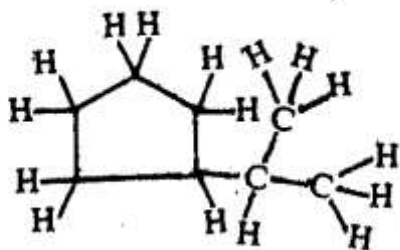
SELF ASSESSMENT EXERCISE 1

Write the condensed formulas for the following compounds:

1.



2.



3.3 Orbital Hybridisation

Properties and chemical reactions of most organic molecules can be easily explained by considering the molecules to be formed by sharing of electron pairs between the atoms. Another approach to formation of molecules is the molecular orbital method. Organic chemists have for many years employed a bonding model that combines elements of molecular orbital theory with Lewis model of formation of covalent bond by electron sharing. This model was proposed by Pauling in 1930 and is based on the concept of orbital hybridization. This model uses the terminology of molecular orbital theory but treats the bonds between the atoms as though they are localized, as in the case of diatomic molecules. In other words, it is a sort of **localized molecular orbital treatment of the bond**.

You have already studied that various types of orbital hybridization is possible depending upon the number and nature of the orbitals involved. In this unit, we will restrict our discussion to the hybridization involving s and p orbitals. Let us now study each type of hybridization involving s and p orbitals, in detail, to understand this concept and its use in explaining the formation of molecules.

Recall that: Hybridization is a theoretical concept which enables as realistic modelling of molecular structure as possible.

The orbitals which undergo hybridization should not be energetically much different.

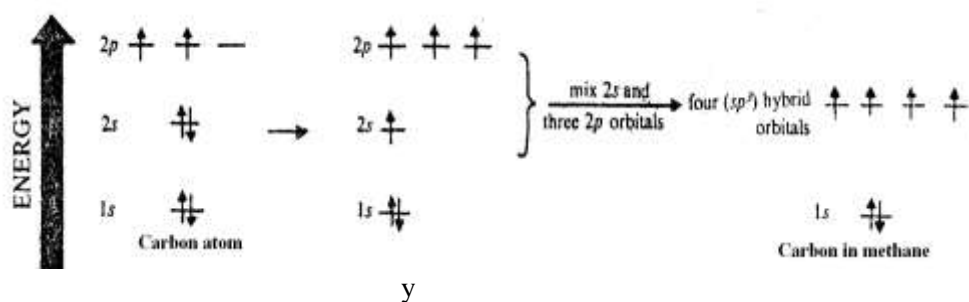
The number of hybrid orbitals generated is always equal to the number of atomic orbitals combined

Sp^3 is pronounced as s - p -three and not sp cube.

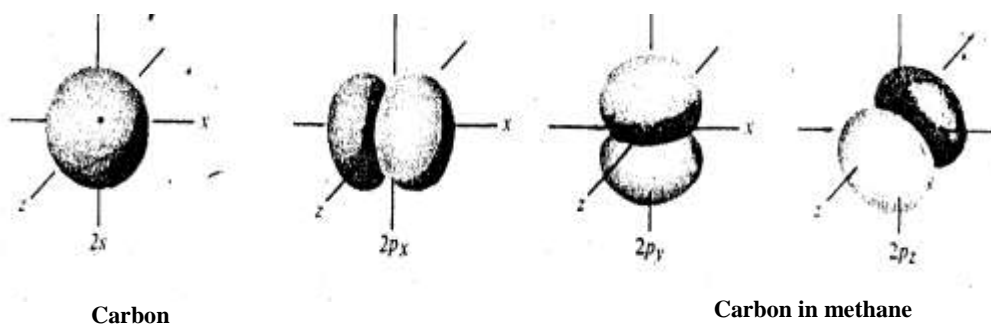
The hybrid orbitals are obtained by mathematical combinations of atomic orbitals.

3.3.1 sp^3 -Hybridisation

Let us consider the simplest organic compound, methane, having the molecular formula CH_4 . You can recall that carbon has the electron configuration $1s^2 2s^2 2p_x^1 2p_y^1$. Since only two unpaired electrons are there, one may expect that it should form only two bonds with two hydrogen atoms to form CH_2 . But actually it forms four bonds with four hydrogen atoms to give CH_4 . Pauling proposed that this could be explained by using orbital hybridization. In this method, atomic orbitals are mixed to yield the new hybrid orbitals. In this case, in the first step one of the $2s$ electrons is promoted to the $2p_z$ orbital, electron configuration can then be written as $2s^1 2p_x^1 2p_y^1 2p_z^1$. Bond formation with these pure atomic orbitals would lead to the situation where the bond formed by one $2s$ electron will be different from the bonds formed by three $2p$ electrons. But, in methane molecule, all the four bonds are equivalent. In order to explain this, the idea of orbital hybridisation was invoked. In this process, one $2s$ and three $2p$ orbitals on hybridization yield a set of four new equivalent orbitals. These new orbitals are called **hybrid orbitals**. Since they are formed by combining one s and three p orbitals, they are called sp^3 hybrid orbitals. All the four sp^3 hybrid orbitals are of equal energy and each one of them has 25% s character and 75% p character.



These sp^3 hybrid orbitals are shown in Fig. 1.1. You can see in Fig. 1.1 (a) that the



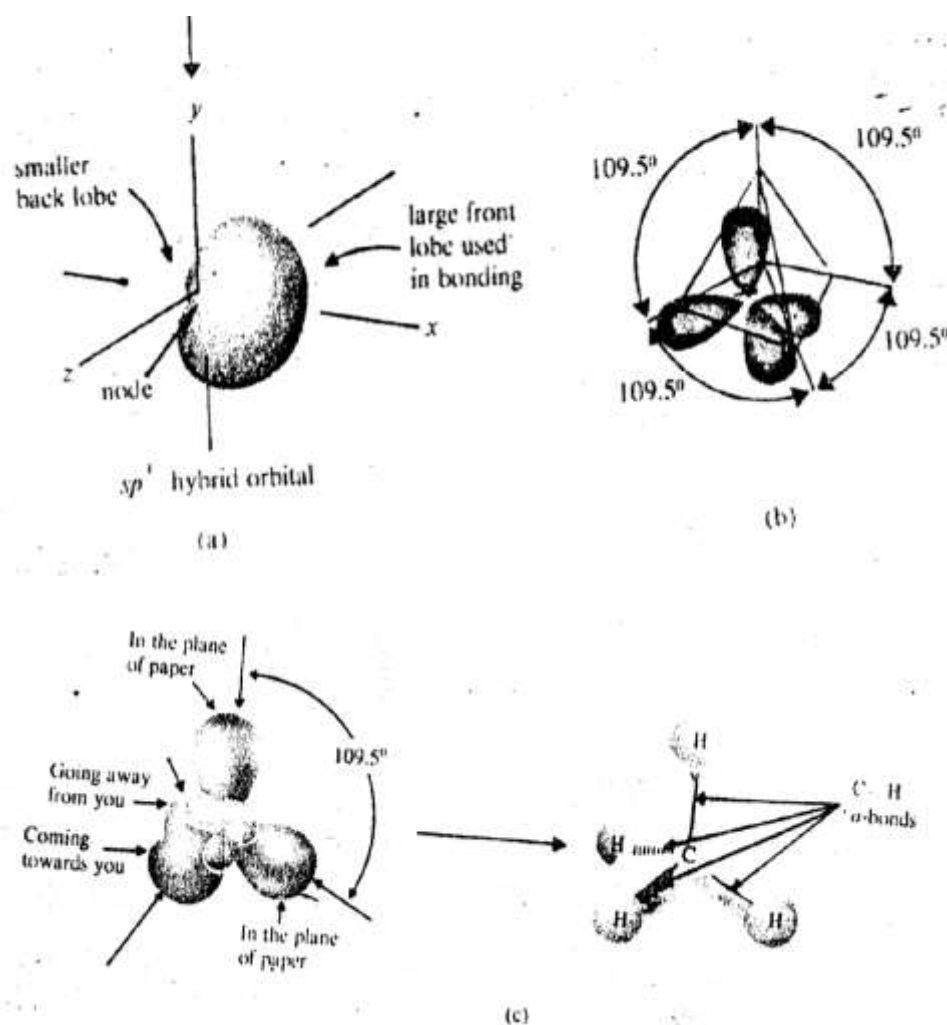


Fig. 1.1: a) Hybridisation of one $2s$ and three $2p$ orbitals to yield four sp^3 hybrid orbitals. b) Four sp^3 hybrid orbitals directed towards the corners of a tetrahedron: small back lobes are not shown. c) Formation of methane molecule.

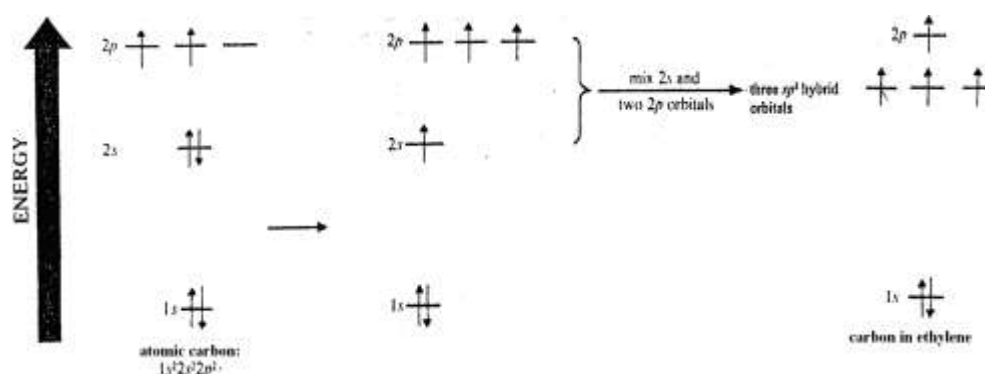
Sp^3 hybrid orbital has two lobes of unequal size separated from each other by a node. This situation is similar to a p orbital but with the difference that here one lobe is very small and the other is very large. In other words, in sp^3 hybrid orbitals, the electron density is concentrated in one direction which leads to greater overlap as compared to pure atomic orbitals. Hence, the bonds formed by such orbitals will be stronger and more stable in comparison to those formed by using pure atomic orbital. The spatial orientation of these orbitals is obtained by mathematical calculations and is shown in Fig. 1.1 (b). This is in accordance with the VSEPR theory which you had studied. You can see in the figure that these orbitals are directed towards the corners of a tetrahedron and the bond angle between any two sp^3 hybrid orbitals is 109.5° . In methane molecule, each of the four sp^3 hybrid orbitals overlaps with $1s$ orbital of four hydrogens as shown in Fig. 1.1 (c).

Note that the bonds so formed, i.e: the C – H bonds, are σ (sigma) bonds. If instead of combining with hydrogens, the hybrid orbital forms a bond with the similar hybrid orbital of another carbon atom, then a C – C bond will result instead of the C – H bond. The C-C has a bond length of 154 pm and a bond energy of 348 kJ mol^{-1} . You will study more about the compounds involving sp^3 hybridisation in the latter part of this course.

3.3.2 Sp^2 -Hybridisation

In a molecule like ethylene, where there are not enough hydrogen in the molecule to form six C - H bonds, another type of hybridization has to be thought of.

In this type of hybridization, as the name indicates, the $2s$ orbital of the carbon is hybridized with only two of the three available $2p$ orbitals, as shown below.



Since three orbitals are hybridized, three equivalent sp^2 hybrid orbitals are obtained. We shall now explain sp^2 hybridisation using ethylene as an example.

According to the VSEPR theory, these orbitals are oriented in space making an angle of 120° with each other as shown in Fig. 1.2(a). Note that the three sp^2 hybrid orbitals are in one plane. The third p orbital which is not utilized for hybridization is perpendicular to the sp^2 hybrid orbitals and is shown in red colour in Fig. 1.2(a).

When two such sp^2 hybridised carbon atoms form a bond, the C – C bond formed is again a σ bond. If the rest of the sp^2 hybrid orbitals on each carbon atom overlap with $1s$ orbital of the two hydrogen atoms, then as shown in Fig. 1.2 (b) the two unhybridised p orbitals on the two carbon atoms are parallel to each other. These p orbitals can overlap sideways to yield a second bond, known as π (pi) bond which is shown in Fig. 1.2(c). The C = C bond length for ethylene molecule so obtained is 134 pm. You can compare this value with C – C single bond length as

given before in case of ethane. You will study in detail, the compounds having sp^2 hybridised carbon atoms such as **alkenes** and **dienes**.

- (a) You are aware that:
- δ bonds are formed by the edge-on overlap of pure (s and p) or hybrid orbitals. The electron density in δ bonds is maximum along the internuclear axis.
 - π bonds are formed by sideways overlap of p orbitals. π bonds have maximum electron density above and below the internuclear axis.

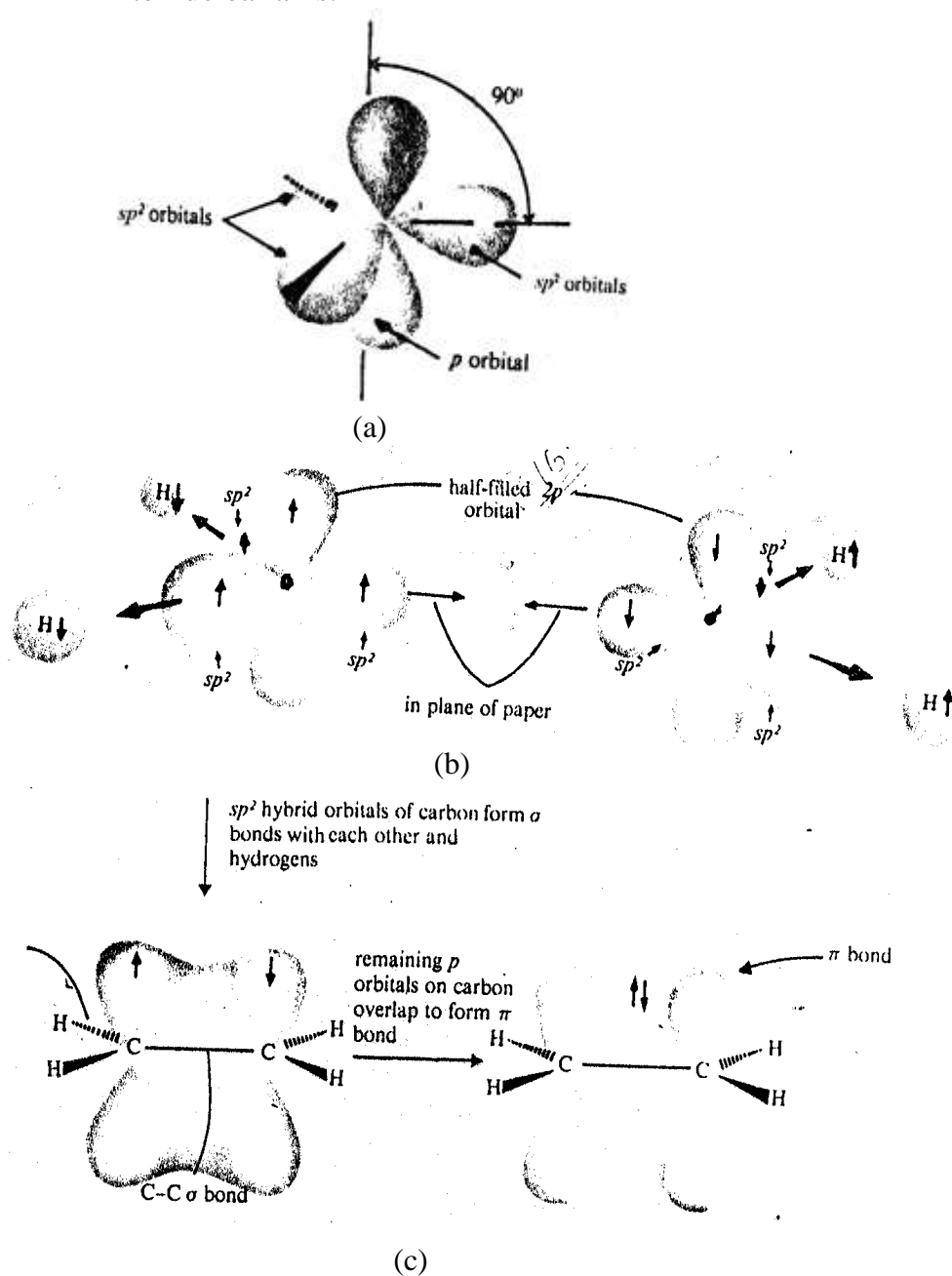


Fig. 1.2: (a) sp^2 hybrid orbitals. (b) Formation of $C - C \delta$ bond. (c) Formation of a π bond in ethylene molecule.

Activity

Make a model of ethylene molecule and convince yourself that it is flat in shape with the two carbons and their substituent hydrogens lying in one plane. However, the π bond is at right angles to this plane.

SELF ASSESSMENT EXERCISE 2

Predict the percentage of s and p character in sp^2 hybrid orbitals.

3.3.3 sp -Hybridisation

Let us now consider the third type of hybridization involving s and p orbitals in cases where a triple bond is stipulated. In carbon atom when $2s$ and only one of the three $2p$ orbitals hybridise as shown below, the hybridization is known as sp - hybridization. This leads to two new equivalent sp hybrid orbitals as shown in fig 1.3(a)

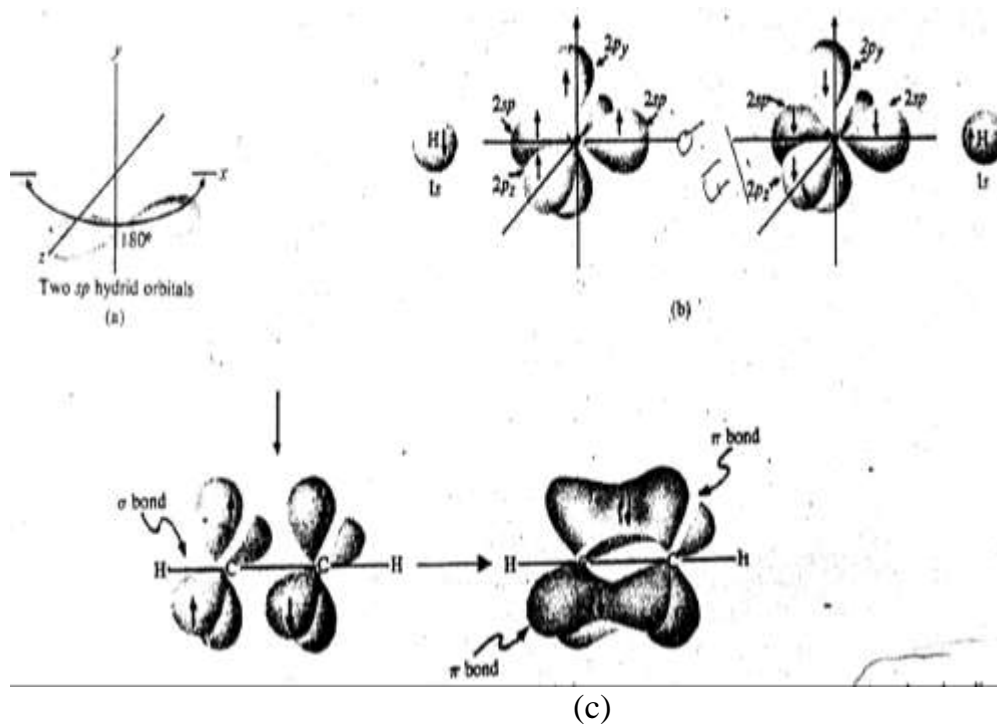


Fig. 1.3: (a) two sp hybrid orbitals. (b) Formation of one σ (sigma) bond. (c) Formation of two π bonds.

Acetylene is a linear molecule having cylindrically symmetrical π electron density about the internuclear axis.

These two orbitals are oriented in space at an angle of 180° according to the VSEPR theory. Let us study sp -hybridisation using acetylene as an example. When one of the two sp hybrid orbitals on each carbon atom

combines with another, a C – C sigma bond is formed. The second sp hybrid orbital on each carbon forms a sigma bond with $1s$ orbitals of two hydrogens, as shown in Fig. 1.3 (b). This leaves two p orbitals on each carbon atom which are not used in sp hybridization. These p orbitals are perpendicular to each other and also to the sigma bond. These p orbitals can overlap laterally to give rise to two π bonds. Such a bond is called a triple bond and we get the acetylene molecule, as shown in Fig. 1.3 (c) The C = C bond in acetylene has a bond length of 120 pm and the H – C – C angle is 180° which shows that it is linear. Compounds having triple bond are called **alkynes** and will be dealt with in detail in Unit 5 of module 2. We can sum up the above information as shown in Table 1.3

Table 1.3: Bond characteristics and hybridization of carbon in simple molecules

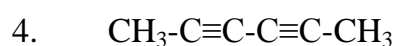
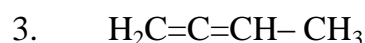
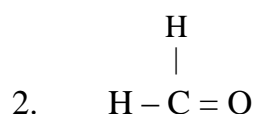
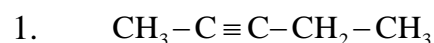
Compound	Hybridisation of carbon atom	Bond length in pm	Bond angle	Nature of carbon-carbon bonds
Ethane	Sp^3	154	109.5°	Single
Ethylene	Sp^2	134	120°	Double
Acetylene	Sp	120	180°	Triple

From the data given in the Table 1.3 we can conclude that

- (i) in the hybrid orbitals, as the s character increases, bond length decreases.
 - (ii) as the bond order increases, the bond length decreases
- Before proceeding to the next section, answer the following SAQ.

SELF ASSESSMENT EXERCISE 3

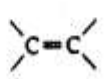
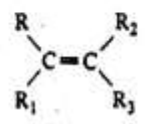
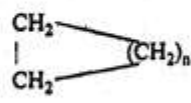
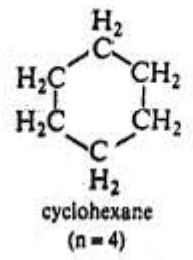
Indicate the type of hybridization for each of the carbon atoms in the following compounds:

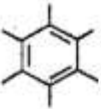
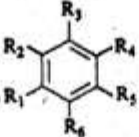
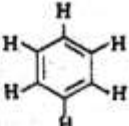
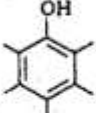
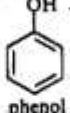




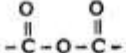






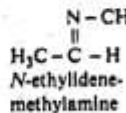



3.4 Functional Group Classification

A systematic study of chemistry or for that matter any other branch of science, is not possible without arranging the subject matter in a logical manner when sufficient data has accumulated. In case of inorganic chemistry, formulation of the periodic table stimulated not only the search for missing elements but also led to the understanding of the periodic behaviour. In organic chemistry, as the number of known organic compounds runs into millions, it is very difficult to study each and every compound individually. Thus, by grouping similar compounds together in a class or a family, it is easier to understand their properties, reactions etc. One way of such classification is based on the functional groups. A **functional group** can be defined as an atom or a group of atoms in a molecule which exhibits characteristic chemical properties. Such chemical properties exhibited by the functional group are more or less constant for various transformation of the functional group and do not affect the rest of the molecule. The advantage of such a classification based on functional groups is that in addition to logically systematizing the organic compounds, the properties of the compounds can be predicted just by looking at their structures, i.e., by knowing the type of functional group present. Table 1.4 lists a number of important functional groups. You will study each class of compounds in detail in the forthcoming blocks of this course.

Table 1.4: Functional Groups

Class	Functional Group	General structural formula	Example	IUPAC suffix or prefix
<i>Containing C and H only</i>				
Alkane	none	R - H	CH ₄ methane	-ane
Alkene			H ₂ C = CH ₂ ethylene	-ene
Alkyne	-C≡C-	R - C≡C - R ₁	H - C≡C - H acetylene	-yne
Cycloalkane	none			cyclo - ... -ane

Aromatic Compounds				—
<i>Containing C, H and O</i>				
Alcohol	-OH	R-OH	CH ₃ -OH methanol	-ol
Phenol		Ar-OH	 phenol	-ol
Ether	-O-	R-O-R'	CH ₃ -O-CH ₃ dimethyl ether	alkoxy-
<i>Carbonyl compounds</i>				
Aldehyde		RCHO	CH ₃ CHO acetaldehyde	-al
Ketone		R-C(=O)-R'	CH ₃ -C(=O)-CH ₃ acetone	-one
Carboxylic acid		R-C(=O)-OH	CH ₃ -C(=O)-OH acetic acid	-oic acid
Ester		R-C(=O)-OR'	CH ₃ -C(=O)-O-CH ₃ methyl acetate	-oate
Anhydride		R-C(=O)-O-C(=O)-R'	CH ₃ -C(=O)-O-C(=O)-CH ₃ acetic anhydride	-oic anhydride
<i>Containing C, H and N</i>				
Amine		 (primary amine)	CH ₃ NH ₂ methylamine	} -amine or Amino-
		 (secondary amine)	H ₃ C-NH-CH ₃ dimethylamine	
		 (tertiary amine)	H ₃ C-N-CH ₃ trimethylamine	
Imine				—
Nitrile	-C≡N	R-C≡N	CH ₃ -C≡N acetonitrile	-nitrile
<i>Containing C, H, N and O</i>				
Nitro compounds	-NO ₂	R-NO ₂	CH ₃ -NO ₂ nitromethane	Nitro-
Amide		R-C(=O)-NH ₂	CH ₃ -C(=O)-NH ₂ acetamide	-amide

Containing C, H and other elements				
Halide	-X	R-X	CH ₃ -Cl methyl chloride	Halo-
Acyl halide	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{X} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{X} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C}-\text{Cl} \end{array}$ acetyl chloride	-oyl halide
Thiol	-SH	R-SH	CH ₃ -SH methanethiol	-thiol
Sulphonic acid	-SO ₂ -OH	R-SO ₂ -OH	CH ₃ -SO ₂ -OH methanesulphonic acid	-sulphonic acid

- Here, X stands for halogens (F, Cl, Br and I), R stands for the alkyl group and Ar stands for the aryl group.
- The names given in Column 4 are common names.
- At this stage, you should not worry about the last column of the table. We will refer back to this column while studying nomenclature of organic compounds in the next section.


The compounds which are listed in the first category in Table 1.4 are the compounds which contain only carbon and hydrogen. These compounds are also called **hydrocarbons**. The hydrocarbons can be classified as **aliphatic**, **alicyclic** or **aromatic**. In the *aliphatic* hydrocarbons, the carbon atoms are linked to each other to form chains (straight or branched). The *aliphatic* hydrocarbons can be further classified as saturated or *unsaturated*. The saturated hydrocarbons contain the carbon and hydrogen atoms linked to each other by single bonds and are called **alkanes**. The unsaturated hydrocarbons are of two **types**: the one containing double bond as the functional group are named as **alkenes**; the other containing a triple bond as the functional group are known as **alkynes**.

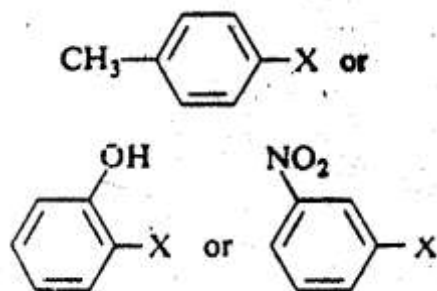
In the *alicyclic hydrocarbons*, the carbon atoms are arranged in rings to yield cyclic structures. These compounds are also known as **cycloalkanes**.

The *aromatic hydrocarbons* include benzene and those compounds which resemble benzene in their properties.

In fact, the hydrocarbons provide a backbone to which various functional groups may be attached to yield an enormous variety of organic compounds.

The alkyl groups, generally represented by R, are derived from **alkanes** by removing one hydrogen. The simplest alkyl group is methyl group (CH₃-C) which is derived alkane, methane (CH₄). Common alkyl groups are listed in Table 1.7, Similarly, aryl groups denoted by Ar, are obtained from benzene and its derivatives by removing one hydrogen.

The simplest aryl group is phenyl group (C_6H_5-  and is abbreviated as Ph. In general, aryl halide (Ar-X) can refer to any of the following:



Let us now study about the structural features of some classes of aliphatic compounds. The compounds in which the carbon and oxygen atoms are linked by a single bond can be classified as **alcohols** or **ethers**, depending upon the number of alkyl groups attached to oxygen. In alcohols, oxygen is linked to only **one** alkyl group and one hydrogen; but in ethers, oxygen has two alkyl groups attached to it. The compounds containing carbon and oxygen linked by a double bond (i.e. $>C=O$, which is called **carbonyl group**, can be classified as **aldehydes** or **ketones**, depending on whether the number of alkyl groups attached to carbonyl carbon is one or two, respectively. If instead of an alkyl group, one hydroxyl (-OH) group is attached to the carbonyl group, a class of compounds known as **carboxylic acids**.

$\begin{array}{c} O \\ || \\ R - C - OH \end{array}$ is obtained. A number of carboxylic acid derivatives are obtained by

replacing the hydroxyl group by halogens, $-NH_2 - O - \begin{array}{c} O \\ || \\ C - R \end{array}$ or $-OR$ groups.

Accordingly, these compounds are called **acid halides** ($R - C - X$), amides

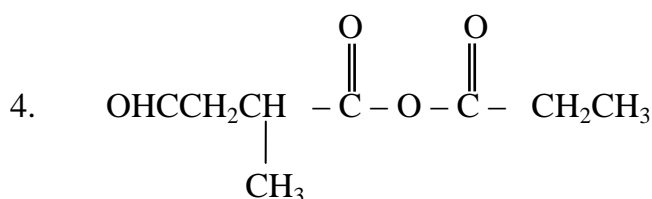
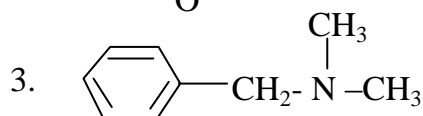
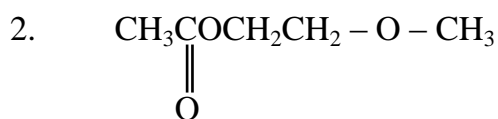
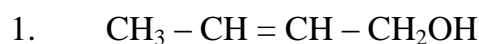
$\begin{array}{c} O \\ || \\ R - C - NH_2 \end{array}$, **anhydrides** ($R - C - O - \begin{array}{c} O \\ || \\ C - R' \end{array}$) and esters ($R - C - \begin{array}{c} O \\ || \\ OR' \end{array}$). They are also called functional derivatives of carboxylic acids, as they are obtained by the changes in the functional group.

In a similar manner, compounds having carbon-nitrogen single bond are called **amines**. The amines can be of three types: **primary**, **secondary** and **tertiary** amines depending upon whether the number of alkyl groups attached to nitrogen is **one**, **two** or **three**. The carbon-nitrogen double bond is characteristic of the class of compounds known as **imines** while compounds having carbon-nitrogen triple bond are called **nitriles**. Then we have **alkyl halides** which have their unique importance in the transformation of functional groups which you will realize when you study their reactions in the following blocks. The sulphur analogs of alcohols and carboxylic acids are known as **thiols** and **suphonic acids**, respectively.

Parallel to the classes discussed above for aliphatic compounds, we have **aromatic compounds** in which benzene forms the backbone to which various functional groups mentioned above can be attached to yield similar classes of aromatic compounds, like aryl halides, arylamines, phenols, aromatic carbonyl compounds, aromatic acids and their derivatives, etc. As you have seen in Table 1.4, R is generally used to represent **an alkyl group**; the corresponding aromatic compounds are obtained by replacing R by Ar which denotes an aryl group; this is shown in Table 1.4 in case of alcohol and phenol. In the next section, we will study about the nomenclature of these compounds. Before that attempt the following SAQ to check your understanding about the functional groups.

SELF ASSESSMENT EXERCISE 4

Encircle and name the functional groups present in the following compounds:



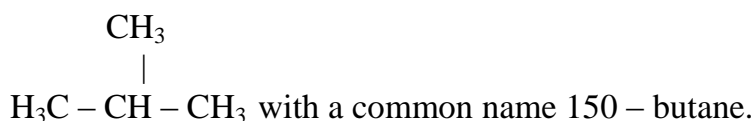
3.5 Nomenclature of Organic Compounds

The earliest attempts to name organic compounds were based either on their origin or on their properties. For example, citric acid was named so because of its occurrence in *citrus* fruits. The aromatic compounds were called so because of their characteristic odour (Greek: **aroma**, fragrant smell). Examples are oil of wintergreen and vanillin (a constituent of vanilla also used as a flavouring agent) which were called aromatic due to their characteristic fragrance. With the advancement and growth in the knowledge of chemistry, the number of known organic compounds has increased rapidly. Also, with the increase in the number of carbon atoms, the number of possible isomers for hydrocarbons (without any functional group) becomes very large (see Table 1.5).

Isomers are the compounds that have identical molecular formulas but differ in the ways in which the atoms are bonded to each other. For example, four carbons in a hydrocarbon having molecular formula C_4H_{10} can be arranged in the two different ways:

Straight chain $H_3C - CH_2 - CH_2 - CH_3$

Common name; normal butane or n-butane



Thus, n-butane and isobutane are isomers.

Table 1.5: Possible Number of Isomers for Hydrocarbons

Number of carbon Atoms in the Hydrocarbon	4	5	6	7	8	9	10	12	15	20
Number of possible Isomers	2	3	5	9	18	35	75	355	4,347	366,319

Having learned about the variety of functional groups, you can imagine that the nature and position of functional groups present can raise these numbers many fold. Under such a situation, it is next to impossible to learn the names randomly assigned to the compounds, especially when there is no correlation of the name to the structure of the compound. This necessitated the need to have a **systematic nomenclature** for which the International Committee of Chemists met at Geneva in 1892. The work was carried on by the **International Union of Chemists (I.U.C.)** which gave its report in 1931, known as the I.U.C. system of nomenclature. As the nomenclature is always undergoing modifications and revisions, 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 (I.U.P.A.C.)**. We will now study this system in detail.

Since the nomenclature of other classes of compounds is based on the nomenclature of alkanes, let us start the study of nomenclature with the alkanes. **Alkanes** are represented by the general formula C_nH_{2n+2} where n can be 1,2,3,4... etc. The first four alkanes retain their original or nonsystematic names. The names of alkanes higher than these start with a prefix (Greek or Latin words) which indicates the number of carbon atoms in the chain and end with suffix-ane. The IUPAC names for various alkanes having different chain lengths are given in Table 1.4. The unbranched alkanes have their common names as normal alkanes or n-alkanes.

Compounds that differ from each other in their molecular formulas by the unit $-CH_2-$ are called members of a homologous series. Thus, the compounds listed in Table 1.6 belong to a homologous series.

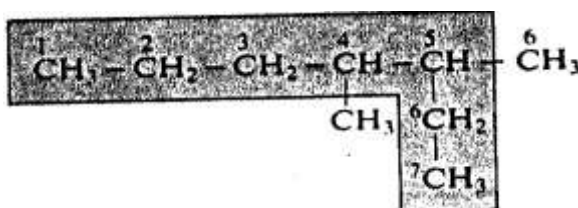
Table 1.6: IUPAC Names of straight chain alkanes having general formula C_nH_{2n+2}

n.	Formula	Name	n.	Formula	Name
1	CH ₄	methane	11	CH ₃ (CH ₂) ₉ CH ₃	undecane
2	CH ₃ CH ₃	ethane	12	CH ₃ (CH ₂) ₁₀ CH ₃	dodecane
3	CH ₃ CH ₂ CH ₃	propane	13	CH ₃ (CH ₂) ₁₁ CH ₃	tridecane
4	CH ₃ (CH ₂) ₂ CH ₃	butane	14	CH ₃ (CH ₂) ₁₂ CH ₃	tetradecane
5	CH ₃ (CH ₂) ₃ CH ₃	pentane	15	CH ₃ (CH ₂) ₁₃ CH ₃	pentadecane
6	CH ₃ (CH ₂) ₄ CH ₃	hexane	20	CH ₃ (CH ₂) ₁₈ CH ₃	icosane
7	CH ₃ (CH ₂) ₅ CH ₃	heptane	30	CH ₃ (CH ₂) ₂₈ CH ₃	triacontane
8	CH ₃ (CH ₂) ₆ CH ₃	octane	40	CH ₃ (CH ₂) ₃₈ CH ₃	tetracontane
9	CH ₃ (CH ₂) ₇ CH ₃	nonane	50	CH ₃ (CH ₂) ₄₈ CH ₃	pentacontane
10	CH ₃ (CH ₂) ₈ CH ₃	decane	100	CH ₃ (CH ₂) ₉₈ CH ₃	hectane

* Prior to 1979 version of IUPAC rules, icosane was spelled as eicosane.

The branched chain alkanes are named by using the following steps:


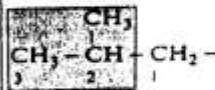
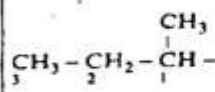
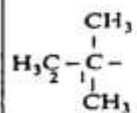
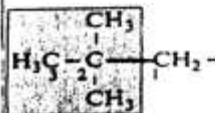
1. The longest continuous chain of carbon atoms is taken as the parent hydrocarbon. For example, in the compound shown below, the parent hydrocarbon is heptane and not the hexane.



2. Identify the substituent alkyl groups attached to the parent chain.

Some common alkyl groups are listed in Table 1.7. You can locate that both the substituents in the example cited above are methyl groups.

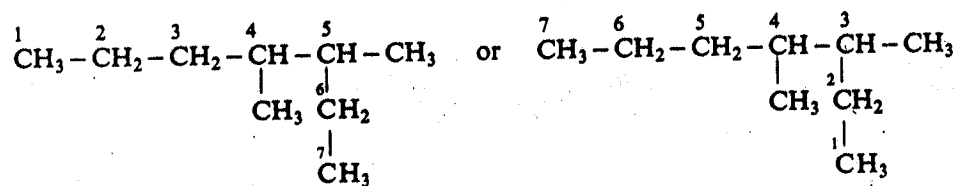
Table 1.7: Common Alkyl groups

Alkyl group	Common name	IUPAC name
CH_3	methyl	methyl
CH_3CH_2-	ethyl	ethyl
$\text{CH}_3\text{CH}_2\text{CH}_2-$	<i>n</i> -propyl	propyl
	isopropyl	1-methylethyl
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$	<i>n</i> -butyl	butyl
	isobutyl	2-methylpropyl
	sec-butyl	1-methylpropyl
	tert-butyl	1, 1-dimethylethyl
	neopentyl	2, 2-dimethylpropyl

The IUPAC system of nomenclature has retained some of the older names for branched alkyl groups such as isopropyl, isobutyl, sec-butyl, and neopentyl.

Note that the numbering of carbon atoms is from the point of attachment of the group to the parent chain.

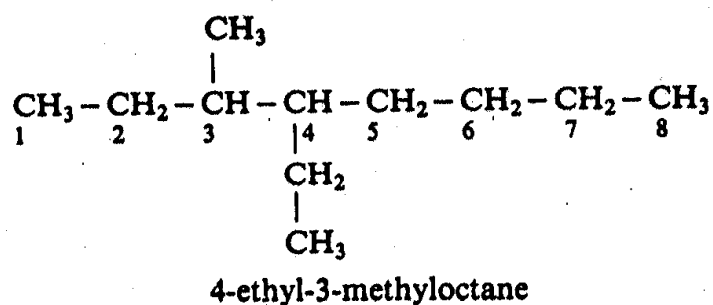
- The parent carbon chain is then numbered in such a way that the substituents get the lowest possible numbers. The carbon atoms in the above compound can be numbered as;



Can you guess which of the two numbering systems is correct: The first possibility locates the methyl groups at carbons 4 and 5 and the second, at carbons 3 and 4. Certainly, the second way of numbering the carbon chain is correct.

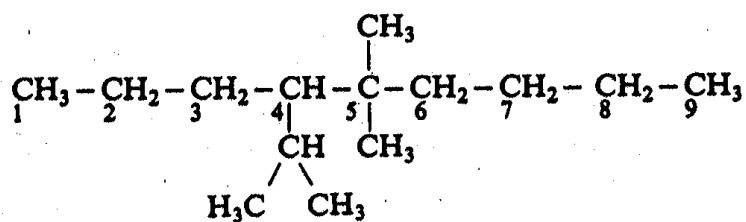
- Prefixes *di*, *tri*, *tetra*, *penta* etc, are used when the substituents occur more than once. Since in the above compound the methyl substituent is occurring twice, the name is prefixed with *di* for the above compound.
- The name of the compound is written by writing the location and name of the substituents followed by the name of the parent alkane. Thus, the above compound can be named as 3, 4-dimethylheptane. Note that a comma is used to separate the two numbers and the numbers are separated from names of groups by a hyphen. Also note that there is no blank space between the name of the last substituent and the parent alkane.
- When more than one type of alkyl groups are present, then they are cited in the name in the alphabetical order, regardless of their location in the principal chain.

The numerical prefixes *di*, *tri*, *tetra*, etc. and hyphenated prefixes such as *sec-tert* – are not considered in determining the alphabetical order but prefixes *iso*, *neo*, *cyclo* are considered for alphabetizing. To understand it, let us consider the examples given below:



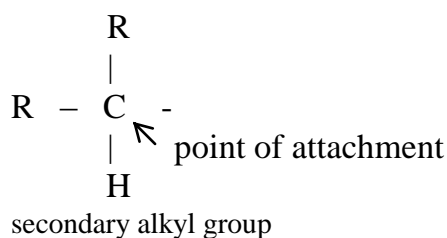
Note that here *ethyl* is cited before *methyl*, in spite of its higher location number.

Similarly, the compound shown below,

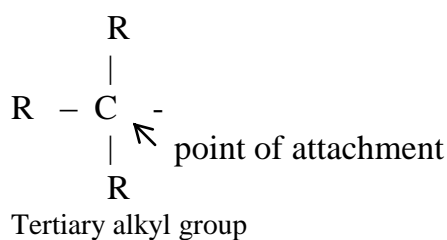


can be named as 4-isopropyl-5,5-dimethylnonane or 4-(1-methylethyl)-5,5-dimethylnonane.

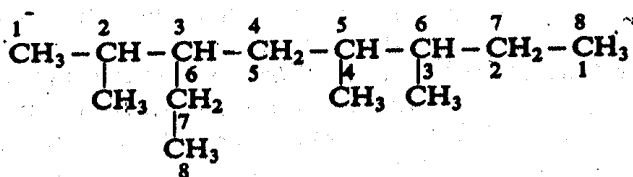
7. The branched chain substituents, such as 1-methylethyl shown in step 6, are numbered starting from the carbon attached directly to the parent chain. Table 1.7 shows the numbering for the branched substituents listed there. The longest carbon chain is selected and the substituents are named according to the rules listed above for compounds having unbranched substituents. Note that the name and numbering of branched substituent is written in brackets in order to separate it from the numbering of the main chain.
8. The alkyl substituents can be further classified as primary, secondary or tertiary. An alkyl group is called a primary alkyl group if the carbon atom at the point of attachment is bonded to only one other carbon. For example, $R - CH_2 -$ is a primary alkyl group. Similarly, a *secondary* alkyl group has two alkyl groups bonded to the carbon atom taken as the point of attachment to the main chain. Thus, a secondary alkyl group can be written as shown below:

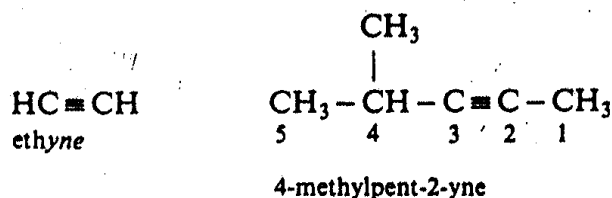


Similarly, a *tertiary* alkyl group has three carbon atoms bonded to the carbon atom taken as point of attachment. Thus, a tertiary alkyl group can be represented as shown below:

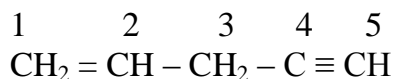


9. When more than one carbon chains of equal length are available, the numbering is done considering the following points:
- (a) The principal chain should have the greatest number of side chains. For example, in the compound shown below;



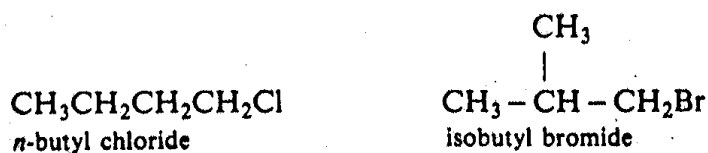


When both double and triple bonds are present, then the double bond gets the lower number. Thus, for the compound show below;

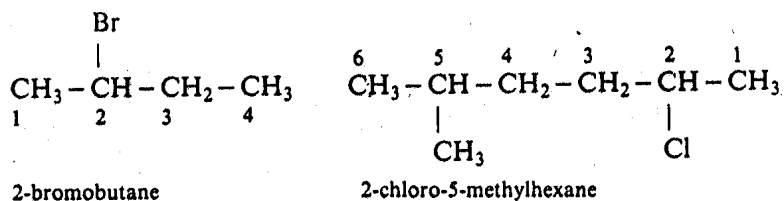


The correct name is pent – 1-ene-4-yne

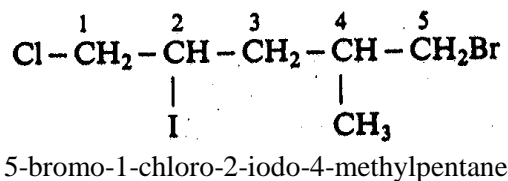
Alkyl halides: The alkyl halides are the halogen derivatives of alkanes. The halogens present are usually F, Cl, Br and I. The common names are arrived at by writing the name of alkyl group followed by the name of the halide. Examples are shown below:



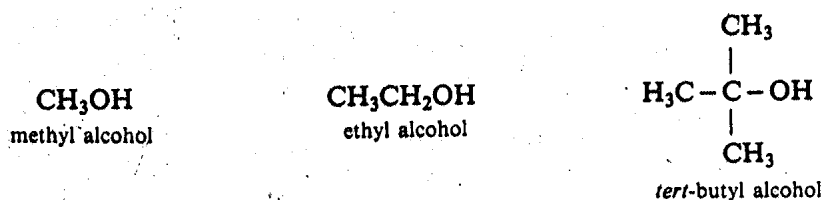
In the IUPAC system of nomenclature, prefix *halo-* (i.e., *fluoro*, *chloro*-, *bromo* or *iodo-*) is used to give the lowest number to the carbon atom to which the halogen is attached. For example, some halogen compounds are named below:



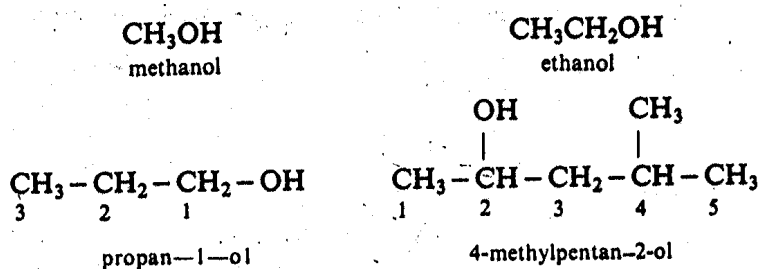
When more than one type of halogen atoms are present, their names are arranged in alphabetical order as shown in the next example,



Alcohols: Alcohols are the compounds having hydroxyl (-OH) group attached to the alkyl chain. The common names of the alcohols are written by specifying the alkyl group followed by the word alcohol, e.g.



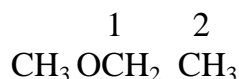
In the IUPAC nomenclature, suffix *ol* is used instead of final *e* of the parent hydrocarbon. The position of the hydroxyl group is given by assigning the lowest possible number to the carbon atom carrying it. Some examples are:



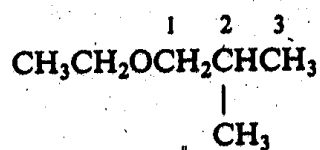
Ethers: The common names for ethers are derived by naming the two alkyl groups in alphabetical order followed by the word ether. This is illustrated in the examples given below:



In the IUPAC system, ethers are named *as alkoxyalkanes*. The larger of the two alkyl groups is chosen as the hydrocarbon chain. For example, the compound,



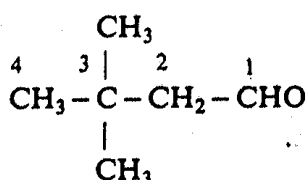
is named as 1-methoxyethane and not as ethoxymethane. Similarly, the compound,



has the name 1-ethoxy-2-methylpropane.

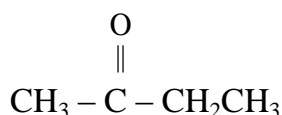
Aldehydes: Lower members of this class are commonly named after the acids that they form on oxidation. For example, HCHO, formaldehyde is named so because it forms formic acid (HCOOH) on oxidation.

In the IUPAC system of nomenclature, they are named as **alkanals**. The simplest aldehyde is methanol. Since the aldehyde group – CHO) is always at the end of the chain, it is always numbered as C – 1 in the chain, but this number is not specified in the name, i.e. the compound.



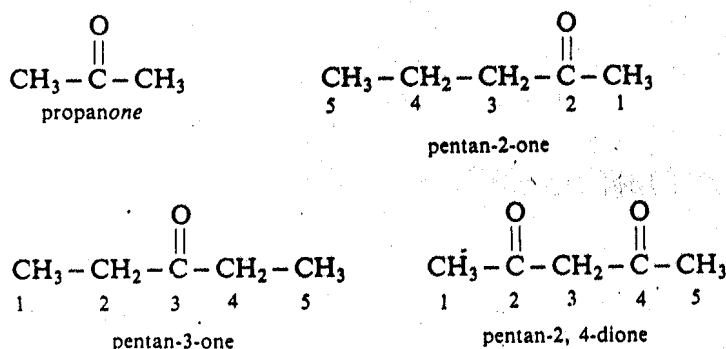
is named as 3, 3-dimethylbutanal.

Ketones: The common names for ketones are written similar to ethers, i.e. the two alkyl groups are written alphabetically followed by the word ketone. For example, the compound,



is commonly known as ethyl methyl ketone.

Thus, acetone, CH_3CCH_3 is also known as dimethyl ketone. The IUPAC names for ketones are derived by using the suffix *one* instead of final *e* of the parent hydrocarbon. As usual, the position of the carbonyl group is indicated by the lowest possible number. A few examples are,



Carboxylic acids: Nowhere else in organic chemistry, the common names are so prevalent as they are among carboxylic acids. Some examples are listed in Table 1.8 along with both their common and IUPAC names. For monocarboxylic acids,

O
||

[i.e. acids having one carboxy (- C – OH) group], the IUPAC names are derived by replacing *e* ending of the alkane by *oic acid*. As for aldehydes, the carboxyl carbon is numbered 1. However, in case of the dicarboxylic acids, the final *e* of the hydrocarbon is not dropped.

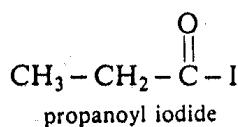
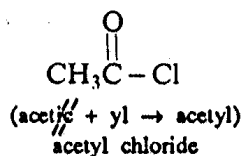
Table 1.8: Some Carboxylic Acids

Structure	Common Name	IUPAC Name
O HCOH	Formic acid	Methanoic acid
O CH ₃ – C – OH	Acetic acid	Ethanoic acid
OH O CH ₃ CHCOH	Lactic acid	2-hydroxypropanoic acid
CH ₃ (CH ₂) ₁₆ COOH	Stearic acid	Octadecanoic acid
HO ₂ C – CO ₂ H	Oxalic acid	ethanedioic acid
HO ₂ C(CH ₂) ₄ CO ₂ H	Adipic acid	Hexanedioic acid
O CH ₂ = CHCOH	Acrylic acid	Propenoic acid
OH HOOC – CH – CH – COOH OH	Tartaric acid	2,3-dihydroxybutanedioic acid

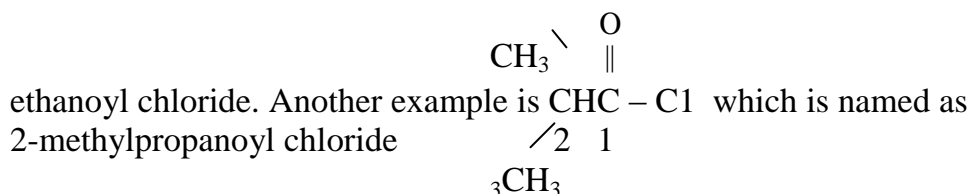
Acyl halides: Acyl halides are commonly named by placing the names of the halide after the name of the acyl group. The acyl group is obtained from the carboxylic acid by removal

O O
|| ||

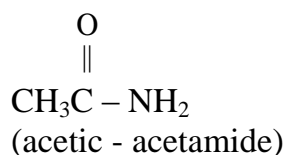
of its hydroxyl portion, i.e. R – C – OH leads to R – C – acyl group. The acyl group is named by using *yl* as the ending instead of ending *ic* in the carboxylic acid. Some examples are:



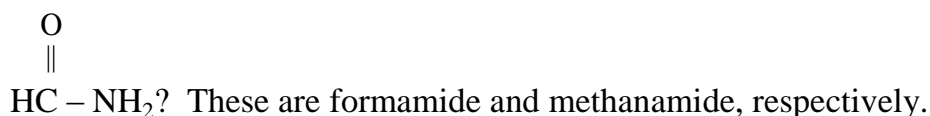
IUPAC names for acyl groups use the ending *oyl* instead of *yl* in the name of the corresponding hydrocarbon. The acetyl chloride has the IUPAC name



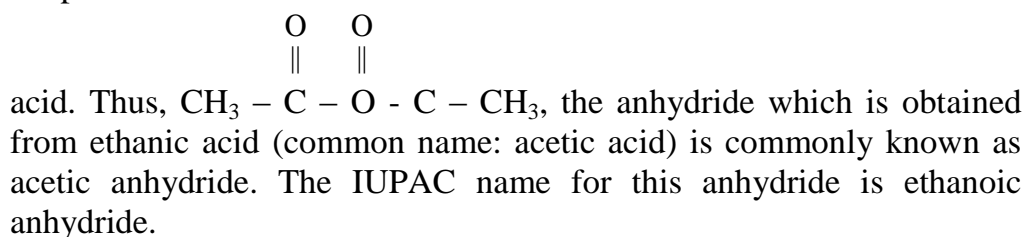
Acid amides: The common names for acid amides are derived by replacing the suffix *ic* or *oic* of the carboxylic acid by the suffix *amide* as shown below:



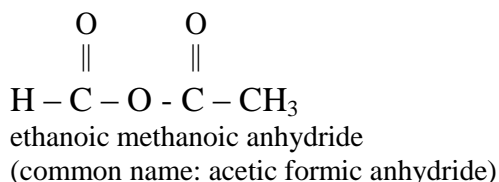
The IUPAC name for an amide is derived by appending the suffix *amide* to the parent hydrocarbon with the final *e* dropped. Thus, acetamide has the IUPAC name ethanamide. Having done this, can you give common and IUPAC names for



Acid anhydrides: A symmetrical anhydride is named as anhydride of the parent



For mixed anhydrides, both the parent carboxylic acids are cited in alphabetical order, followed by the word *anhydride*, as illustrated below:



Ethers: As the ethers contain alkyl and alkanoyl (acyl) groups, they are named as alkyl alkanoates. The alkyl group is cited first, followed by the name of the alkanoyl (acyl) portion which is named by replacing the *ic* ending of the carboxylic acid by the suffix *ate*.



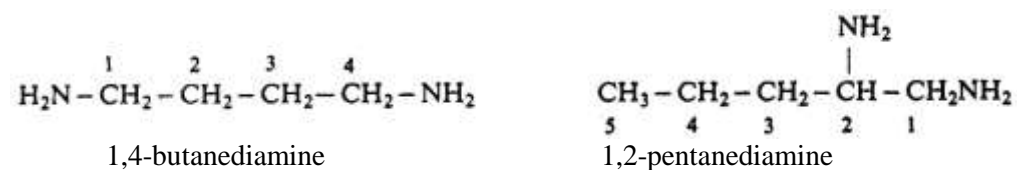
Amines: There are two systems of naming amines. One method names them as **alkylamines** and the other calls them as **alkanamines**. The alkanamine naming system was introduced by **Chemical Abstracts** and is easier to use as compared to the earlier IUPAC system of alkylamine names. The latest revision of **IUPAC** rules accepts both systems and examples below are named in both ways.

Bonding, Functional Group Classification and Nomenclature

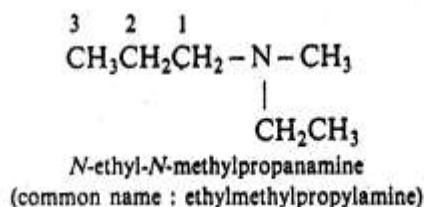
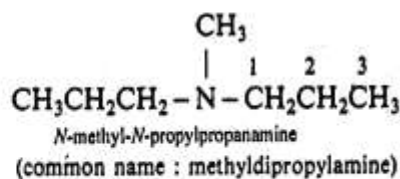
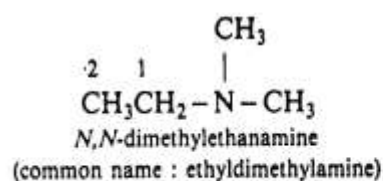
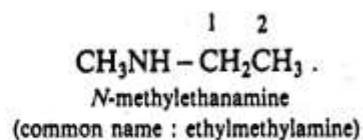
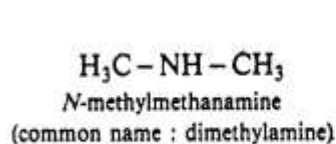


(Note that the numbering starts at the carbon and not at the nitrogen of the amine part).

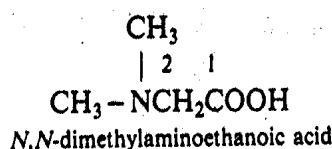
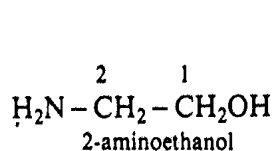
Primary diamines are named by using the suffix **diamine** after the name of the hydrocarbon.



For the secondary and the tertiary amines, the longest alkyl group present is considered as the parent chain. The remaining alkyl groups are named as substituents attached to the nitrogen and a prefix N- is used with the name of the alkyl group.

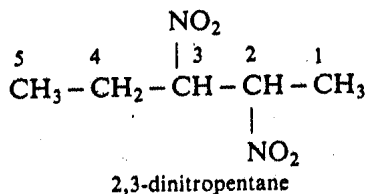
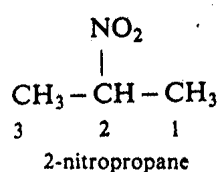
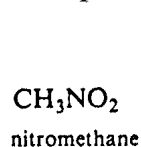


When used as a substituent, the $-\text{NH}_2$ group is named as amino and is prefixed with a number indicating the carbon atom to which it is attached.

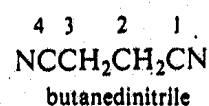
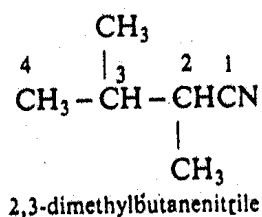
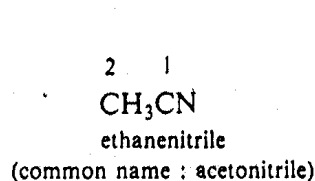


Nitro compounds: The nitro compounds are named as nitroderivatives of the corresponding hydrocarbons.

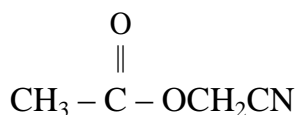
Examples being,



Nitriles: Nitriles are named in the IUPAC system by using the suffix – nitrile to the name of the hydrocarbon corresponding to the longest carbon chain. Note that here the carbon of the nitrile group is included in the numbering of carbon chain and is numbered as position 1. Some examples are given below:

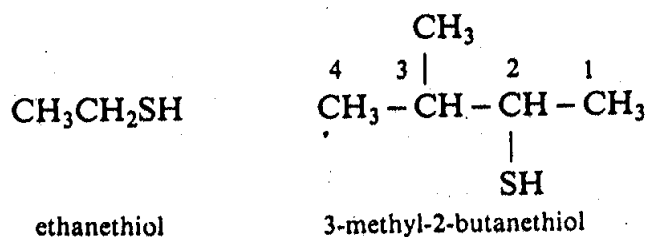


When named as a substituent, the $-\text{CN}$ group is called a cyano group. For example, the compound.

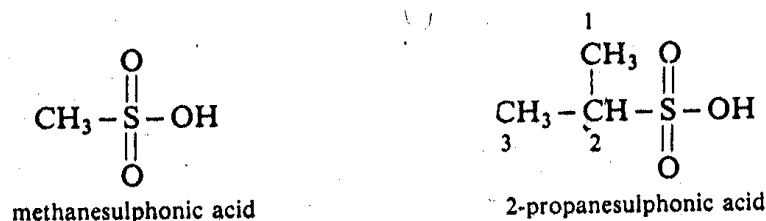


is named as cyanomethyl ethanoate.

Thiols: In naming thiols, an ending *thiol* is used as a suffix to the name of the corresponding hydrocarbon; for example,



Sulphonic acids: The names of sulphonic acids use the suffix sulphonic acid with the name of the corresponding hydrocarbon.



Till now, you have studied about the nomenclature of monofunctional compounds, i.e. the compounds which contain only one functional group. In polyfunctional compounds where more than one functional groups are present, one group is identified as the principal functional group and this principal functional group is used as a suffix in the name of the compound. The priorities for selection of principal functional group are given below in the order of decreasing precedence. The order is carboxylic acid, sulphonic acid, ester, acid anhydride, acyl halide, amide, nitrile, aldehyde, ketone, alcohol, thiol, amine, alkyne, alkene, ethers, halides, nitro.

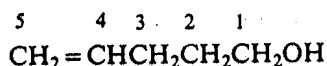
The order of priority for various functional groups is decided by considering the following points:

- (i) Functional groups that have an IUPAC suffix and terminate a carbon chain, have highest priority, e.g. carboxylic acids and their derivatives.

- (ii) Next are the groups that have a suffix and can be located at any position in the molecule, e.g. hydroxyl and amino groups.
- (iii) Groups having no suffix and which are named as substituents, are given the lowest priority, Example being the halogens.

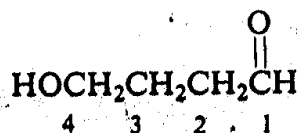
Let us study the examples given below which illustrate the nomenclature of polyfunctional compounds.

Example 1



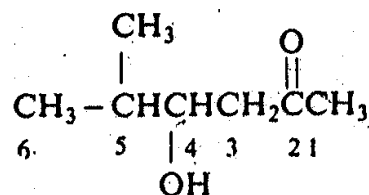
Here, the functional groups present are a hydroxyl group (- OH) and a double bond. As per the order given above, the hydroxyl group is the principal functional group and hence the compound should be named as an alcohol (and not as an alkene). Hence, its name is pent-4-ene-1-ol.

Example 2



Now, in this case the carbonyl group or more specifically the aldehyde functional group (- CHO) is to be given priority over the hydroxyl group. Hence, this compound is named as 4-hydroxybutanal.

Example 3



The principal functional group is the keto group. Hence, as shown in the structure, the numbering of the carbon chain will be done so as to give this function the lowest number. Thus, the name of this compound will be 4-hydroxy-5-methyl-2-hexanone.

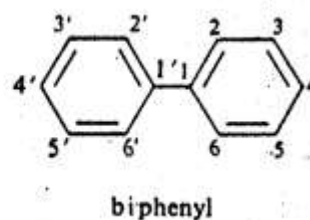
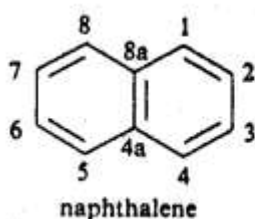
Let us now study the nomenclature of aromatic compounds. The aromatic compounds can have any of the following types of basic skeletons:

(a) Compounds Containing One Aromatic Ring

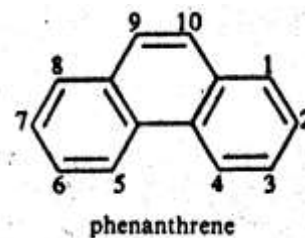
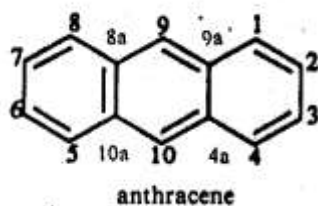
This class includes benzene and its derivatives. The derivatives of benzene include the compounds which can have any of the functional groups discussed before attached to the benzene ring.

**(b) Compounds Containing Two Aromatic Rings**

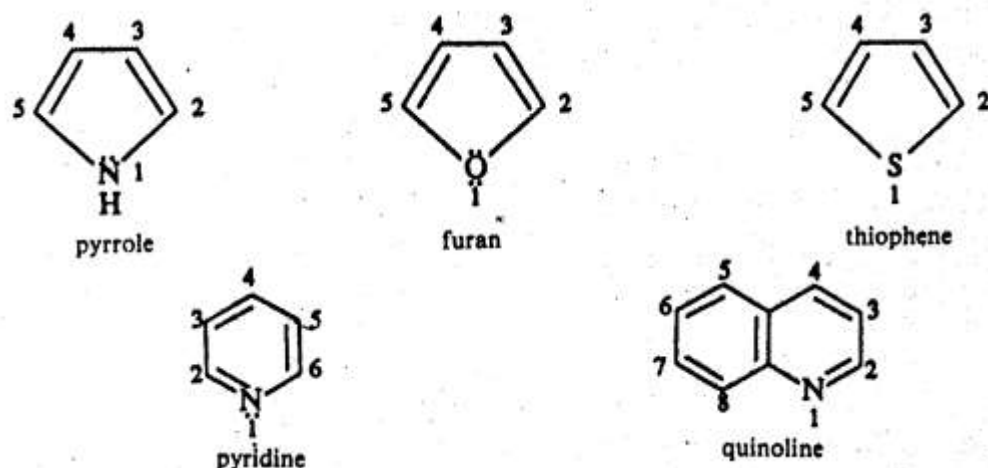
Examples being naphthalene and biphenyl.

**(c) Compounds Having More Than Two Aromatic Rings**

Examples are:

**(d) Heterocyclic Compounds**

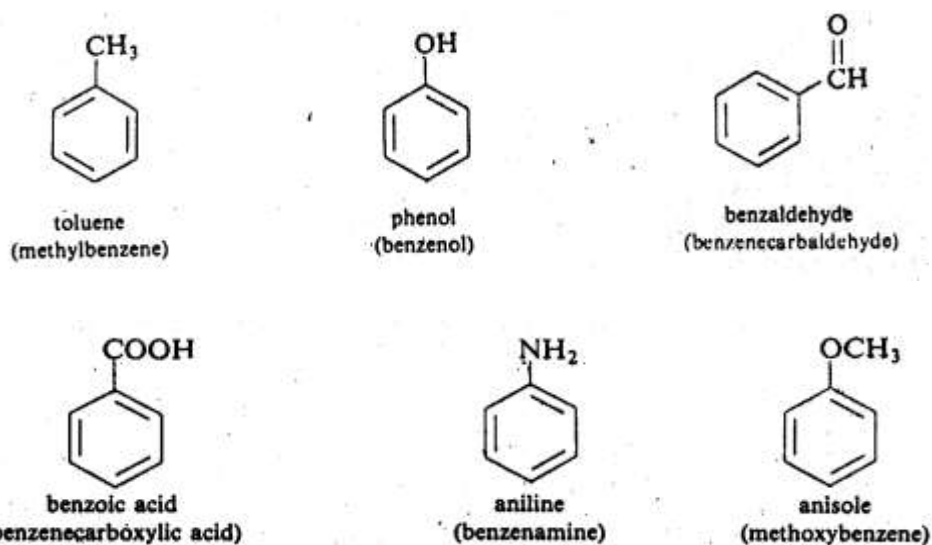
Aromatic compounds containing heteroatoms such as O, N or S in the aromatic ring are called heterocyclic compounds. Some heterocyclic compounds are shown below:



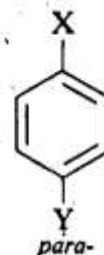
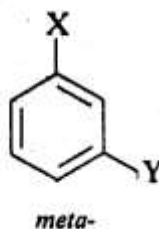
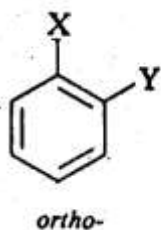
At this stage we will study in detail the nomenclature of benzene and its derivatives only. Although the carbon skeletons for the type of compounds shown in the categories (b), (c) and (d) are numbered here, their nomenclature will be dealt at appropriate places in later units of this course.

(a) Benzene and its Derivatives

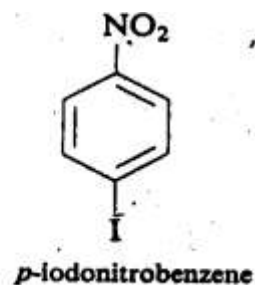
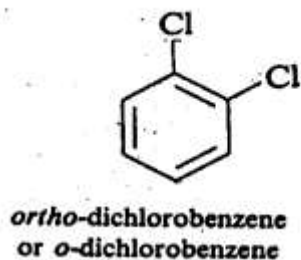
A number of monosubstituted benzene derivatives are known by their special names. These names are in common use for long and hence are approved by IUPAC. Some examples of these compounds are given below along with their common and IUPAC names (in brackets).



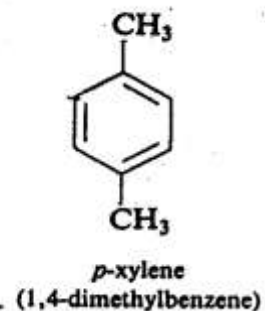
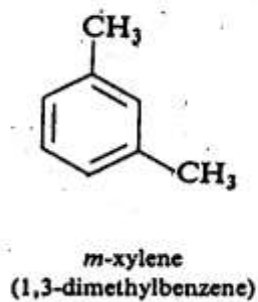
For disubstituted benzene derivatives, the following three arrangements of the substituents are possible.



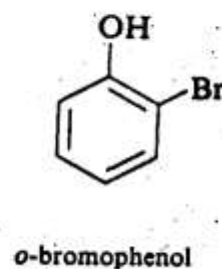
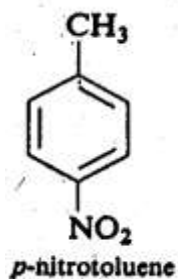
These arrangements are named using the Greek prefixes *ortho-*, *meta-* and *para* which are abbreviated as o-, m- and p-. The substituents are then named in the alphabetical order. This is illustrated in the examples below:



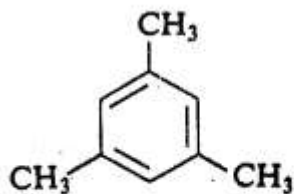
Dimethyl derivatives of benzene are known as xylenes. The three xylenes are;



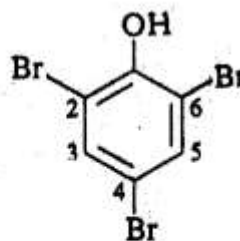
When one substituent is such that it corresponds to the monosubstituted benzene that has a special name, then this substituent is called the principal functionality and the compound is named as a derivative of that parent functionality. For example,



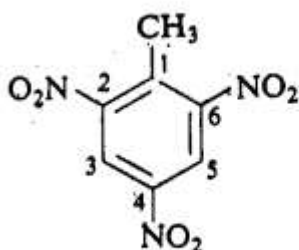
The polysubstituted benzenes are named by identifying the principal functions and then numbering is done such as to keep the principal function as number. The other substituents are then given the lowest possible numbers. This is illustrated in the following examples.



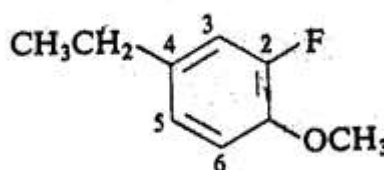
1,3,5-trimethylbenzene
(common name : mesitylene)



2,4,6-tribromophenol



2,4,6-trinitrotoluene (TNT)

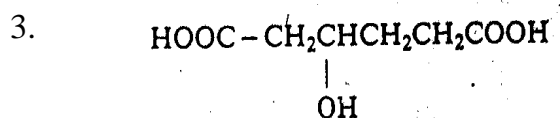
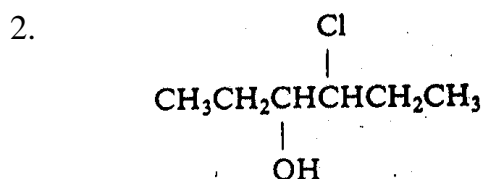
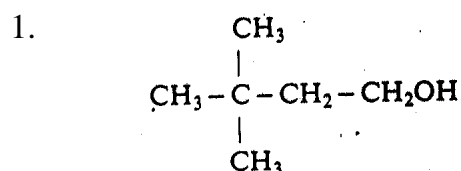


4-ethyl-2-fluoroanisole

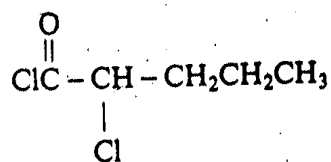
Having studied the nomenclature in detail, attempt the following SAQs to check your understanding about it.

SELF ASSESSMENT EXERCISE 5

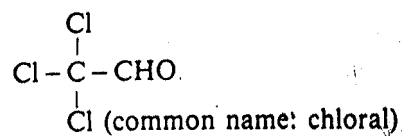
Name the following compounds according to the I.U.P.A.C. system of nomenclature.



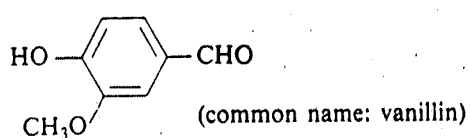
4.



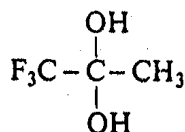
5.



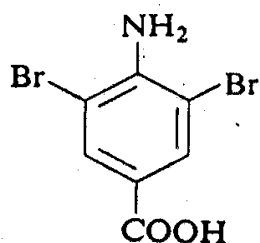
6.



7.



8.



SELF ASSESSMENT EXERCISE 6

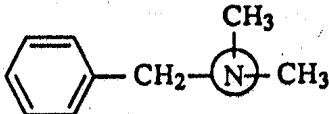
Given below are the names of some compounds. Write their structures

- (1) 3-ethyl-3-pentanol
- (2) 3-methyl-2-butene-1-ol
- (3) 2-bromo-4-nitrotoluene
- (4) 5-hexyne-2-one
- (5) benzoic anhydride
- (6) ethyl formate

4.0 CONCLUSION

We have studied the general features of bonds and defined bond lengths, angles and energy. In addition, the functional groups in molecules have been identified.

ANSWER TO SELF ASSESSMENT EXERCISE 4

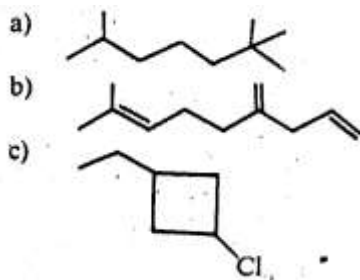
4. a) $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{OH}$
Double bond and hydroxyl group
- b) $\text{CH}_3\text{COCH}_2\text{CH}_2-\text{O}-\text{CH}_3$
Ester and ether groups
- c) 
Tertiary amine
- d) $\text{OHCCH}_2\text{CH}(\text{CH}_3)-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-\text{CH}_2\text{CH}_3$
Aldehyde and anhydride functional groups.

ANSWER TO SELF ASSESSMENT EXERCISE 5

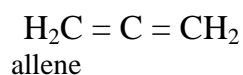
- (a) 3,3-dimethylbutanol
(b) 4-chloro-3-hexanol
(c) 3-hydroxyhexanedioic acid
(d) 2-chloropentanoyl chloride
(e) 2,2,2-trichloroethanal
(f) 4-hydroxy-3-methoxybenzaldehyde
(g) 1,1,1,3,3,3-hexafluoro-2,2-propanediol
(h) 4-amino-3,5-dibromobenzenecarboxylic acid

6.0 TUTOR-MARKED ASSIGNMENT

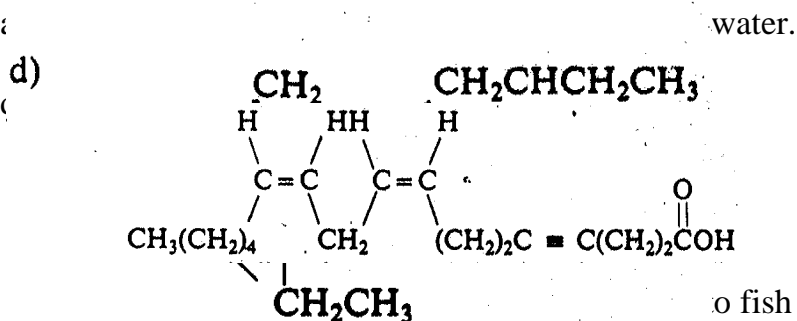
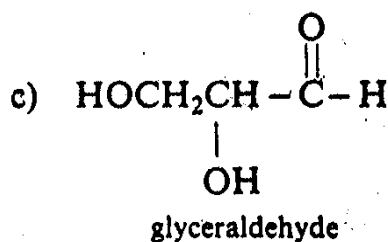
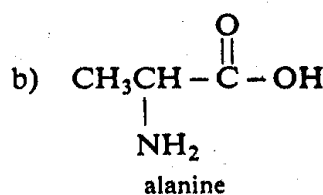
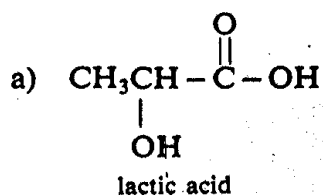
1. Expand the following line structures.



2. The structural formula for allene is shown below; illustrate the formation of bonds in allene by showing the overlap of the orbitals using a diagram.



3. Many compounds isolated from natural sources often show more than one functional group, given below are some such compounds. Identify the functional groups present in these compounds.



4. For compounds having molecular formula, $\text{C}_3\text{H}_5\text{Cl}_3$, write structural formulas for all possible isomers and name them.

5. Write the structural formulas and IUPAC names for the following compounds:
- (a) butanoic acid
 - (b) and its
 - (i) acid chloride
 - (ii) acid anhydride
 - (iii) acid amide
 - (iv) methyl ester

7.0 REFERENCES/FURTHER READING

R.T. Morrison and R.N. Boyd, *Organic Chemistry*, (6th Ed.), India: Prentice-Hall Pvt. Ltd.

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UNIT 2 ALKANES

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- 2.0 Objectives
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 - 3.1.2 Fractionation of Petroleum
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- 7.0 References/Further Reading

1.0 INTRODUCTION

Alkanes are saturated aliphatic hydrocarbons. You have already learnt in your previous 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 hybridized 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, 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, "Paruum 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 toward reagents such as acids, alkanes, oxidizing and reducing agents, halogenation, pyrolysis, aromatization, etc. Many of these reactions proceed through the formation of highly reactive free radicals.

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

2.0 OBJECTIVES

After studying this unit, you should be able to:

- describe the composition and fractionation of petroleum
- define octane number and cetane number
- discuss the physical properties of alkanes,
- list the characteristic spectral peaks of alkanes in uv, ir, nmr and mass spectra
- list the methods for preparation of alkanes and cycloalkanes
- discuss the important chemical reactions of alkanes and cycloalkanes.

3.0 MAIN CONTENT

3.1 Petroleum: A Source of Alkanes

Petroleum is the chief of source of many acyclic as well as cyclic alkanes. This complex mixture of alkanes occurs abundantly in various natural deposits in the earth.

Petroleum is an oily, thick inflammable and usually dark coloured liquid. The origin of the word petroleum is from the Latin words *petra* (rock) and *oleum* (oil), as it is found in abundance near the surface of the earth trapped by rock structure.

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 Nigeria.

Petroleum industry in Nigeria has made headway only after independence. In the last 30 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 a small percentage.

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.

3.1.1 Composition

The composition of petroleum varies with the locality of its occurrence but all samples contain mixtures of alkanes ranging in size from methane with only one carbon atom to long chain hydrocarbon containing upto 40 carbon atoms. Cyclohexane, naphthalenes and other aromatic hydrocarbons are also present in small amounts. In addition to hydrocarbons, oxygen, nitrogen and sulphur containing compounds as well as metallic constituents may also be present. In fact, as many as 500 compounds have sometimes been detected in a single of petroleum. Liquefied petroleum gas (LPG) contains a mixture of propane and butane.

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

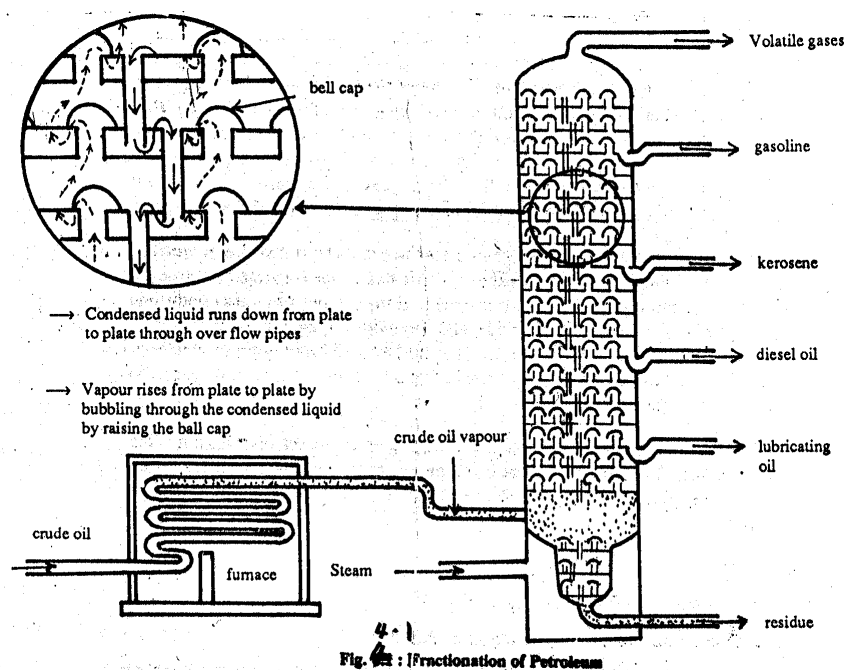


Fig. 2.1 Fractionation of Petroleum

The petroleum obtained directly from the ground is not readily usable, since it is a mixture of many compounds. Separating the crude petroleum into useful components is called **refining**. The first step in refining is fractional distillation.

3.1.2 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 volatilized by lowering the pressure. The vapours are then passed through a tall bubble tower. This tower is filled with horizontal stainless steel trays. Each tray is provided with chimneys covered with a loose cap called **bell cap** (Fig.2.1). As the vapours 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 2.1.

Table 2.1: Fractionation of Petroleum

Name	B.P. (K)	Approximate Composition	Uses
Natural gas	293-373	C ₁ – C ₄	Refinery and domestic fuel
Light petrol	343-363	C ₅ – C ₇	Solvent
Benzene	353-393	C ₆ – C ₇	Dry cleaning
Ligroin	343-473	C ₆ -C ₈	Solvent
Petrol (gasoline)	473-573	C ₆ -C ₁₁	Motor fuel
Kerosene (paraffin oil)	above 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)		C ₃₀ -C ₄₀	Asphalt tar, petroleum coke

3.1.3 Synthetic Petroleum

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. Following processes have shown some promise.

Bergius Process: In this process, finely powdered coal is hydrogenated in presence of catalysts, such as tin and lead to give a mixture of liquid hydrocarbons. During this process, the carbon rings in coal undergo fission to give smaller fragments which are then hydrogenated to open chain and cyclic hydrocarbons. Gasoline (bp up to 473) and kerosene (bp up to 573 K) are obtained on fractional distillation of hydrogenation products.

Fischer-Tropsch Process: This method was developed in 1923 by two German chemists, Franz Fischer and Has Tropsch. Water gas, which is a mixture of carbon monoxide and hydrogen, is obtained by the reaction of steam with red hot coke. The water gas is mixed with half its volume of hydrogen and the catalyst used in the process is a mixture of cobalt (100 parts), thoria (5 parts), magnesia (8 parts) and kieselguar (100 parts). This water gas when hydrogenated and passed over a catalyst at 470-870 K under 1-10 atm pressure yields crude petroleum.



The crude oil obtained is refined by the fractional distillation process as described earlier.

3.1.4 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 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.

Thus 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. Mixtures of these two compounds are used to define octane numbers between 0 and 100. Octane number is the percentage of 2, 2, 4-trimethylpentane 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 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.

Various additives, such as tetraethyllead, $(C_2H_5)_4 Pb$ and *tert*-butyl methyl ether, $(CH_3)_3COCH_3$, are used to boost the octane number of gasoline. The use of tetraethyllead is being curtailed for environmental reasons.

3.1.5 Cetane Number

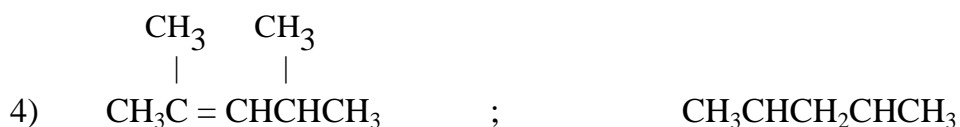
The working of diesel engine differs from that of gasoline engine. In diesel engines, fuels having a lower octane number are much more useful than those having a higher octane number. In other words, the straight chain hydrocarbons constitute a superior fuel than the branch chain hydrocarbons. Quality 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 fuel required for modern diesel engine has cetane number greater than 45.

SELF ASSESSMENT EXERCISE 1

State which compound has best octane rating in each of the following pairs.





3.2 Physical Properties

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 alkane molecule is the nonpolar or very weakly polar. Their physical constants like boiling points densities, etc., increase with increase in the number of carbon atoms. Except for the few members, the boiling point increases by 20 to 30 degrees for each CH_2 unit that is added to the chain. 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 in 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.

	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ butane		$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$ pentane
BP (K)	273		309
	$\begin{array}{c} \text{CH}_3\text{CHCH}_3 \\ \\ \text{CH}_3 \end{array}$ 2-methyl propane	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CHCH}_2\text{CH}_3 \end{array}$;	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CCH}_3 \\ \\ \text{CH}_3 \end{array}$ 2,2-dimethyl propane
BP	261	245	274.5

Unlike boiling point, 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 is given here. The carbon atoms in alkanes are sp^3 hybridised state with a bond angle of $109^\circ 28'$. The terminal carbon atoms in a carbon chain with an odd number of carbon

atoms lie on the same side, whereas those in a carbon chain with an even number of carbon atoms lie on the opposite site. This means that the packing efficiency and the interaction between the molecules in the solid state is less in alkanes containing an odd number of carbon atoms as compared to those with an even number of carbon atoms. This is reflected in the lower melting points of alkanes with odd number of carbon atoms. The maximum density of alkane is about 0.8, thus, all alkanes are lighter than water. Alkanes are soluble in nonpolar solvents but insoluble in polar solvents.

SELF ASSESSMENT EXERCISE 2

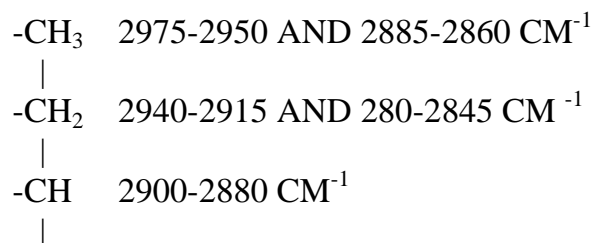
Fill in the blanks:

1. Alkane molecules are very weakly polar or nonpolar because there is very little -----difference between the carbon and hydrogen atoms.
2. Boiling point of alkanes ----- with the increase in the length of the carbon chain
3. Branching in the carbon chain ----- the boiling point.
4. Alkanes are soluble in ----- solvents.

3.3 Spectral Properties

UV spectroscopy is not of much help in the characterization of alkanes, since the alkanes do not show any absorption band above 200 nm.

In the infrared (ir) spectra of alkanes, the position of C-H stretching band depends on whether the hydrogen atom is attached to a primary, secondary or tertiary carbon atom. Thus, we have the following regions:



Some C – H deformation absorption frequencies are – CH₃, 1435 and 1385-1370 cm⁻¹ and >CH₂, 1480-1440 cm⁻¹. Two useful skeletal vibrations are: (CH₃)₂CH-, 1175-1165 cm⁻¹ and (CH₃)₃C-, 1255-1245 cm⁻¹, it is thus possible to detect the presence of these groups in a molecule.

The nmr spectra of alkanes give characteristic signals at, δ 0.9 (CH₃), δ 1.4 (-CH₂) and δ 1.5 (-CH).

Let us now examine the mass spectra of alkanes. The stability of the radical ions can also be presumed in the order tert > sec > p, hence, the fission of bonds in alkanes occurs preferentially at the branched carbon atom. When alternative fissions can occur, it is the heaviest side chain that is eliminated preferentially. Since alkyl radical ions are formed, all those with ^1H and ^{12}C will give peaks of odd masses in their mass spectra. In particular, alkanes give a series of peaks separated by 14 mass units (CH_2). The relative abundances of these peaks is usually the greatest for C_3H_7^+ (43), C_4H_9^+ (57) and $\text{C}_5\text{H}_{11}^+$ (71), and decreases fairly regularly for the larger masses.

3.4 Preparation of Alkanes and Cycloalkanes

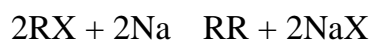
Alkanes are generally obtained from natural sources: petroleum and natural gas. However, synthetic methods are more practical when a pure alkane is required. Alkanes can be prepared from: (a) alkenes or alkynes, (b) alkyl halides, and (c) carboxylic acids. You have already studied about the preparation of alkanes and cycloalkanes in your earlier classes. Here we recall only the important methods. General methods for the preparation of alkanes and cycloalkanes are summarized in Table 2.2.

Table 2.2 Reactions for the preparation of alkanes and cycloalkanes

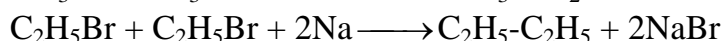
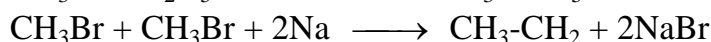
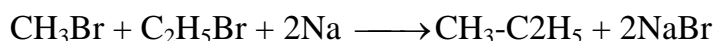
ALKANES	
Wurtz reaction	
$2\text{RX} + 2\text{Na} \longrightarrow \text{RR} + 2\text{NaX}$	
Kolbe's electrolytic method	
$\text{R}'\text{COOK} + \text{RCOOK} \longrightarrow \text{R}'\text{R} + 2\text{CO}_2$	$+ \text{H}_2 + 2\text{KOH}$
at anode	at cathode
Hydrogenation of unsaturated hydrocarbons	
$\text{RCH} = \text{CHR} + \text{H}_2 \xrightarrow{\text{catalyst}} \text{RCH}_2\text{CH}_2\text{R}$	
Reduction of alkyl halides	
$\text{RX} \xrightarrow[\text{agent}]{\text{reducing}} \text{RH}$	
Decomposition of Grignard's Reagent	
$\text{RX} + \text{RMgX}$	$\xrightarrow[\text{H}_2\text{O}]{\text{H}^+} \text{RH} + \text{Mg(OH)X}$
Decarboxylation of Carboxylic acids	
$\text{RCOONa} + \text{NaOH}$	$\text{RH} + \text{Na}_2\text{CO}_3$

3.4.1 Wurtz Reaction

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



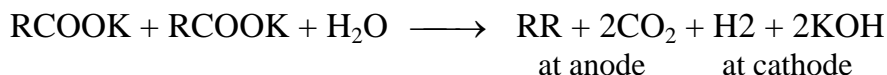
This reaction is useful only when two identical alkyl halide molecules are used. When a mixture of two different alkyl halides is used, a mixture of three different alkanes is obtained. For example, if you take a mixture of bromomethane and bromoethane, you will get three different products, viz.



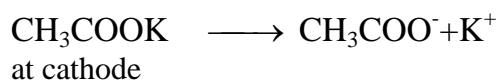
The separation of such a mixture into individual alkanes is quite difficult. Thus, the Wurtz reaction between two different alkyl halides is normally useless in practice. When a single alkyl halide is used, the synthesized hydrocarbon contains an even number of carbon atoms. In other words, we can say 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 reactions is the formation of many side products when an alkane with an odd number of carbon atoms is desired.

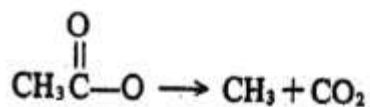
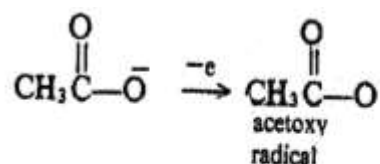
3.4.2 Kolbe's Electrolytic Method

When a concentrated solution of sodium or potassium salt of a carboxylic acid is electrolysed, an alkane is formed. The method is known as Kolbe's electrolytic method.

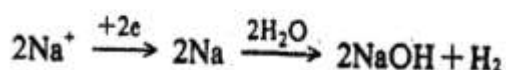


The following mechanistic pathway illustrates this method:

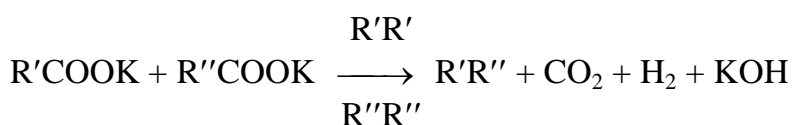




At cathode



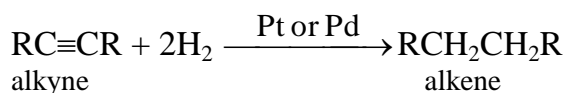
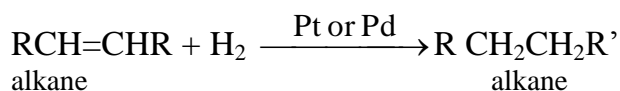
In case a mixture of salts of two carboxylic acids is electrolysed, a mixture of alkanes is formed:



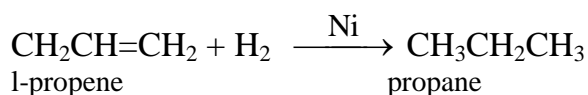
This reaction has limited synthetic applications because of the formation of many side products as a result of other reactions of the free radicals formed.

2.4.3 Hydrogenation of Unsaturated Hydrocarbons

Alkanes or cycloalknes can be prepared by hydrogenation of unsaturated hydrocarbons using platinum or palladium as a catalysts. The general reaction to the reduction of alkene is:



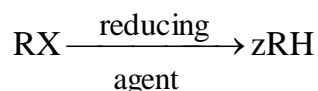
Hydrogenation of an alkene can also be carried out by using nickel catalyst but relatively higher temperature and pressure are required for this reaction. This reaction is called Sabatier Senderen's reaction. An example is given below:



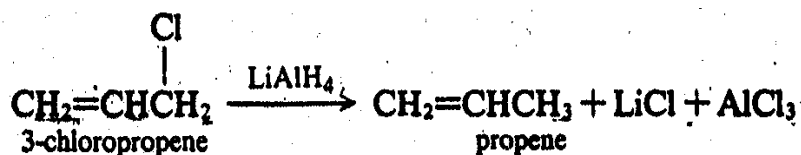
This is a very useful synthetic method and the yield is nearly 100%.

3.4.4 Reduction of Alkyl Halides

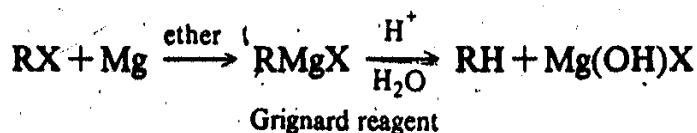
Alkanes can also be prepared by the reduction of alkyl halides by various methods. Reducing agents like zinc and acetic acid and zinc-copper couple give good yields of alkanes.



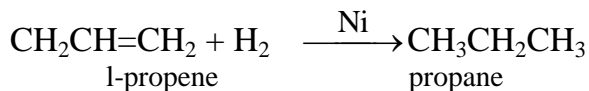
Lithium aluminium hydride, LiAlH_4 , is an excellent reducing agent. Though it reduces many unsaturated functional groups, such as CO_2 , $\text{C}=\text{N}$, etc, it does not attack isolated double bond or triple bond. Dry ether is the commonly used solvent. For example,



Alkyl halide in ether reacts with magnesium to form alkylmagnesium halide (Grignard reagent) which, on treatment with water or dilute acid, decomposes to give alkanes. We will take up the preparation and properties of Grignard reagents in Unit 11 of this course.



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-Senderen's reaction. An example is given below:



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

3.4.5 Decarboxylation of the Carboxylic Acids

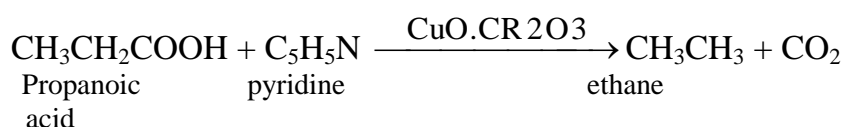
Alkanes may be prepared through decarboxylation of carboxylic acids by heating a mixture of the sodium salt of a carboxylic acid with soda lime. Soda lime is a mixture of NaOH and CaO . The active ingredient is NaOH , CaO helps in keeping the reaction mixture porous.



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.

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

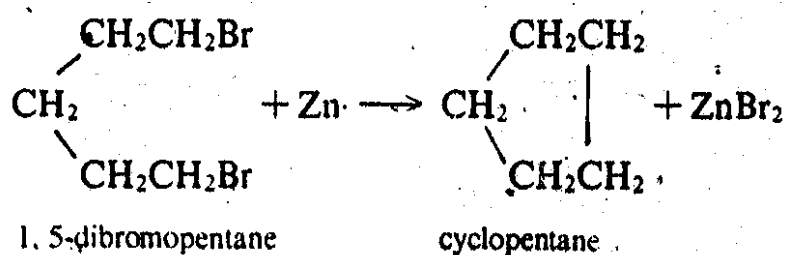
Sometimes decarboxylation of the acid itself is more effective than that of its salt. The direct decarboxylation of a carboxylic acid can be carried out by heating it with an organic base, such as pyridine using copper chromite ($\text{CuO} \cdot \text{Cr}_2\text{O}_3$) as catalyst



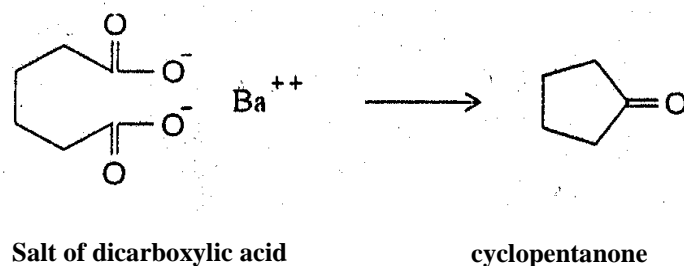
Next we discuss two methods of preparation of cycloalkanes.

3.4.6 Preparation of Cycloalkanes

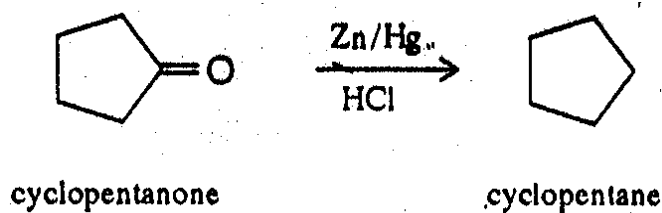
- (i) When 1,5 -dihalogen derivatives of alkanes are treated with sodium or zinc, the corresponding cycloalkane is formed, e.g. 1, 5-dibromopentane would form the cyclopentane.



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



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



SELF ASSESSMENT EXERCISE 3

Write the equation showing synthesis of the following alkanes from the starting materials indicated. Write your answer in the space given below:

1. Cyclohexane from cyclohexene

2. Undecane from the sodium salt of dodecanoic acid, $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$

3. Cyclopropane from 1, 3-dibromopropane

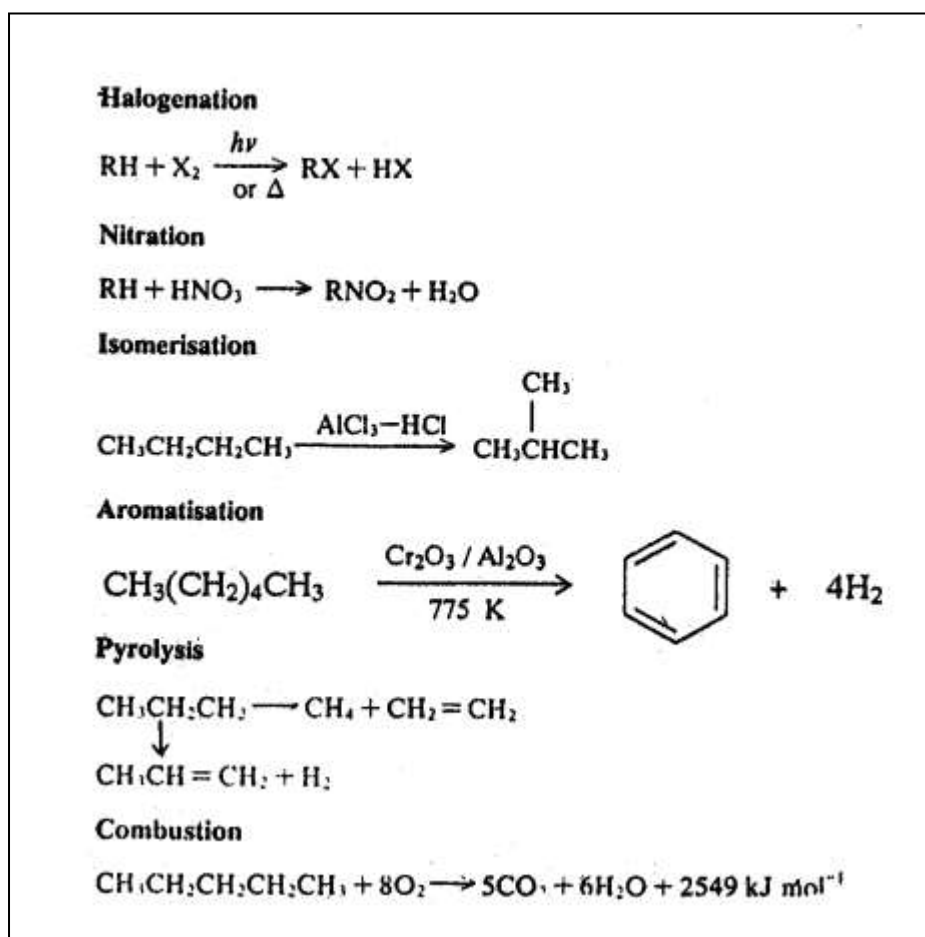
4. Butane from 1-chlorobutane

3.5 Reactions of Alkanes

Alkanes are relatively unreactive to 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 encountered in alkanes

are almost nonpolar 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 chain 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 peroxide. The chemical reactions which take place in the presence of light are called photochemical reactions. In substitution reactions, one or more of the H atom(s) of alkanes are substituted by halogen or some other groups. Some important reactions of alkanes are given in Table 2.3

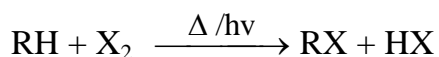
Table 2.3: Reactions of Alkanes



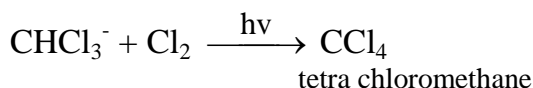
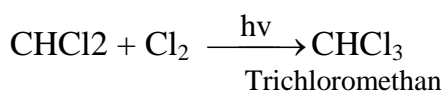
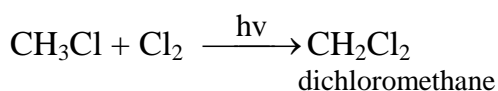
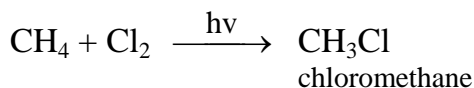
Let us discuss these reactions in detail.

3.5.1 Halogenation

Halogenation of alkane 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)

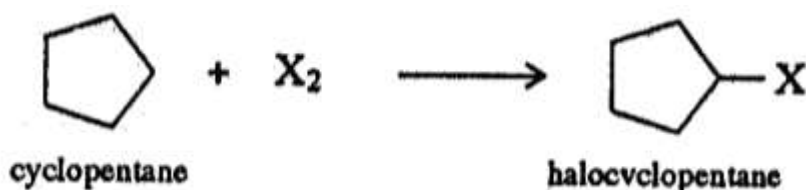


The reaction does not take place in dark but a vigorous reaction occurs when the mixture of alkane and halogen is exposed to light or heated to a high temperature. But in most cases, the reaction is of limited synthetic value because a mixture of products is obtained. Multiple substitutions may occur.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



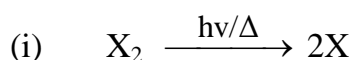
The yield of the monosubstituted product may increase by using an excess of alkane.

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

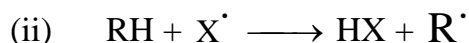


The mechanism of halogenation is supposed to involve the following steps:

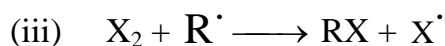
In the first step, the halogen molecule undergoes homolysis forming free radicals. This step is called chain initiation:



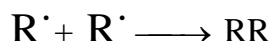
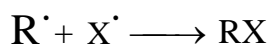
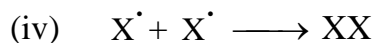
In the next step, the halogen atom abstracts a hydrogen atom from the alkane molecule thereby producing an alkyl radical.



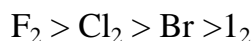
The alkyl radical on collision with another molecule of halogen abstracts a halogen atom from it generating a molecule of the alkyl halide and a halogen atom. These two steps are called propagation. They are repeated in sequence till the reactants are consumed.



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



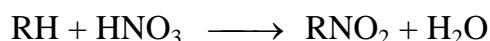
The order of reactivity of halogen in halogenation of alkanes is:



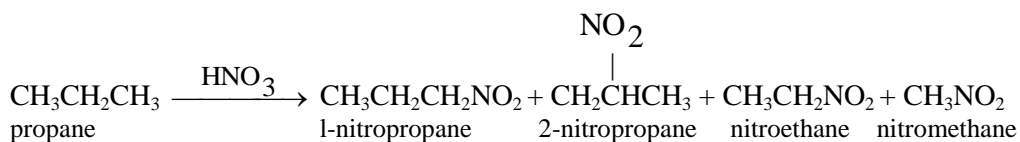
However, the fluorination reaction is too violent to be practical, and iodine actually does not react at all.

3.5.2 Nitration

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

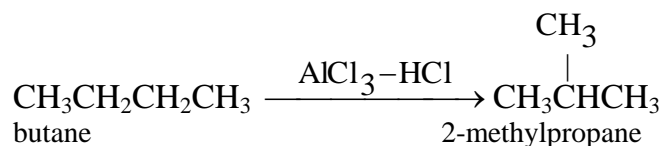


In this reaction, the product is usually a mixture of nitroalkanes including those with smaller carbon chain than the parent alkane.



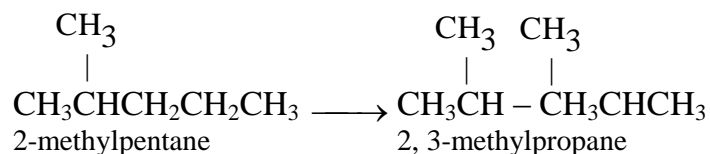
3.5.3 Isomerisation

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



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

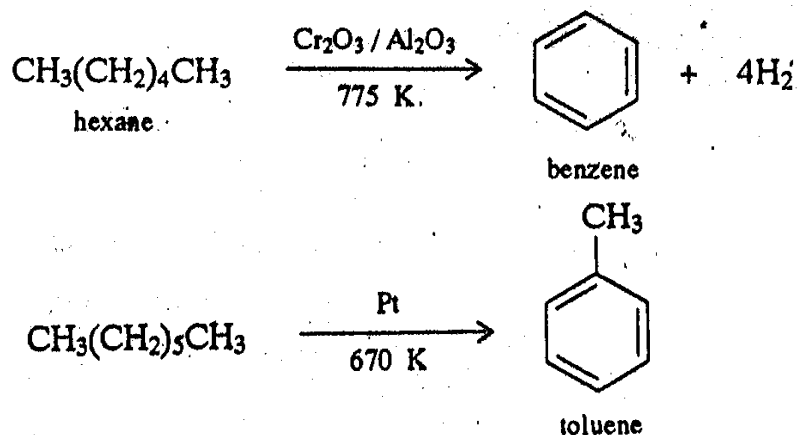
Thus:



Isomerization is used to increase the branched chain content of lower alkanes produced by cracking; you have studied in subsec 2.2.4 that branched chain alkanes are more valuable than straight chain alkanes as motor fuel.

3.5.4 Aromatization

This is a process of converting aliphatic or acyclic 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, isomerization and dehydrogenation. Aromatization of gasoline increases their octane number from 40 to 95 because unsaturated hydrocarbons are better fuels.



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

3.5.5 Pyrolysis

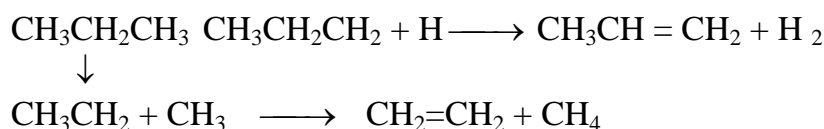
This is a process of decomposing an organic substance by heating it to high temperature in the absence of oxygen. The word pyrolysis is taken from the Greek words **pyro** (fire) and **lysis** (disintegration). The pyrolysis of alkanes, particularly where petroleum is concerned, is known as cracking.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

decomposes into smaller molecules. For example, on cracking propane, the possible products are:



Large quantities of high boiling fractions of petroleum are converted into low boiling gasoline by cracking. Propane 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.

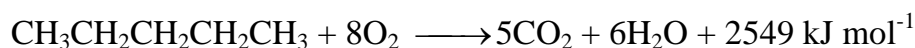
The mechanism of cracking is still obscure, but it is believed to be a free radical as illustrated below:



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

3.5.6 Combustion

Alkane's burn in excess of air or oxygen to give carbondioxide and water. This reaction is known as combustion and is the most important of all their reactions. Combustion is highly exothermic and accounts for their use as valuable fuels. It is a free radical chain reaction and requires a very high temperature for its initiation. Once the reaction is started, the subsequent chain-carrying steps proceed readily with the evolution of a large amount of energy. For example, the heat of combustion of pentane is 2549 kJ mol^{-1} .

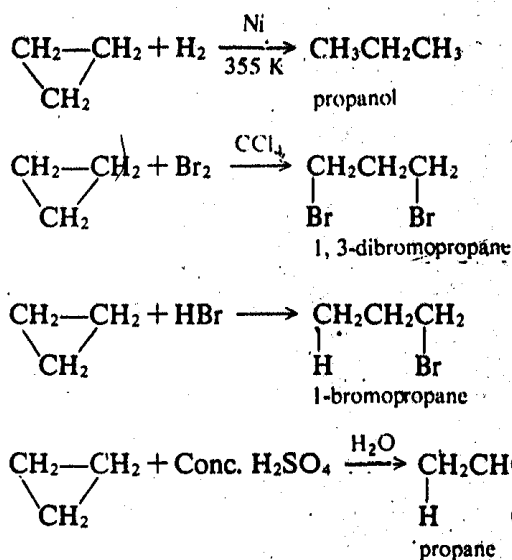


The large quantity of heat evolved can be a source of extensive power. Hence, the use of petrol, diesel etc., as fuels in internal combustion engines. The burning of alkanes also produces carbon black, which is used in the manufacture of Indian ink, printer's ink, black pigments and as a filler in rubber compounding.

3.5.7 Reactions of Small Ring Compounds

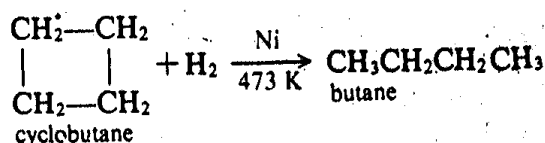
Let us now study the reactions characteristic of small ring compounds, such as cyclopropane and cyclobutane.

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 previous classes that the bonding in cyclopropane and cyclobutane is not as strong as that in higher homologues. Hence, the bonds in cyclopropane and cyclobutane are vulnerable to attack by certain reagents. 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. These addition reactions destroy the cyclopropane and cyclobutane ring system, and yield open chain products. Some examples are given below:



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

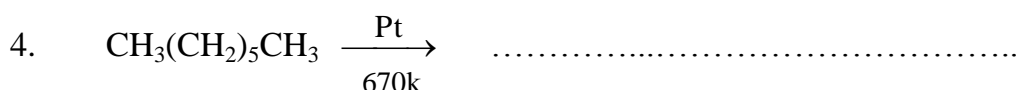
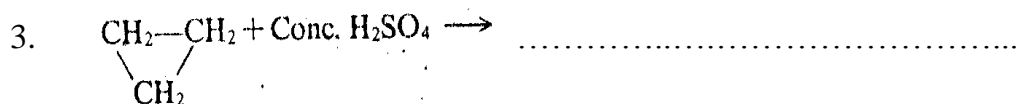
Cyclobutane does not undergo most of the ring opening reactions of cyclopropane; it gets hydrogenated under vigorous conditions.



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

SELF ASSESSMENT EXERCISE 4

Complete the following reactions:

**4.0 CONCLUSION**

The alkanes are a group of relatively inactive compounds whose general formula is $\text{C}_n\text{H}_{2n+2}$. The primary source of alkanes is by fractionation of petroleum.

5.0 SUMMARY

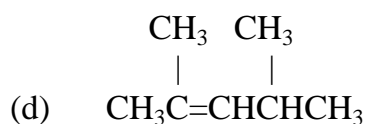
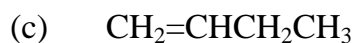
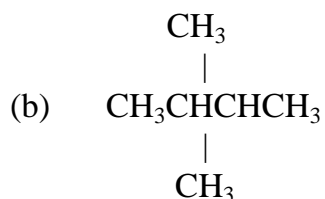
In this unit you have learnt that:

Alkanes are compounds of the general formula $\text{C}_n\text{H}_{2n+2}$. Cycloalkanes contain a ring of carbon atoms and have the general formula C_nH_{2n} .

- The chief source of alkanes is petroleum.
- The performance of gasoline for internal combustion engines is rated by octane number. Cetane number is a measure of the quality of diesel.
- Alkanes are nonpolar compounds. Their physical constants like boiling point, density, etc., increase with increase in the number of carbon atoms. Branching in the chain decreases the boiling point.
- Alkanes are prepared by: (i) 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.
- The main reaction of alkanes is combustion; heat for power production is its chief outcome.

- 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 aluminum chloride and hydrogen chloride.
- When an alkane is heated to a high temperature (at about 875 K), it decomposes into small molecules. This process is known as paraffin cracking.
- When alkanes with six or more carbon atoms are heated under pressure in the presence of a catalyst, aromatic hydrocarbons are produced.

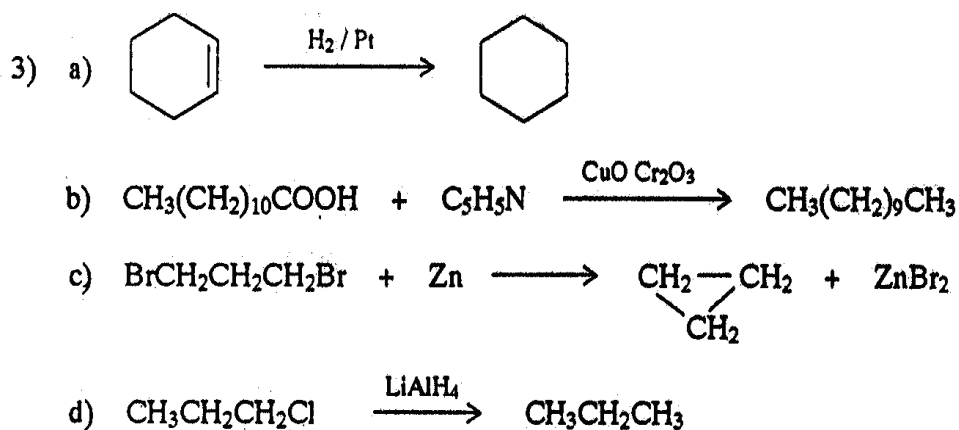
ANSWER TO SELF ASSESSMENT EXERCISE 1



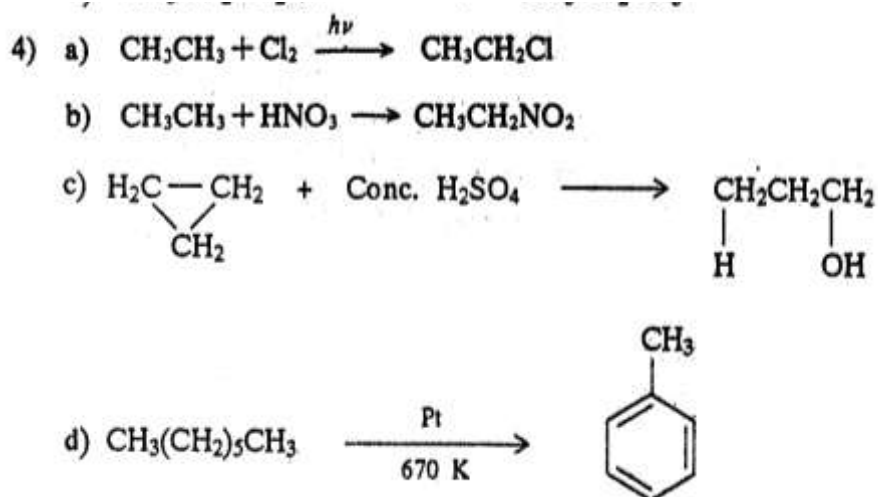
ANSWER TO SELF ASSESSMENT EXERCISE 2

- (a) electro negativity
 (b) increases
 (c) decreases
 (d) nonpolar

ANSWER TO SELF ASSESSMENT EXERCISE 3

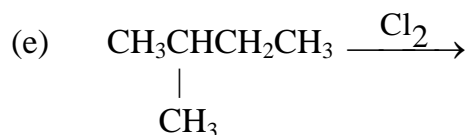
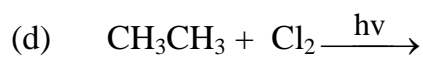
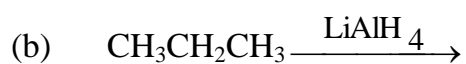
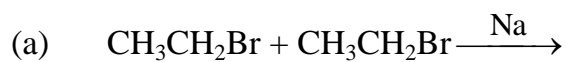


ANSWER TO SELF ASSESSMENT EXERCISE 4

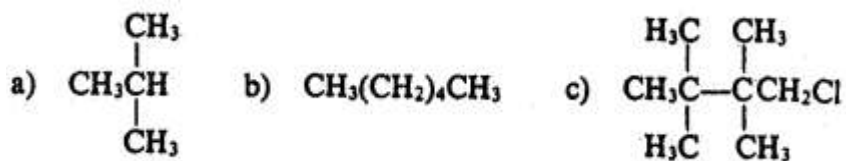


6.0 TUTOR-MARKED ASSIGNMENT

1. Give the products of the following reactions:

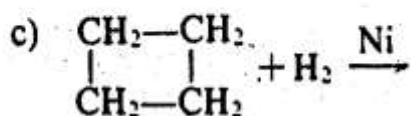
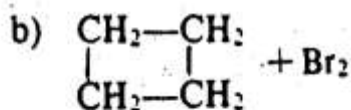
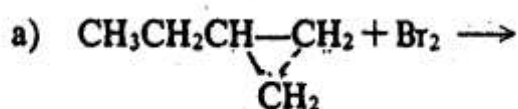


2. Starting with $\text{CH}_2=\text{CHCH}_2\text{Br}$ or $(\text{CH}_3)_3\text{CCl}$, how would you prepare the following compounds:



3. Write the equation to show Wurtz reaction:

4. Complete the following equations:



7.0 REFERENCES/FURTHER READINGS

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UNIT 3 ALKENES

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- 3.0 Main Content
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 - 3.2 Physical Properties
 - 3.3 Spectral Properties
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 - 3.5.7 Epoxidation
 - 3.5.8 Addition to Conjugated Diene
 - 3.5.9 Diels-Alder Reaction
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor-Marked Assignment
- 7.0 References/Further Reading

1.0 INTRODUCTION

In this unit, we shall discuss their chemistry in detail. Ethene, the simplest alkene, was known to chemists in the eighteenth century and was obtained in pure form in 1794. Alkenes, also called olefins, are hydrocarbons which contain one or more carbon-carbon double bond(s). Since alkenes evidently 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 induces ripening in fruit.

In this unit, we will discuss structure of alkenes, their spectral and physical properties, different methods for their preparation and finally, we will study their important chemical reactions.

2.0 OBJECTIVES

After studying this unit, you should be able to:

- classify the types of alkenes
- explain the structure of monoenes and dienes
- list their spectral and physical properties
- list the different methods for their preparation, and
- write down the important chemical, reactions of alkenes.

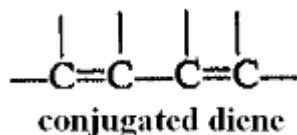
3.0 MAIN CONTENT

3.1 Classification of Alkenes

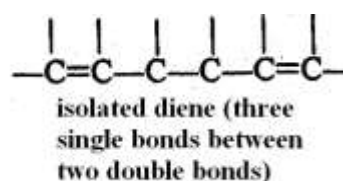
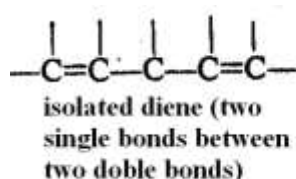
Alkenes can be classified on the basis of the number of double bonds present in the molecule. Hydrocarbons containing one carbon-carbon double bond are called monenes. The monoenes have the general formula C_nH_{2n} .

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.

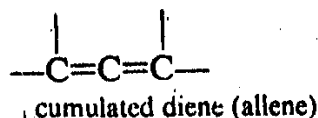
Dienes are divided into three main classes depending on the relative positions of the two double bonds in the molecule: isolated or non-conjugated dienes conjugated dienes and cumulated dienes. In conjugated dienes, the two double bonds are separated by a single bond. A typical conjugated diene skeleton is given below:



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



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



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 this unit, 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 important functional group in organic chemistry. The shape of the organic molecule is influenced by the presence of the double bond which is also the site of most of the chemical reactions that alkenes undergo. So it is necessary to understand the structure of these molecules.

Carbon-carbon double bond is the distinguishing feature of the monoenes and dienes. You have already studied about the bonding of monoenes in Unit 1 of this course and learnt that 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. 5.1). Bonding in dienes with isolated double bonds is similar to monoenes. Thus here we shall discuss π bonds in conjugate and cumulated systems.

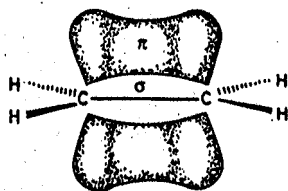


Fig 3.1: Orbital picture of ethene

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



Each of the four carbon atoms of butadiene contains unhybridised p -orbitals. The sideways overlap of unhybridised p -orbitals gives rise to two localized π bonds, i.e. the bonds between C_1 and C_2 and C_3 and C_4

(Fig. 5.2). 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 electron clouds of the p -orbitals of C_2 and C_3 . This give rise to completely delocalised π -orbitals spread over all the four carbon atoms. It is this delocalization of π electrons which imparts stability to 1,3-butadiene.

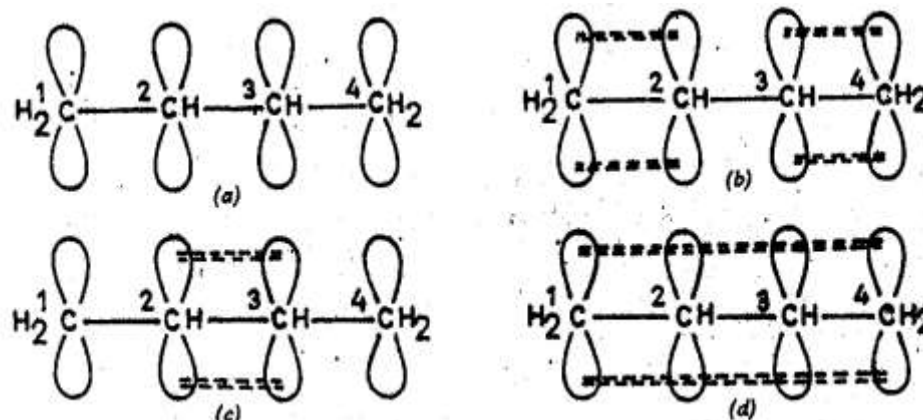


Fig 3.2: Orbital structure of 1, 3-butadiene

In the allene molecule, the central carbon atom is sp hybridized while the terminal carbon atoms are sp^2 hybridised. The central carbon atom forms a bond with each of the *terminal* sp^2 hybridised carbon atom. The remaining two p -orbitals of this carbon form two π bonds by sideways overlapping with the p -orbitals of the terminal carbon atoms

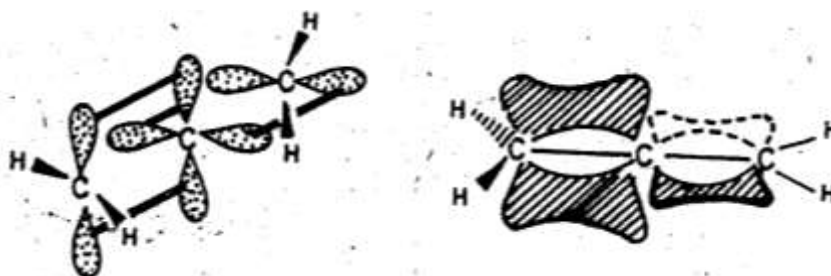


Fig. 3.3. Molecular orbital picture of allene

SELF ASSESSMENT EXERCISE 1

Fill in the blank in the spaces given below:

1. Dienes are isomeric with
2. Polyenes contain more thandouble bonds
3. Double bonds that alternate with single bond aredienes
4. In allene the central atom ishybridised and the terminal atoms are hybridized.

3.2 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 20-30K per CH₂ group except for the very homologues. Like alkanes, branching in an alkene also lowers the boiling point. Lower alkenes, from ethane to butane, are colourless gases, higher ones, from C₅ - C₁₅, are liquids and the rest are solids at temperature.

Alkenes are slightly more soluble in water than the corresponding alkanes because the π -electrons are attracted to the partially positive hydrogen of the water molecules.

3.3 Spectral Properties

In the UV spectrum, although the ethylenic chromophore shows an absorption band below 200 nm, yet it is not of much practical value as measurement of UV spectrum in this region is influenced by the absorption of air and solvent molecules.

The ir spectra are quite useful for structure determination of alkenes. The unsymmetrical alkenes are polar and absorb in the region between 160 and 1700 cm⁻¹, whereas the symmetrical ones, being nonpolar, do not absorb in this region. Further, depending upon the substituent, one or more bands of medium intensity appear in the region between 3000 and 3100 cm⁻¹ for >C=C-H stretching. The *cis*- and *trans*-isomers of the type RCH=CHR may be distinguished by C-H deformation frequencies. The *cis*-isomer absorbs at 675-730 cm⁻¹ and the *trans*-isomer at 960-975 cm⁻¹.

In the ir spectra of allenes, a band near 1950 cm⁻¹ appears for the C=C stretching vibration. The strong band at 850 cm⁻¹ arises from >C=CH₂ wagging and is characteristic of allene. The characteristic -C=C- stretching frequencies in conjugated systems is lower and appears around 1600 cm⁻¹.

In the nmr spectra, the chemical shifts of olefinic protons are shifted towards lower field than those of alkane protons. The exact position of absorption depends on the location of the double bond in the hydrocarbon chain. In general, proton on the terminal alkenyl carbon absorb near δ 4.7 ppm, while the protons on the nonterminal carbon absorb slightly farther downfield at δ 5.3 ppm. The protons α to a double bond (CH₂CH = CHCH₂) appear at δ 2.06 ppm.

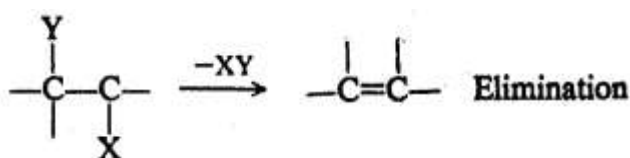
In conjugated dienes, the olefinic protons are more deshielded and consequently resonance due to these protons occurs downfield. In conjugated dienes, the signal due to CH₂ = protons appears at δ 5.3-5.7

ppm and that due to H – C = C proton at δ 4.0-4.5 ppm. In the nmr spectra of the allenes, the alkene hydrogen give rise to signals at δ 5.7-4.7 ppm.

In the mass spectra of alkenes, the molecular ion peak is usually distinct. The fragmentation of interest for alkenes is the allylic cleavage.

3.4 Preparation of Alkenes

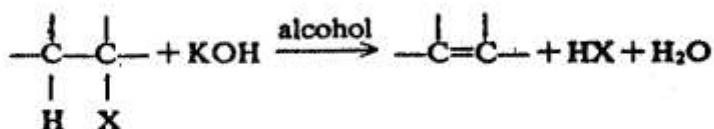
Synthetically, alkenes are prepared by introducing a double bond in saturated hydrocarbons through elimination of atoms or groups from two adjacent carbon atoms. The result is the formation of a double bond between these two carbon atoms.



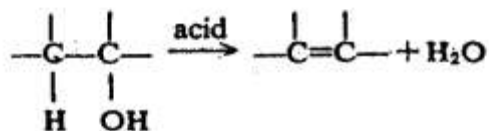
Alkenes can be prepared from alkyl halides, alcohol and ketones and through cleavage reactions. Some important methods for the preparation of alkenes are summarized in

Table 3.1 Preparation of alkenes

Dehydrohalogenation of Alkyl Halides



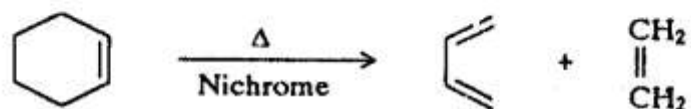
Dehydration of Alcohols



Wittig Reaction



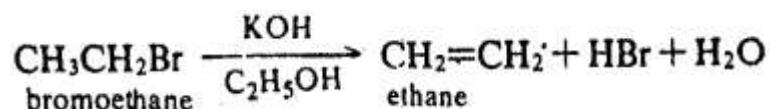
Retro Diels-Alder Reaction



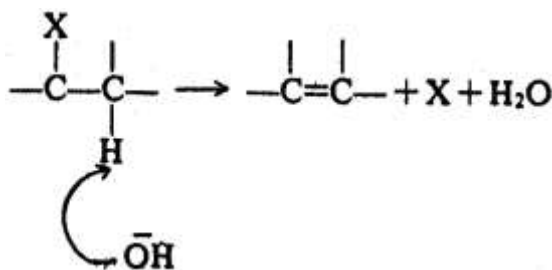
Let us discuss each method in detail.

3.4.1 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.

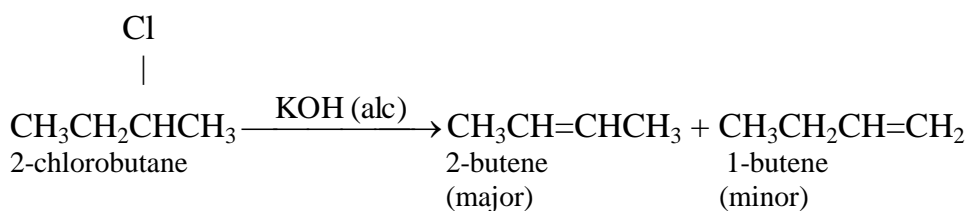
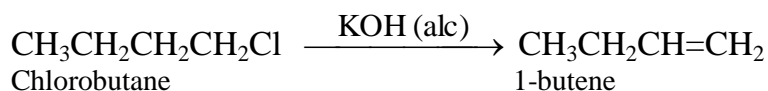


The function of hydroxide ion is to abstract hydrogen from the carbon atom next to the halogen bearing carbon. The carbon halogen bond then cleaves resulting in double bond formation.



Ease of hydrohalogenation of alkyl halides is: *tert* > *sec* > *p*

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 nonterminal carbon atom and both adjacent position have hydrogen atoms yield a mixture of alkenes.

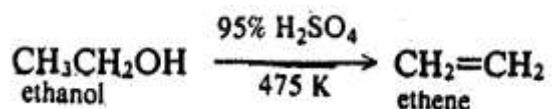


In the first reaction, chlorobutane can lose hydrogen only from C₂; therefore, it gives only one product, i.e. 1-butene. However, in the second reaction, 2-chlorobutane can lose hydrogen from any of the two-β-carbon atoms and, hence, it gives a mixture of 2-butene (80%) and 1-butene (20%). Now you may ask why 2-butene is the major product. Dehydrohalogenation follows Saytzeff rule which says that the more highly substituted alkene is the dominant product.

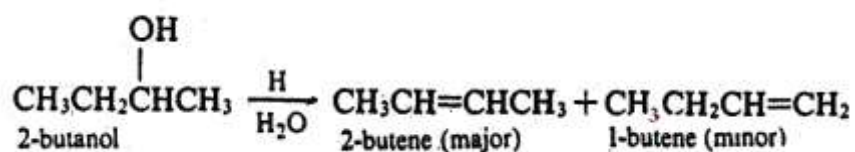
3.4.2 Dehydration of Alcohols

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 475 K. Dehydration is also brought about by passing the alcohol vapour over alumina (Al₂O₃) at 625-675 K, e.g.,



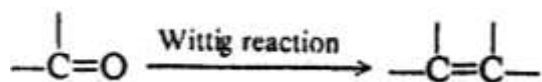
In the case of secondary and tertiary alcohols other than 2-propanol, there exists the possibility of the formation of more than one alkenes. For example, in 2-butanol, hydrogen elimination can occur either from C₁ or C₂. The direction and the rate of reaction again follow the Saytzeff rule and hence 2-butenes, the more substituted alkene, is the major product and 1-butene the minor one.



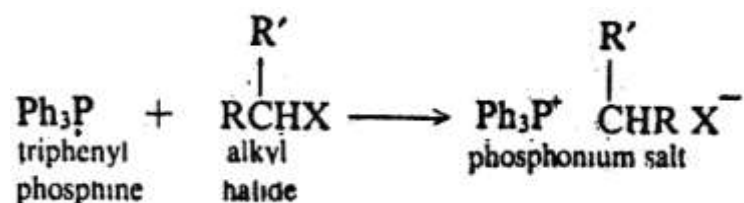
The ease of dehydration of various alcohols has been found to follow the order: tert > sec > p.

3.4.3 Wittig Reaction

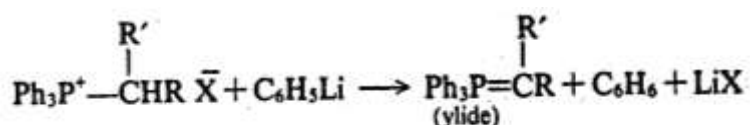
In 1954, George Wittig reported a method of synthesising alkenes from carbonyl compounds. This reaction is applicable to aldehyde and ketones and leads to replacement of carbonyl oxygen by the group=CRR' (where R and R' are hydrogen or alkyl group).



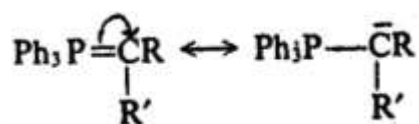
There are two main steps in Wittig reaction. In the first step, the nucleophilic reagent triphenylphosphine reacts with primary or secondary alkyl halide to give phosphonium salt



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



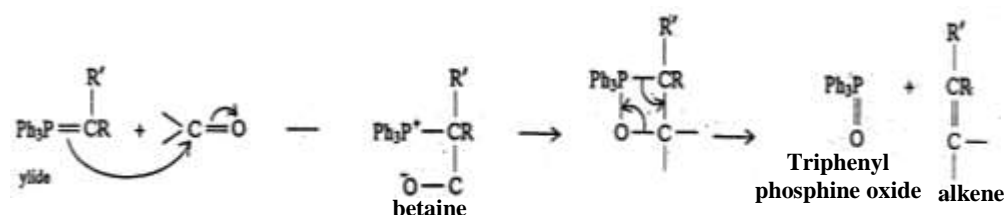
The phosphorous ylide has a hybrid structure and it is the negative charge on carbon that is responsible for their characteristic reactions.



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

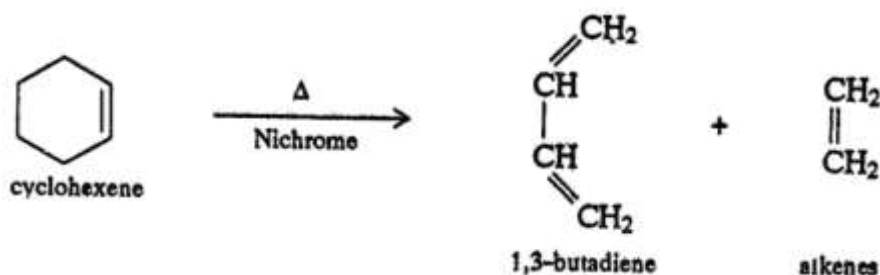
Betain: A molecule having non-adjacent charges opposite.

The mechanism of 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.



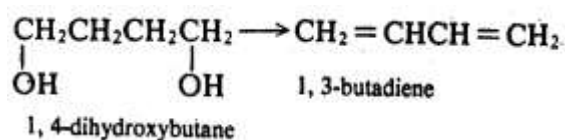
3.4.4 Preparation of Dienes

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.

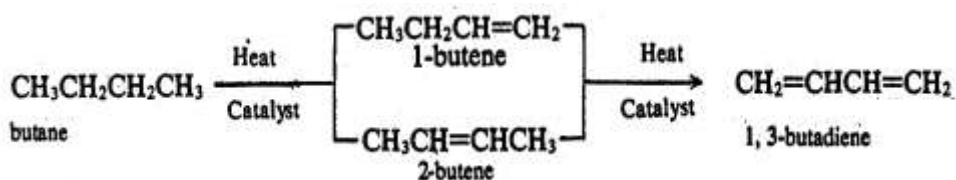


This reaction is also known as the retro Diels-Alder reaction as it is the reversal of the Diels-Alder reaction which you will study in due course.

Other Methods for Preparation of Dienes: 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.

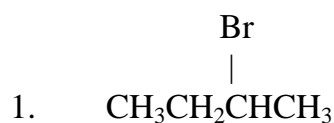


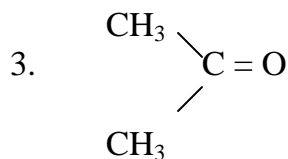
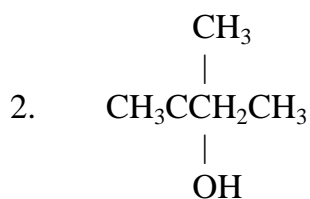
1,3-Butadiene can also be prepared from butane by the cracking process using Cr_2O_3 as illustrated below;



SELF ASSESSMENT EXERCISE 2

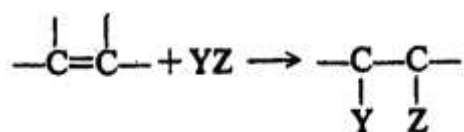
Write equations for the preparation of alkene from the following starting material. If there is more than one product indicate the major one.





3.5 Reactions of Alkenes

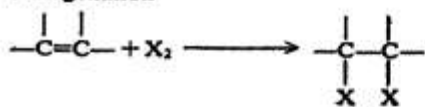
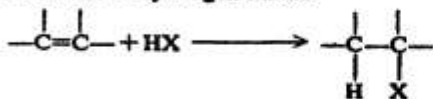
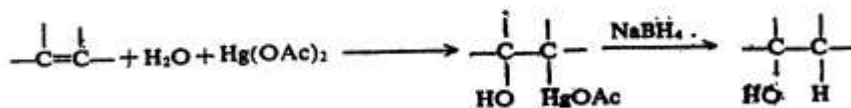
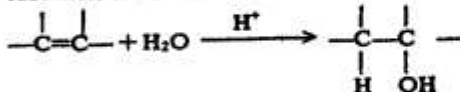
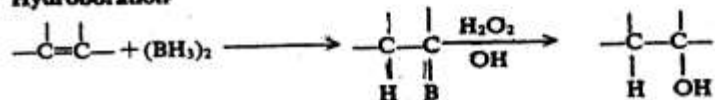
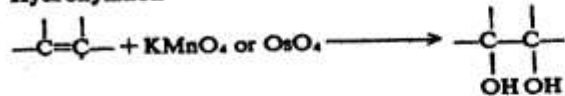
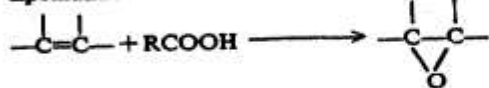
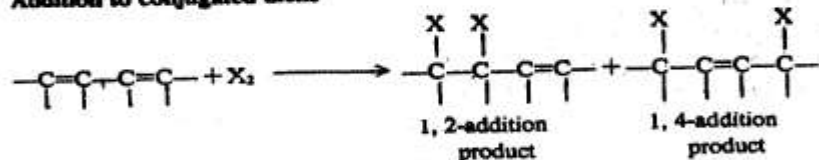
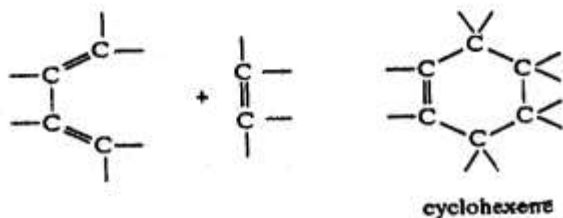
The double bond consists of a strong σ bond and a weak π bond; so most of the reactions of alkenes would involve the breaking of this weaker bond.



In addition reactions of alkene, 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 atoms are rehybridised to sp^3 carbons. Compounds containing π bonds are usually of higher energy than those having σ bonds. Consequently, addition reactions are usually exothermic processes.

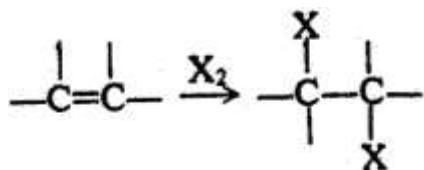
In the region of the double bond, there is a cloud of electrons above and below the plane of bonded atoms. The π electrons are loosely held by the nuclei and are thus easily available to electron-seeking reagent. Such reagents are called electrophilic reagents or electrophiles and the typical reaction of an alkene is the electrophilic addition. Some electrophilic important reactions of alkenes are given in Table 3.2 and discussed below:

Table 3.2: Reaction of Alkenes

Halogenation**Addition of hydrogen halide****Addition of water****Hydroboration****Ozonolysis****Hydroxylation****Epoxidation****Addition to conjugated diens****Diels-Alder Reaction**

3.5.1 Addition of Halogens

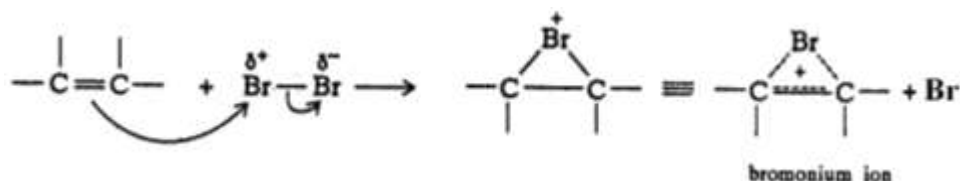
Halogens are quite reactive towards alkenes. Treatment of alkenes with halogens gives 1,2-dihalogenated alkenes.



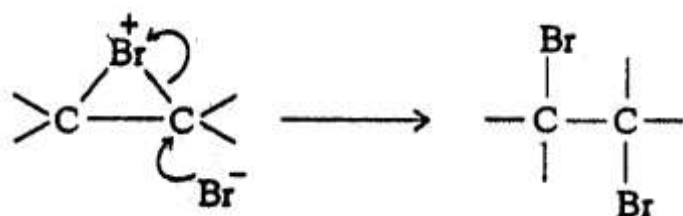
Bromine and chlorine are particularly effective electrophilic addition reagents. Fluorine tends to be too reactive and difficult to control for most laboratory procedures and iodine does not react with alkenes.

Mechanism

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



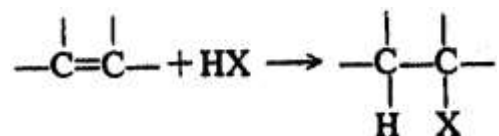
The cyclic structure shields one side of the molecule and, for this reason, Br attacks from the opposite side of the erstwhile double bond to give trans product. This process is known as trans addition. This steric course of the reaction is important in case of alkenes which can give rise to different isomeric products.



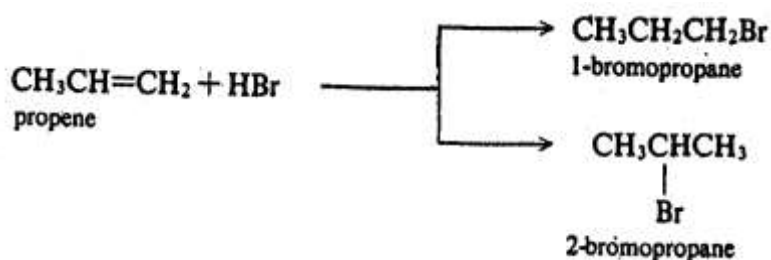
Addition of bromine is extremely useful for detection of carbon-carbon double bond. Rapid decolourisation of bromine solution serves as a test for the presence of the carbon-carbon double bond in a compound.

3.5.2 Hydrohalogenation

An alkene is converted by hydrogen halide (halogen acid) into the corresponding alkyl halide,

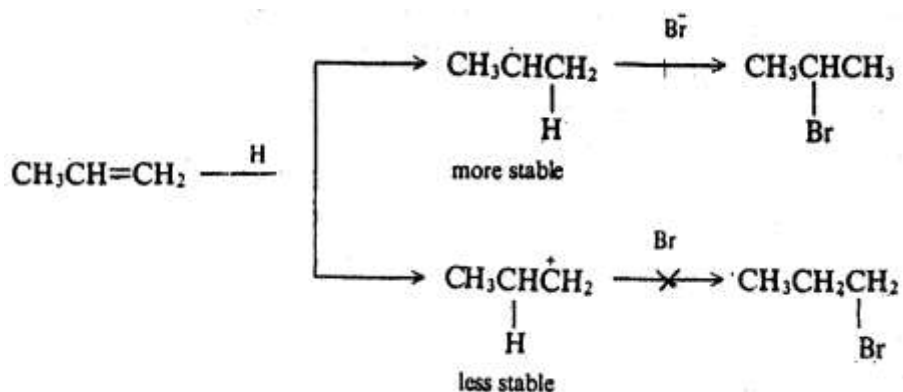


As long as the alkene is symmetrical, we get only one product. In case of unsymmetrical alkene, the position of attachment of nucleophile is governed by the nature of substituents. Addition of HBr to propene should give two products, i.e, 1-bromopropane and 2-bromopropane.



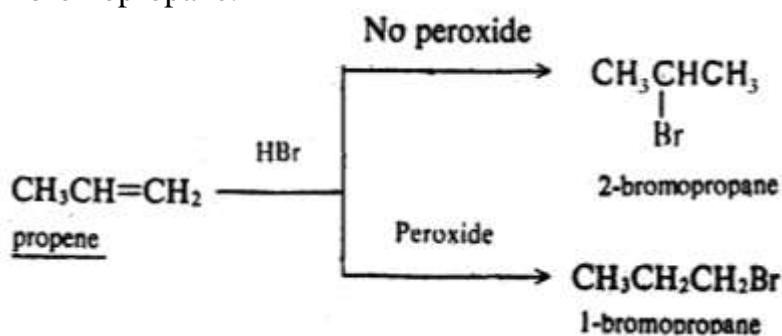
However, only one product, 2-bromopropane, is produced. Such reactions are called regiospecific reactions. Regiospecific: Only one of the two directions of addition is observed. To explain the exclusive formation of the product, the Russian chemist Markownikoff formulated a rule known after him as Markownikoffs rule, which states that addition of a hydrogen halide to an unsymmetrical alkene takes place in such a way that the negative part of the reagent goes to that carbon atom of the alkene which carries the lesser number of hydrogen atoms.

Markownikoffs rule can be explained on the basis of the relative stabilities of carbocations which are of 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 exists the possibility of the formation of either a primary or a secondary carbocation. Since, the secondary carbocation is more stable, addition of H^+ gives exclusively 2-bromopropane via the more stable intermediate.

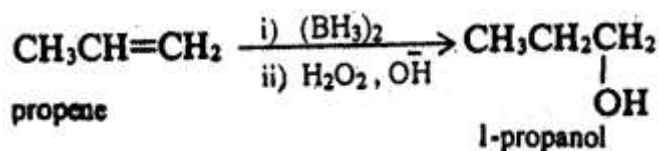


Peroxide Effect

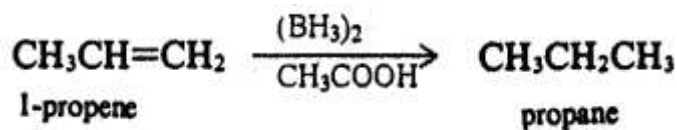
You must be under the impression that addition to alkene always give Markownikoffs product. But it is not so. After an extensive study of the mechanism of addition of HBr to alkene, kharasch and Mayo found that in the presence of peroxide the product obtained was not the one predicted by Markownikoffs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



The reaction intermediate in such additions is a free radical rather than a carbocation. The mechanism is some what similar to that of halogenation of an alkane, which will be dealt in the “Organic Reaction Mechanism” course.



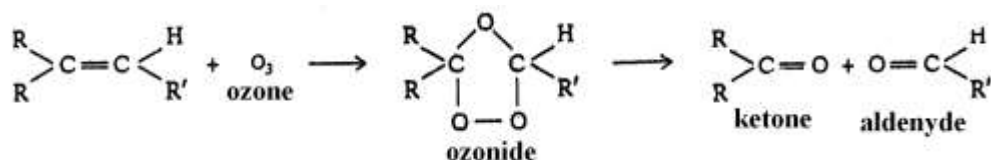
Treatment of organoboranes with a carboxylic acid leads to alkane,



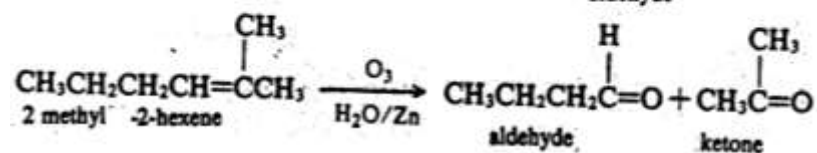
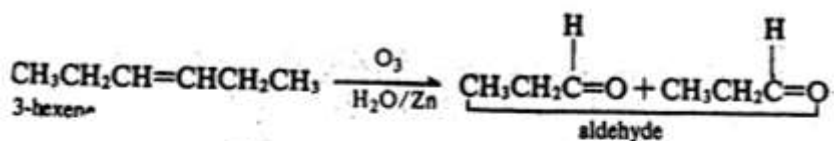
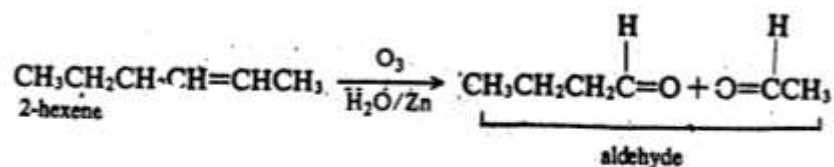
3.5.5 Ozonolysis

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

Ozonolysis consists of two separate reactions, the first is oxidation of alkene by ozone to give an ozonide; and the second is reduction of the ozonide to yield cleavage product.

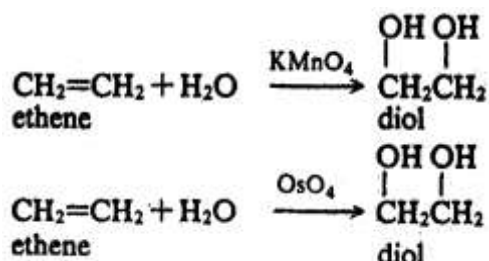


Some examples of ozonolysis are given below:



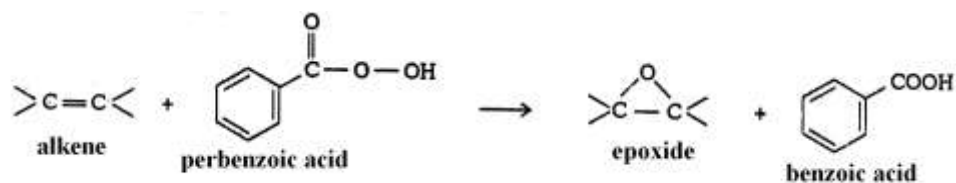
3.5.6 Hydroxylation

Alkenes are readily hydroxylated (addition of hydroxyl groups) to form a dihydroxy compound (diol) known as glycols. The most popular reagent used to convert an alkene to diol is cold alkaline aqueous of potassium permanganate or osmium tetroxide.



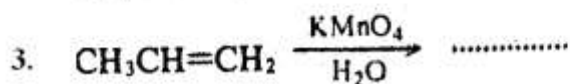
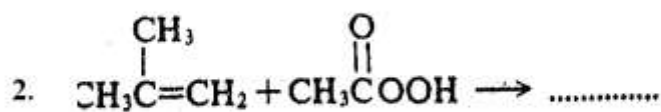
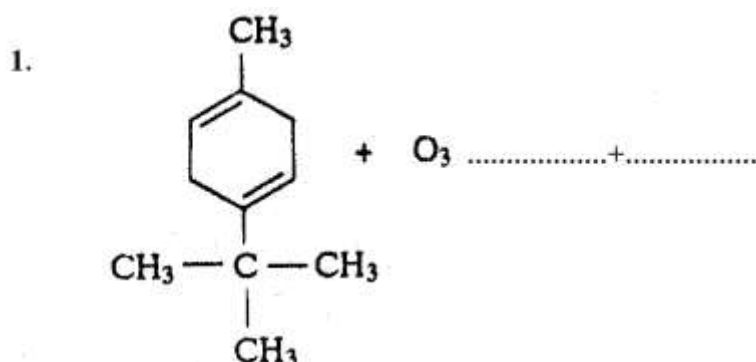
3.5.7 Epoxidation

The double bond in alkene is converted into epoxide by means of peracids. Perbenzoic acid ($\text{C}_6\text{H}_5\text{COO}_2\text{H}$), monopero-phthalic acid ($\text{HO}_2\text{CC}_6\text{H}_4\text{COO}_2\text{H}$) and p-nitroperbenzoic acid have been used, e.g.



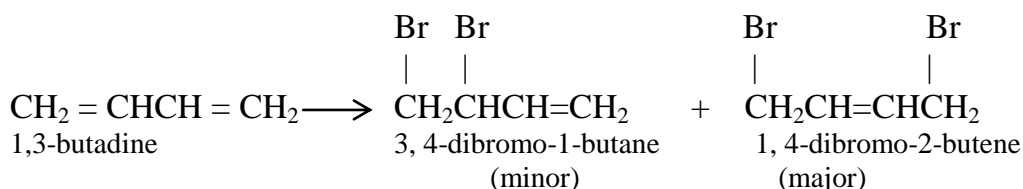
SELF ASSESSMENT EXERCISE 4

Predict the products of the following reactions:

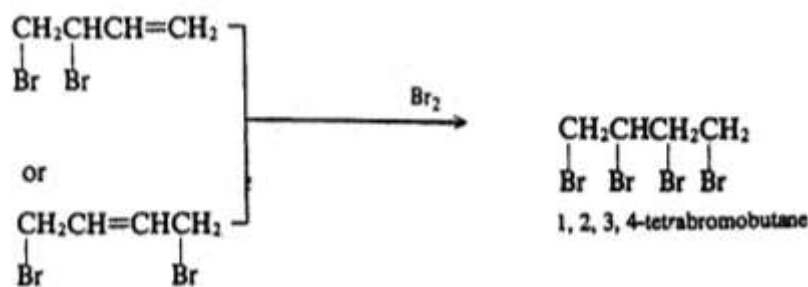


3.5.8 Addition to Conjugated Diene

Alkadienes with conjugated system of double bonds undergo abnormal addition reactions, e.g., when 1,3-butadiene is treated with bromine, two dibromo derivatives are obtained. One of these is 3,4-dibromo-1-butene (due to 1:2 addition) and the other is 1,4-dibromo-2-butene (due to 1:4 addition), a major product.

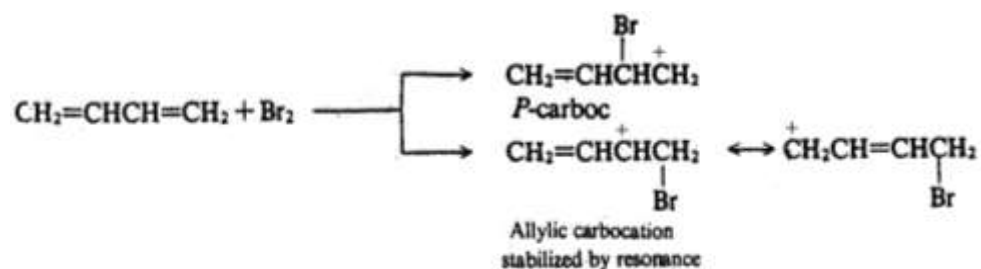


With excess of bromine, the 1,4 addition as well as the 1,2-addition products would yield the same 1,2,3,4-tetrabromobutane.

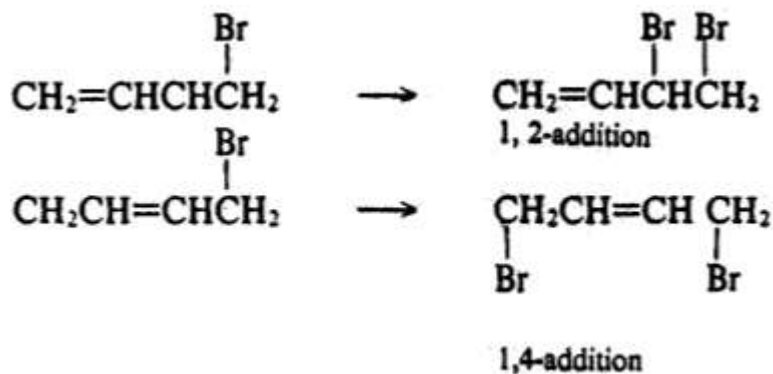


Mechanism

The mechanism of halogenation of 1,3-butadiene is illustrated below:

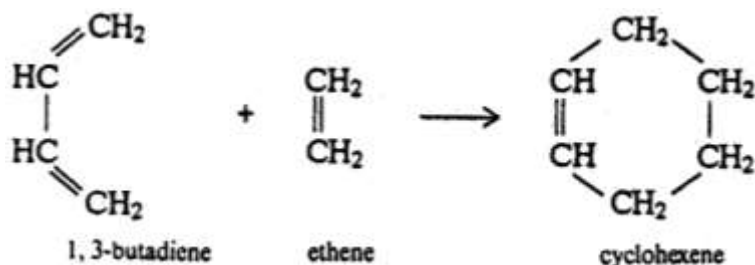


Bromine may attach itself to either C₁ or C₂. The addition of the bromine atom at C₂ would give rise to an unstable primary localized carbocation. But the bromine addition at C₁ results in the formation of resonance stabilized allylic cation. This also explains the enhanced reactivity of dienes over isolated ethylenic double bonds. When the allylic carbocation is attacked by bromine ion (Br⁻) to complete the electrophilic addition reaction, the attack can occur at either C₁ or C₃, since both share the positive charge. The result is a mixture of 1,2- and 1,4-addition products, the latter formed in excess since it has the more highly substituted double bond and is hence more stable.

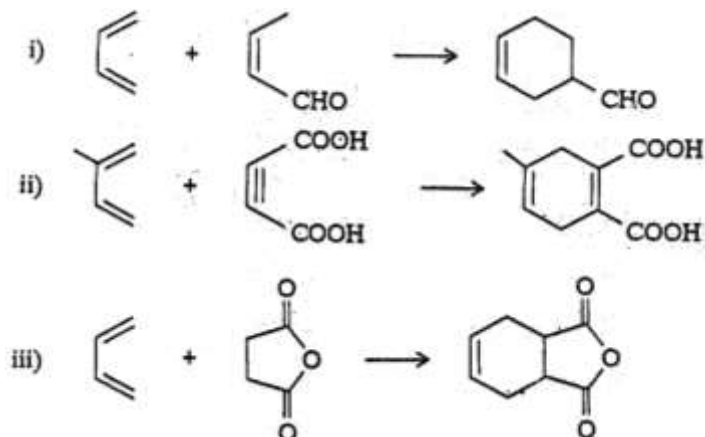


3.5.9 Diels-Alder Reaction

In Diels-Alder reaction, a conjugated diene is treated with an unsaturated compound called the dienophile (diene-lover) to yield, a cyclic system. This reaction is named after the German chemists, Diel and Alder. It is a very useful reaction for synthesizing cyclic systems. The simplest Diels-Alder reaction is the reaction of 1, 3-butadiene with ethene to yield cyclohexene. The resulting product (here cyclohexene) is called the adduct.



This is a very slow reaction and it occurs only under conditions of heat and pressure. Diels-Alder addition take place most rapidly and give the highest yield if the alkene component has electron withdrawing groups or the diene has electron donating groups. The reaction has wide scope because triple bonded systems also may be used as dienophiles. Some important examples of Diels-Alder reaction are given below:



SELF ASSESSMENT EXERCISE 5

1. Write the structure of all possible carbocation intermediates in the addition of HI to 2, 4-hexadiene
2. Which carbocation, of the above problem, would you expect to be more stable?

4.0 CONCLUSION

In this unit, we have studied the classification of alkanes, their physical and chemical properties. In addition, we have explained their structures and methods of preparation.

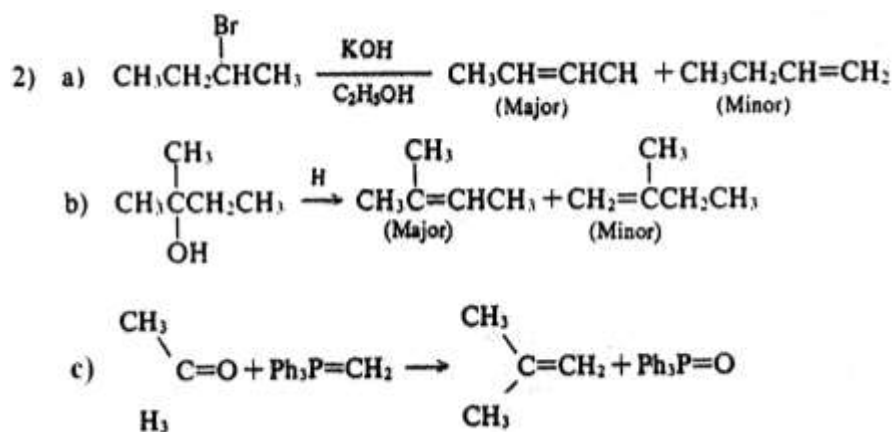
5.0 SUMMARY

- Hydrocarbons containing one carbon-carbon double bond are known as monoene or olefins. Hydrocarbons containing two double bonds are known as alkenes or dienes. 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.
- 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. The ease of dehydrohalogenation of alkyl halide or dehydration of alcohol is:
tert > sec > p
- Alkenes can also be prepared from aldehydes or ketones by Wittig reactions.
- Dienes are prepared by retro Diels-Alder reactions
- The main reactions of alkenes are electrophilic addition reactions. These reactions include addition of halogen, addition of alkyl halide, addition of water, etc.
- Alkenes can be oxidised by ozone, permanganate and osmium tetroxide. Alkenes on ozonolysis give aldehydes or ketones and on oxidation give 1, 2-diol.
- Addition of halogen to conjugated dienes give normal 1, 2-addition product as a minor product and abnormal 1, 4-addition product as a major product.
- Alkenes undergo Diels-Alder reaction.

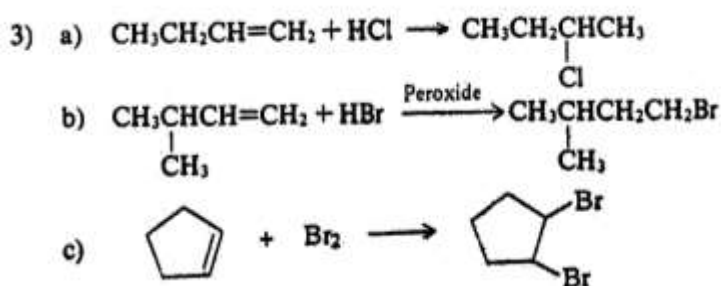
ANSWER TO SELF ASSESSMENT EXERCISE 1

- a) alkyne
 b) four
 c) conjugated
 d) sp ; sp^2

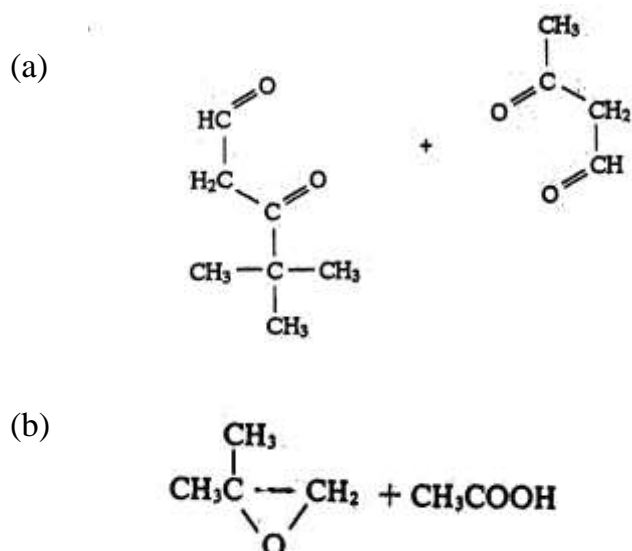
ANSWER TO SELF ASSESSMENT EXERCISE 2

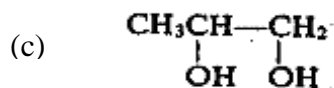


ANSWER TO SELF ASSESSMENT EXERCISE 3



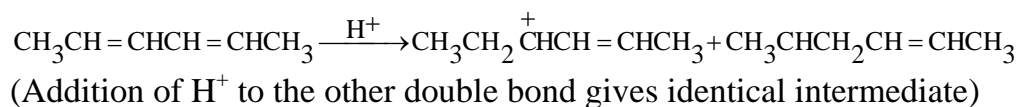
ANSWER TO SELF ASSESSMENT EXERCISE 4



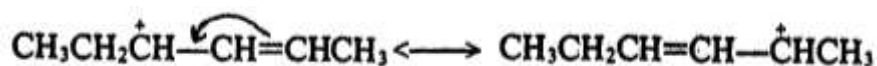


ANSWER TO SELF ASSESSMENT EXERCISE 5

(a)

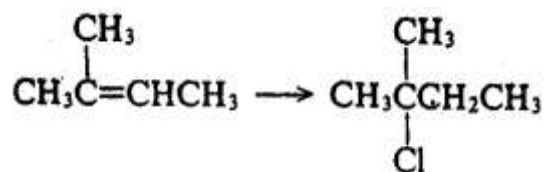


(b) The first carbocation shown would be more stable because it is resonance stabilized allylic carbocation, i.e.

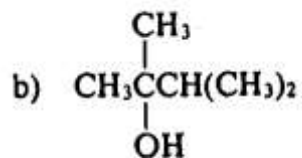
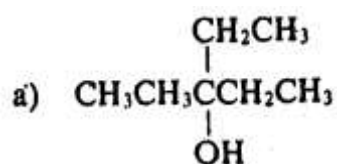


6.0 TUTOR-MARKED ASSIGNMENT

(1) Give a structural formula for the carbocation intermediate that leads to the principle product in following reaction:



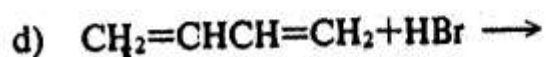
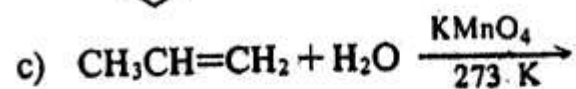
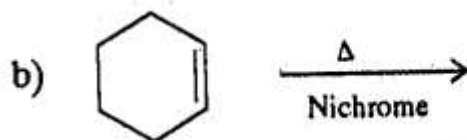
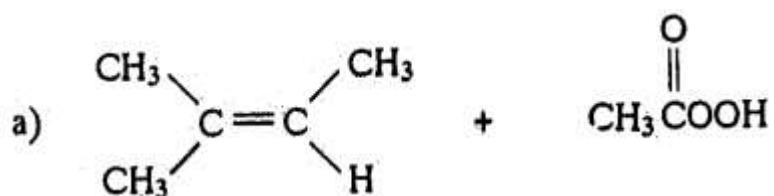
(2) Identify the alkene obtained on hydration/dehydrohalogenation of each of the following compounds:



(3) Give the product formed when HBr react with 2-methyl-2butene in presence of peroxide and in absence of peroxide.

(4) Arrange the following alkenes in order of decreasing stability. $\text{R}_2\text{C}=\text{CR}_2$; $\text{R}_2\text{C}=\text{CH}_2$; $\text{CH}_2=\text{CH}_2$; $\text{R}_2\text{C}=\text{CHR}$; $\text{RHC}=\text{CHR}$; $\text{RCH}=\text{CH}_2$

(5) Complete the following reactions:



7.0 REFERENCES/FURTHER READING

R.T. Morrison and R.N. Boyd, *Organic Chemistry*, (6th Ed.), India: Prentice-Hall Pvt. Ltd.

Lloyd N. Ferguson, *Textbook of Organic Chemistry*, (2nd Ed.), Affiliated East-West Press Pvt. Ltd.

S.M. Mukherji, S.P. Singh and R.P Kapoor, *Organic Chemistry*, Vol. I and II Wiley Eastern Ltd.

P.L. Soni and H.M. Chawla, *Textbook of Organic Chemistry*, (24th Ed.), Sultan Chand and Sons.

UNIT 4 ALKYNES

CONTENTS

- 1.0 Introduction
- 2.0 Objectives
- 3.0 Main Content
 - 3.1 Types of Alkynes
 - 3.2 Physical Properties
 - 3.3 Spectral Properties
 - 3.4 Preparation
 - 3.4.1 Dehydrohalogenation of Dihalides
 - 3.4.2 Dehalogenation of Tetrahalides
 - 3.4.3 Alkylation of Ethyne
 - 3.5 Acidity of Alkynes
 - 3.6 Reactions of Alkynes
 - 3.6.1 Electrophilic Addition
 - 3.6.2 Reduction
 - 3.6.3 Oxidation
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor-Marked Assignment
- 7.0 References/Further Readings

1.0 INTRODUCTION

In the previous two units, you have studied the chemistry of alkanes and alkenes. We shall now study another kind of hydrocarbon known as alkynes which contain carbon-carbon triple bond.

Ethyne, $\text{CH} \equiv \text{CH}$, 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 the preparation of many important chemicals, e.g., ethanoic acid, chloroethene (vinyl chloride), propanone, butanol, ethanol, 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 defiance against infestation.

You will see in this unit that the carbon-carbon triple bond reacts with many of the reagents that react with alkenes. You will also study the most unique aspect of the chemistry of alkynes, the acidity of terminal alkynes.

2.0 OBJECTIVES

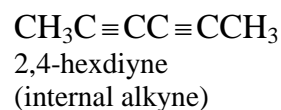
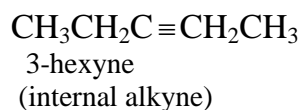
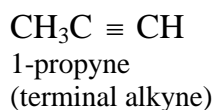
After studying this unit, you should be able to:

- list the various kinds of alkynes
- list the physical and spectral properties of alkynes
- explain the various methods for the preparation of alkynes
- explain the acidity of terminal alkynes
- explain the chemical reactions of alkynes.

3.0 MAIN CONTENT

3.1 Types of Alkynes

Alkynes, also known as acetylenes, constitute the homogenous series of open chain unsaturated hydrocarbons that contain one or more carbon-carbon triple bond. Alkynes may be 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.



3.2 Physical Properties

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. The physical constants like melting points, boiling points and densities increase gradually with the increase in molecular weight. The increase in boiling point with increase in molecular weight is due to increased London forces, as discussed in module 1 of this course. Alkynes have slightly higher boiling points than the corresponding alkenes and alkanes. Terminal alkynes have lower boiling points than the isomeric internal alkynes and 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.

3.3 Spectral Properties

The alkynyl chromophore absorbs below 200 nm ($\pi - \pi^*$ transition) in UV region which is often difficult to detect. Conjugation with a multiple bond, however, results in a bathochromic shift.

The ir absorption region of compounds with a triple bond depends on whether they contain alkyne hydrogen or not. Thus, in terminal alkynes, $\text{RC}\equiv\text{CH}$, there is one absorption band in the region of $3300\text{-}3100\text{ cm}^{-1}$ due to the $\text{C}\equiv\text{CH}$ stretching and another in the region of $2140\text{-}2100\text{ cm}^{-1}$ due to $-\text{C}\equiv\text{C}-$ stretch. In the internal alkynes $\text{RC}\equiv\text{CR}$, there is absorption in the region of $2260\text{-}2190\text{ cm}^{-1}$ corresponding to the $-\text{C}\equiv\text{C}-$ stretching.

The internal alkynes, $\text{RC}\equiv\text{CR}$, have no alkynyl hydrogen, therefore, they have no nmr absorption characteristics of alkynyl hydrogen. The terminal alkynes, $\text{RC}\equiv\text{CH}$, give an absorption signal between δ 2 and 3, characteristic of alkynyl proton. Thus, value for alkynyl proton is less than the value of alkenyl protons. Let us suggest an explanation for this.

The chemical shift of a particular proton depends on the magnetic field felt by it. As you know, the chemical shift as well as the magnetic field felt by a particular proton depends on:

- the electronegativity of the carbon atom to which the proton is attached,
- the way the proton is oriented to the neighbouring π electron cloud, if any.

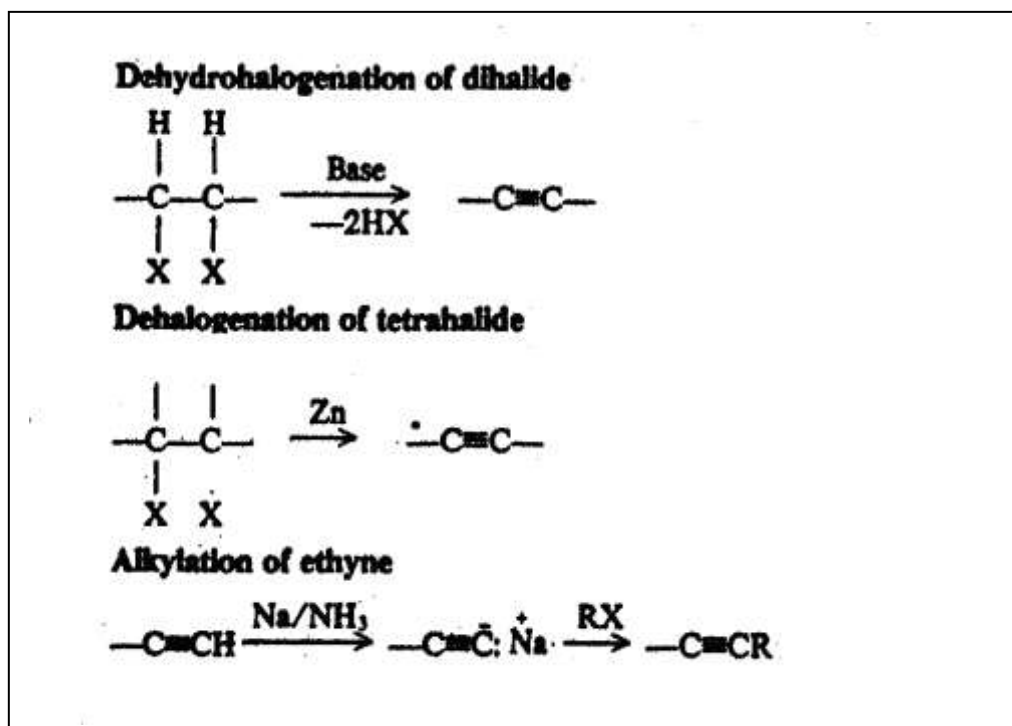
The sp hybridised carbon in alkynes is more electronegative than the sp^2 hybridised carbon in alkenes. Hence, we could expect higher δ value for alkynyl protons than for alkenyl protons. But the orientation of the alkynyl proton to the π electron cloud is unfavourable for higher δ values, as compared to the alkenyl protons.

The mass spectra of an alkyne give distinct molecular ion peak. However, the fragmentation is often complex and not easily interpreted.

3.4 Preparation

Organic synthesis makes use of two major reaction types: one is functional group transformation and the other is carbon-carbon bond forming reaction. Both these strategies are applied to the 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 4.1

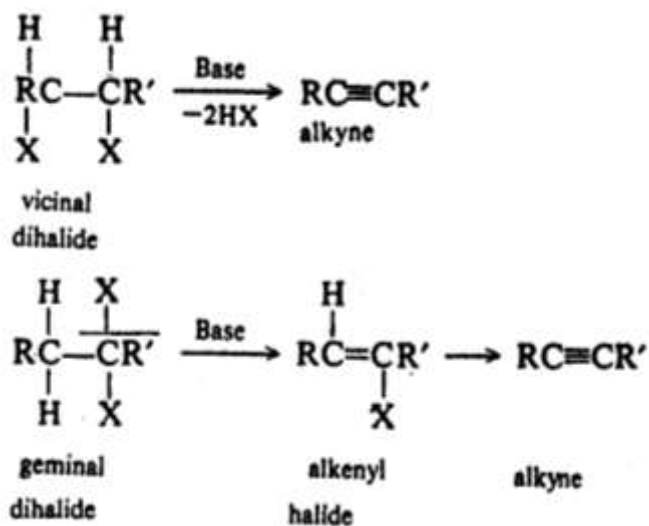
Table 4.1: Preparation of Alkynes



3.4.1 Dehydrohalogenation of Dihalides

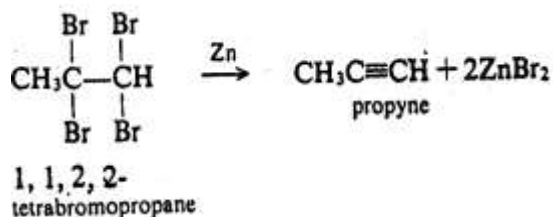
You have already seen in Unit 5 that an alkene can be prepared by the elimination of HX from an alkyl halide. Similarly, an alkyne can be prepared by the elimination of two molecules of HX from a dihalide. The dihalide may be of the geminal or vicinal type. Geminal dihalide: One in which both the halogen atoms are substituted on the same carbon atom.

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



3.4.2 Dehalogenation of Tetrahalides

Alkyne 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.

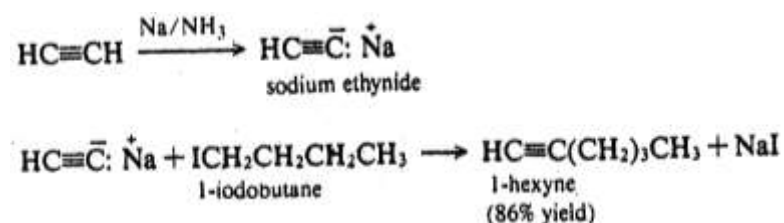


This reaction does not have any synthetic importance, since the tetrahalides themselves are usually prepared from alkynes. However, it provides a method for the purification of alkynes.

3.4.3 Alkylation of Ethyne

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

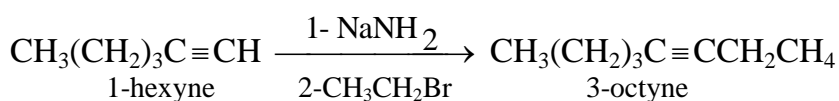
In this sub-section, we shall see how alkynes are prepared by combining smaller units to build larger carbon chains. One of these structural units is ethyne itself. By attaching alkyl group to ethyne, more complex alkynes can be prepared. For example.



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

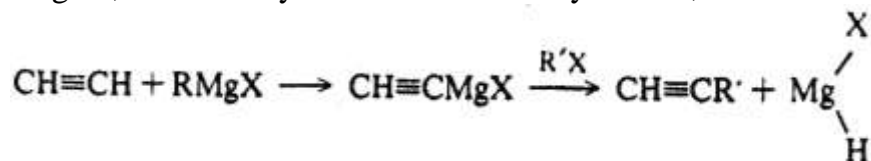
In the second step, sodium ethynide ion attacks the C-I carbon atom of 1-iodobutane and pushes out the iodine ion, yielding the terminal alkyne, 1-hexyne, giving an overall 86% yield.

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.



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,



SELF ASSESSMENT EXERCISE 1

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

1. 2-Heptyne
2. 3-Heptyne

3.5 Acidity of Alkynes

You have already studied the Bronsted-Lowry theory of acids and bases in Unit 2 of this course. According to Bronsted and Lowry, an acid is a species that donates H^+ . In fact, any compound containing a hydrogen atom can act as an acid under suitable conditions. Acid strength can be measured by measuring dissociation constants and expressing the results as values. Strong acids have lower pK_a values than weak acids.

Hydrocarbons are usually not regarded as acids. Nevertheless, we can consider the removal of a proton from a hydrocarbon by a very strong base.



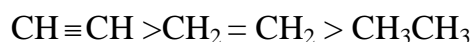
In this equation, the hydrocarbon acts as a Bronsted acid and the conjugate base is a carbon anion or carbanion.

Approximate acidities of different types of aliphatic hydrocarbons have been measured and their pK_a values are given in Table 4.2

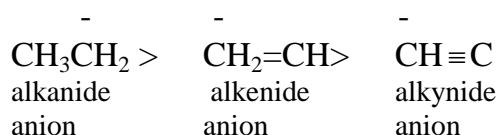
Table 4.2 Acidities of some hydrocarbons

Type	Example	pK_a
Alkane	$\text{CH}_4 \rightleftharpoons \text{C}\bar{\text{H}}_3 + \text{H}^+$	49
Alkene	$\text{CH}_2=\text{CH}_2 \rightleftharpoons \text{CH}_2=\text{C}\bar{\text{H}} + \text{H}^+$	44
Alkyne	$\text{HC}\equiv\text{CH} \rightleftharpoons \text{HC}\equiv\text{C}\bar{\text{H}} + \text{H}^+$	25

From the data given in Table 4.2, we can see that there is a significant difference in the acidity of alkynes and other hydrocarbons. The order of acid strength of these hydrocarbons is:

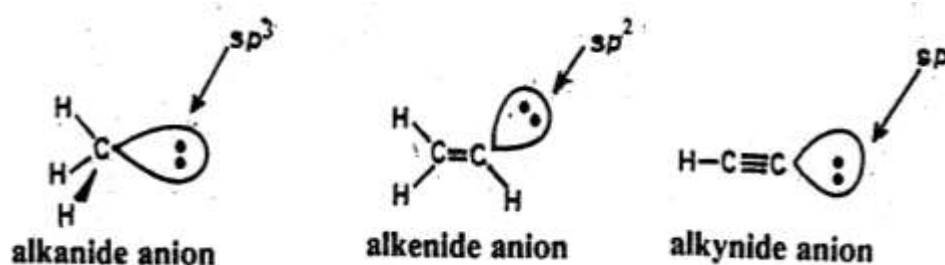


Conversely, the decreasing order of basic strength of the conjugate anions resulting from these hydrocarbons should be:



This decreasing order of acidities and basicities of hydrocarbons can be explained as follows:

Conjugated bases of alkanes, alkenes and alkynes have an electron pair in sp^3 , sp^2 and sp orbitals, respectively, i.e.,



As we proceed from the alkanide anion to alkynide anion, the s character of the hybrid orbital increases and p character decreases. The alkanide anion (sp^3 hybridized) has 25% s character and 75% p character; alkenide anion (sp^2 hybridised) has 33.3% s character 64.6% p character; and alkynide anion (sp hybridized) has 50% s character and 50% p character. You have already studied in your earlier classes that electrons in s orbital are closer to the nucleus than those in p orbital. Since s character is maximum in alkynide anion and minimum in alkanide anion, the electron pair should be held most tightly in alkynide anion and most loosely in alkanide anion. Alkenide anion lies in between. In other words, the electron pair in alkynide anion should be least available for protonation. As you know, the basic strength is more if the electron pair is easily available for protonation.

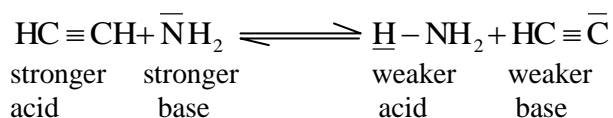
Therefore, in the above series, alkynide anion is the weakest base and alkanide anion is the strongest base. Conversely, alkyne is the strongest acid and alkane the weakest acid.

This can be explained in another way also. On the basis of the above discussion, we can say that the sp hybridized carbon would attract the

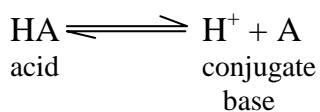
electrons pair constituting the C – H bond of an alkyne more than the sp² and sp³ hybridised carbons in alkene and alkane; respectively. This implies that C – H bond in an alkyne would be more ionic and has a tendency to donate a proton (H⁺), hence, ethyne would be more acidic as compared to ethene or ethane.

Let us now compare its acidity with ammonia and water.

Addition of ethyne to sodamide in ether yields ammonia and sodium ethynide.



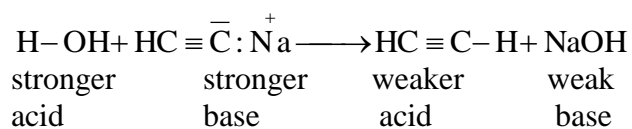
Note:



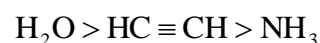
The stronger the conjugate base, the weaker the acid and vice-versa.

The weaker acid, H – NH₂, is displaced from its salt by the stronger acid, HC≡CH. In other words, the stronger base, NH₂⁻ pulls the hydrogen ion away from ethyne to yield a weaker conjugate base, HC≡C⁻, since NH₂⁻ holds the hydrogen ion more tightly than HC≡C⁻, ammonia must necessarily be a weaker acid than ethyne.

Addition of water to sodium ethynide forms sodium hydroxide and regenerates ethyne.



The weaker acid, ethyne, is displaced from its salt by the stronger acid, H₂O. Thus ethyne is a stronger acid than ammonia, but a weaker acid than water, i.e.; the three compounds have the following order of acid strength:



SELF ASSESSMENT EXERCISE 2

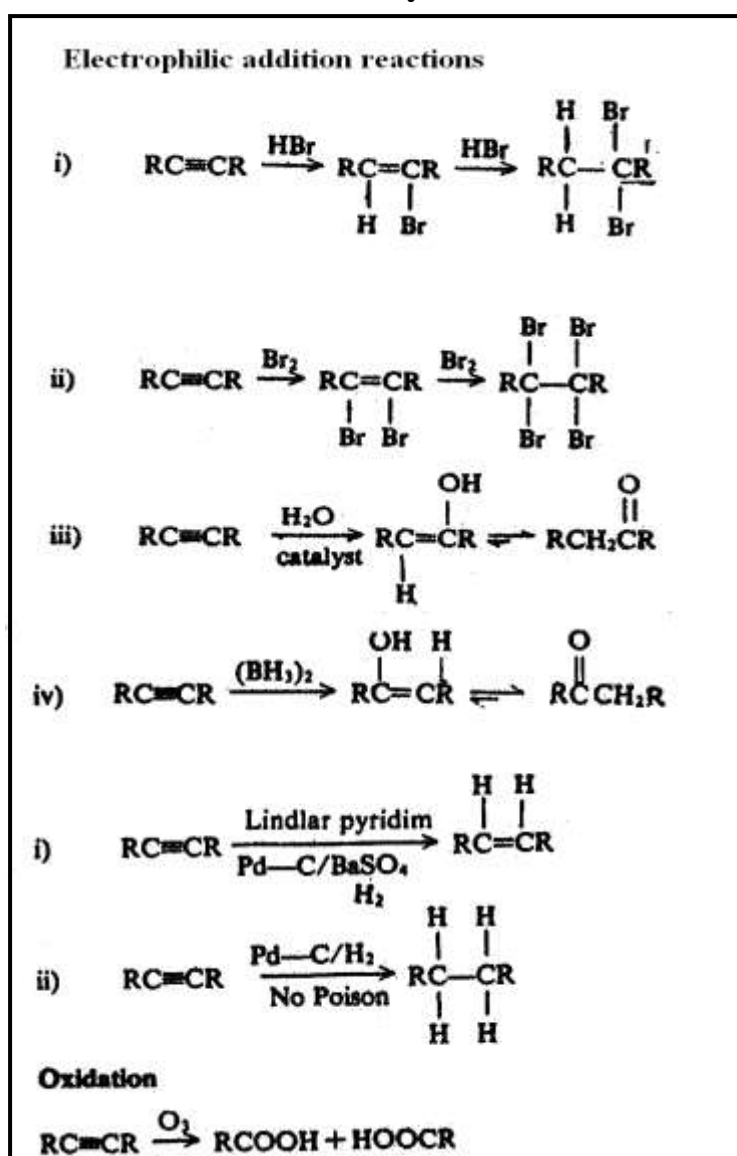
Arrange the following bases in the increasing order of basic strength



3.6 Reactions of Alkynes

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. Characteristic reactions of alkynes include electrophilic additions, reduction and oxidation. Some important reactions of alkynes are summarized in Table 4.3

Table 4.3: Reactions of alkynes

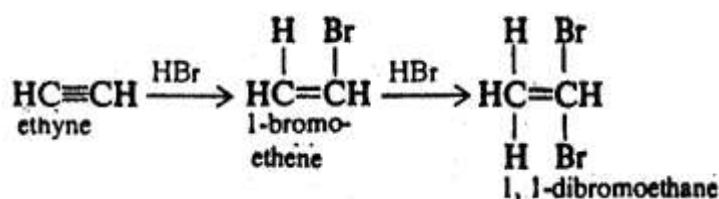


3.6.1 Electrophilic Addition

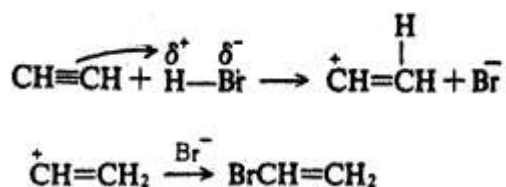
Electrophilic addition reactions are characteristic of alkynes. Some common electrophilic addition reactions are discussed below:

(i) Hydrohalogenation

Alkynes can add on the halogen acid (HX). The addition of halogen acid cannot take place in the dark, but is catalysed by light or metallic halides. Like alkenes, the addition is in accordance with Markownikoffs rule; for example, ethyne combines with hydrogen bromide to form first 1-bromoethene and then 1, 1-dibromoethane.

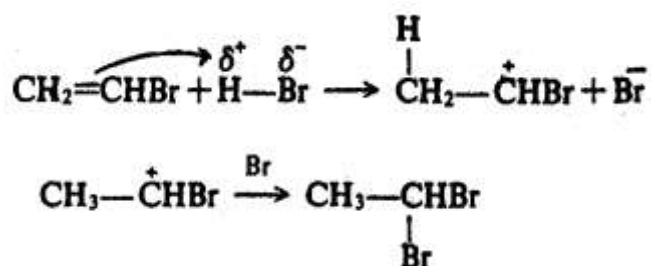


The mechanism of these reactions is the same as in the hydrohalogenation of alkenes, i.e.,



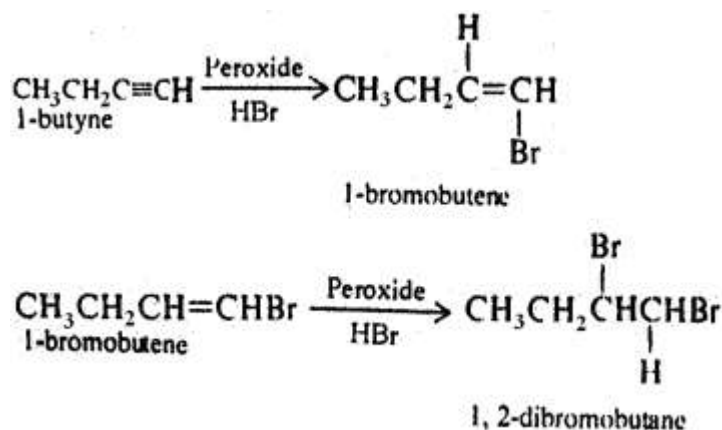
Note: If one of the carbon atoms involved in double bond formation (with another carbon atom) carries a positive charge, then the species is called alkenyl cation.

Addition of another molecule of hydrogen bromide could give either CH_3CHBr^+ (a secondary carbocation) or $\text{CH}_2\text{CH}_2\text{Br}^+$ (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:



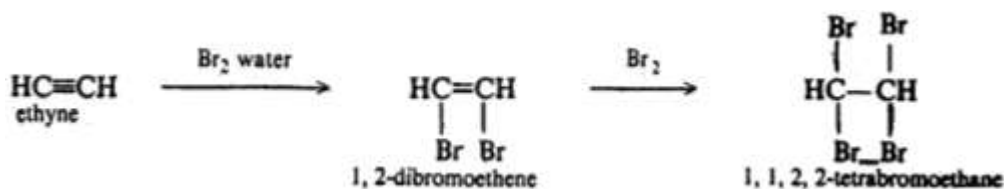
Because of the electron-withdrawing nature of bromine atom, the availability of π electrons in 1-bromoethene is less than that in ethane. Hence, the electrophilic addition (of HBr) to 1-bromoethene is much slower than that to ethene,

In the presence of free radical initiators such as peroxides, anti Markownikoff 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:

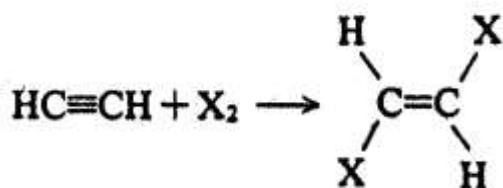


(ii) Halogenation

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, for instance, on treatment with bromine water gives only 1, 2-dibromoethene whereas with bromine alone, it forms 1, 1, 2, 2-tetrabromoethane.



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



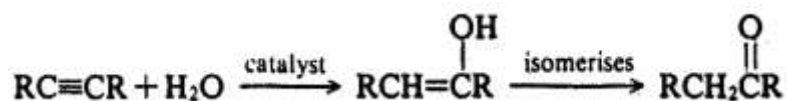
SELF ASSESSMENT EXERCISE 3

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

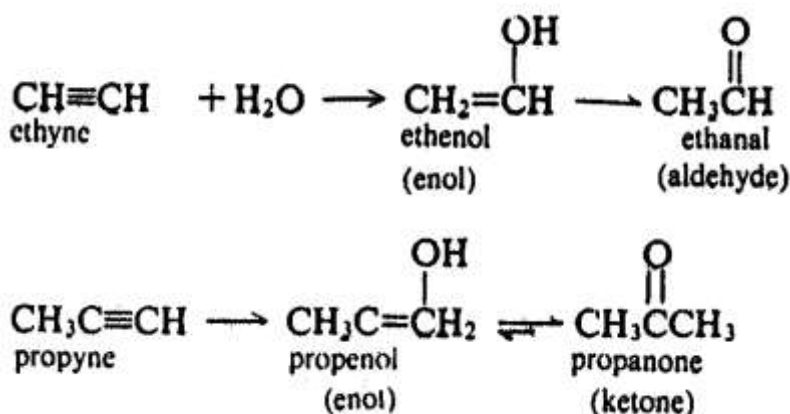
1. HCl
2. Cl₂
3. HBr (in presence of peroxide)

(iii) Hydration

You have seen in previously that 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 double-bonded carbon atom.



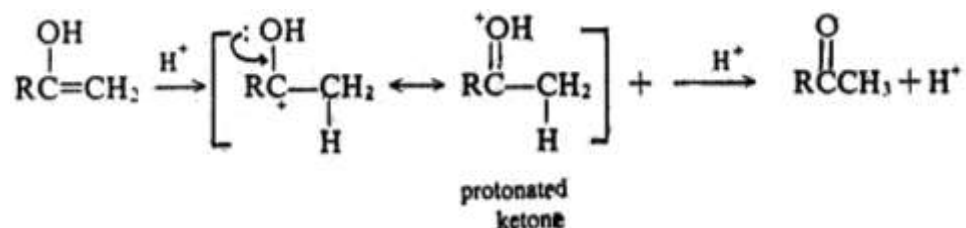
In fact, enols are very unstable and they isomerise (or tautomerise) to give aldehydes or ketones. The process by which enols are converted into aldehydes or ketones is called keto-enol isomerism or keto-enol tautomerism. For example, when ethyne undergoes hydration, it gives an aldehyde, i.e. ethanal,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



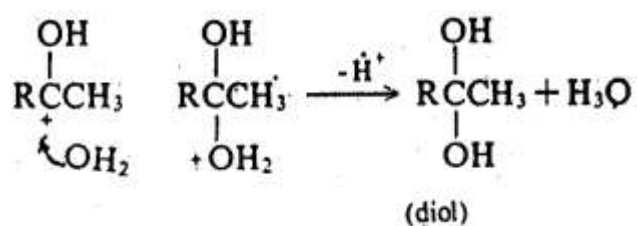
The arrow is longer towards aldehyde or ketone side showing the direction in which the equilibrium is favoured.

In case of unsymmetrical alkyne addition of water place in accordance with Markovnikoff's rule. The enol is converted into aldehyde or ketone by a mechanism similar to the hydration of a double bond. The enol double bond is protonated to give a carbocation. The in the

example shown below is a protonated ketone. Instead of adding water, this ion loses a proton to give ketone.



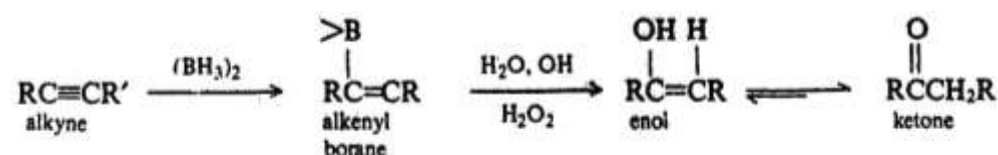
Now you may ask why carbocation is not attacked by water molecule to give a diol, i.e.



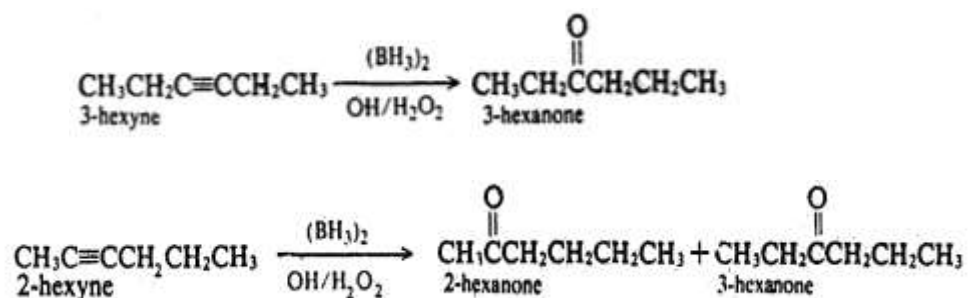
This reaction does not occur, because it is reversible, and the equilibrium between the ketone and the corresponding diol in most cases favours formation of the ketone.

(iv) Hydroboration

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

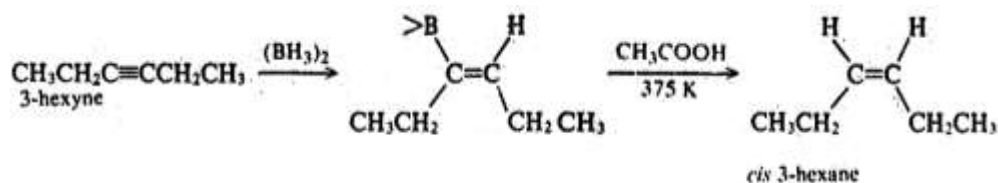


The symmetrical internal alkynes give a single product while unsymmetrical internal alkynes give a mixture of both the possible ketones. For example, 3-hexyne gives 3-hexanone while 2-hexyne gives a mixture of 2-hexanone and 3-hexanone.



The terminal alkynes on hydroboration give aldehydes.

Another reaction of organoboranes is protonolysis. That is, the alkenyl boranes, formed after the addition of borane to alkynes, on treatment with ethanoic acid yield *cis*-alkenes. This reaction sequence provides another method of converting alkynes to *cis*-alkenes.

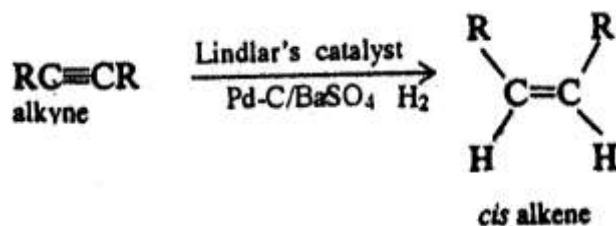


SELF ASSESSMENT EXERCISE 4

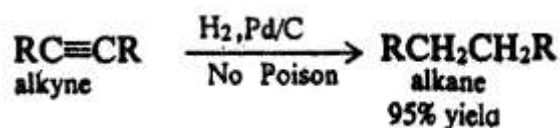
Give the equation for hydroboration of a terminal alkyne.

3.6.2 Reduction

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 gives an alkane. By using a calculated amount of hydrogen and a poisoned catalyst, hydrogenation can be stopped at the alkene stage. A catalyst mixed with a selective inhibiting agent is called a poisoned catalyst. These catalysts selectively block the hydrogenation of alkenes.

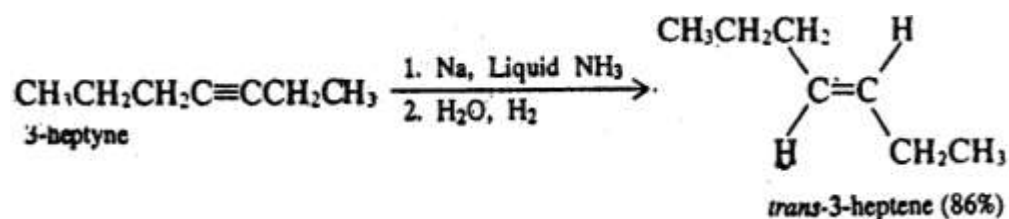


This is a stereoselective addition reaction giving predominantly *cis* alkenes. In the absence of a poison, catalytic hydrogenation of an alkyne gives the alkane. Stereoselective reaction is a reaction which yields predominantly one isomer.

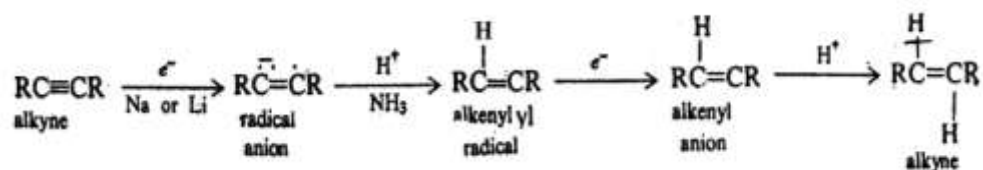


Now you can ask: can we modify the reduction of alkynes so as to get only *trans* alkenes. The answer is yes; we can get only *trans* products, but with a different reducing agent and through a different mechanism.

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. For example, 3-heptyne is reduced to *trans* 3-heptene in the following way:

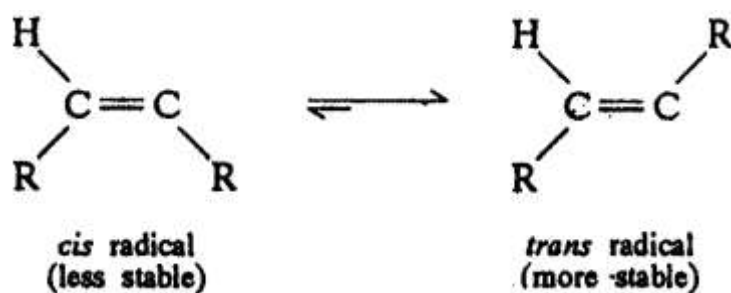


In the first step of this mechanism, the alkyne accepts one electron to give a radical anion. The radical anion is protonated by ammonia solvent to give an alkenyl radical; which gets further reduced by accepting another electron to give an alkenyl anion. This species is again protonated to give the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

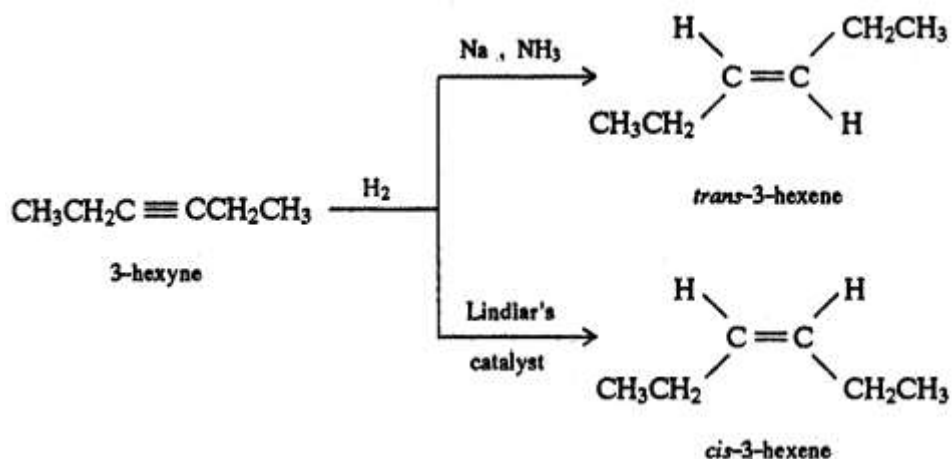


A radical anion has one centre with a negative charge and another, with an unpaired electron.

Formation of the *trans* alkene 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.



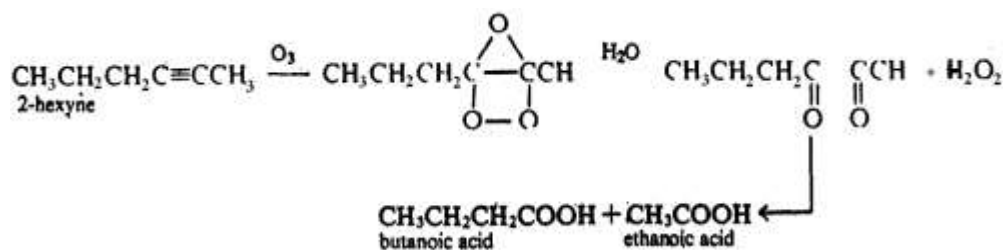
SELF ASSESSMENT EXERCISE 5

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

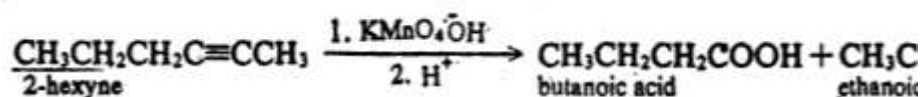
1. *cis*-2-hexene
2. *trans*-2-hexene
3. hexane

3.6.3 Oxidation

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 ozonides on hydrolysis give 1, 2-dicarbonyl compounds, 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.



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



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

SELF ASSESSMENT EXERCISE 6

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



4.0 CONCLUSION

There are various types of alkynes of which acetylene is the most popular. It is used in oxy-acetylene flames for cutting and welding materials. We have given explanation for the acidity of terminal alkynes.

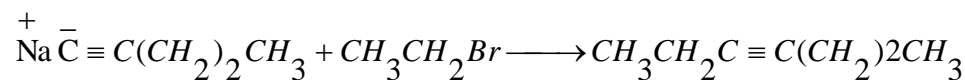
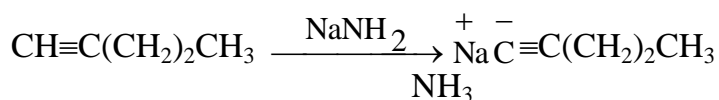
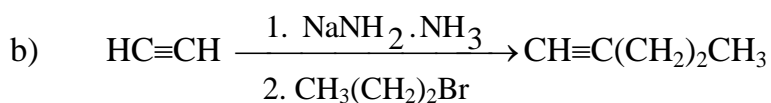
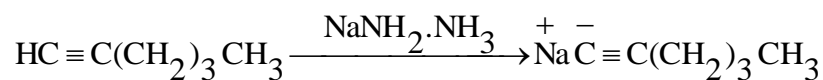
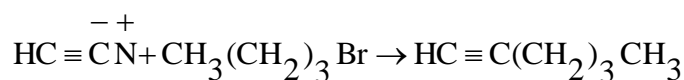
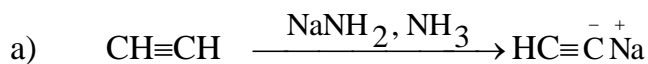
5.0 SUMMARY

- Alkynes are the hydrocarbons with one or more carbon-carbon triple bond
- Alkynes may be of two types, i.e. terminal or internal.
- Physical properties of alkynes are more or less similar to alkenes
- Alkynes are prepared by alkylation of terminal alkynes or by a two-fold elimination of HX from dihalide or by dehalogenation of tetrahalides.
- Terminal alkynes are more acidic than alkanes or alkenes.
- Hydrohalogenation follows Markovnikov's rule.
- Halogens add to alkynes to give tetrahaloalkanes. Using proper reaction conditions dihaloalkene can be isolated.
- Hydration of an alkyne gives an unstable enol which tautomerises to give an aldehyde or a ketone.
- Hydroboration of alkynes may give ketones or aldehydes, depending on reaction conditions and the type of the alkyne.
- 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

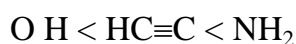
with sodium or lithium in liquid ammonia gives the *trans*-alkene.

- Ozonolysis of alkynes give carboxylic acids.

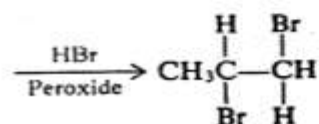
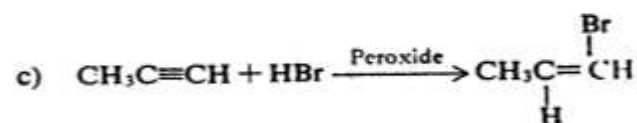
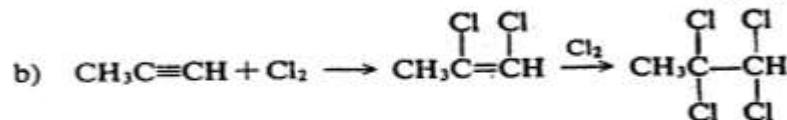
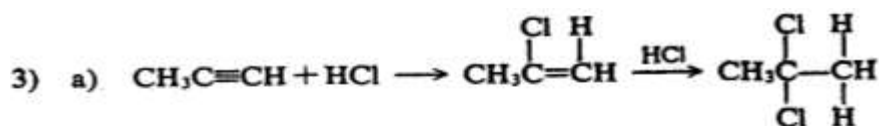
ANSWER TO SELF ASSESSMENT EXERCISE 1



ANSWER TO SELF ASSESSMENT EXERCISE 2

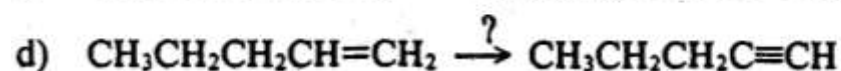
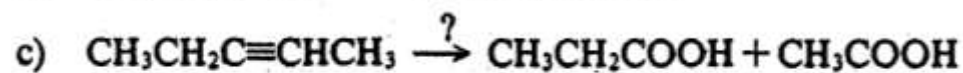
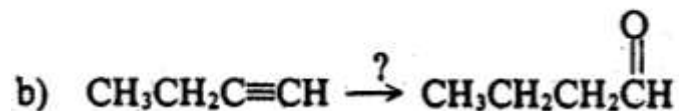
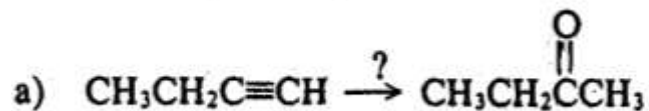


ANSWER TO SELF ASSESSMENT EXERCISE 3

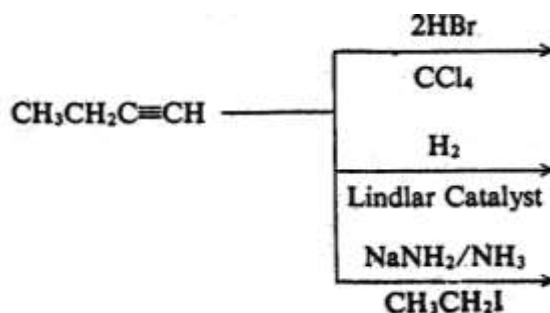


6.0 TUTOR-MARKED ASSIGNMENT

1. How would you carry out the following reactions:



2. Predict the product of the following reactions of 1 – butyne:



3) How will you convert

- 2-Bromopropane to propyne
- 1-Bromopropane to 2-hexyne.

4) Suggest steps for the following transformations:

- 2, 3-dibromopentane to *trans*-2-pentene
- 3-methyl-1-butyne to *trans*-2-methyl-3-heptene

5) Show, by varying appropriate chemical equations, how each of the following compounds could be converted to 1-hexyne:

- 1, 2-Dibromohexane:
- 1-Hexene
- Hexane

7.0 REFERENCES/FURTHER READING

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