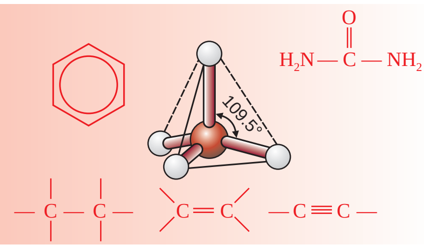
UNIT 1




# Introduction to Organic Chemistry

## Unit Outcomes

*After completing this unit, you will be able to:*

- *know the historical development of organic chemistry and the classification of organic compounds;*
- *know the general formulas of alkanes, alkenes, alkynes, alcohols, aldehydes, ketones, carboxylic acids and esters;*
- *develop skills in naming and writing the molecular and structural formulas of simple alkanes, branched-chain alkanes, simple alkenes, branched-chain alkenes, simple alkynes, alcohols, aldehydes, ketones, carboxylic acids and esters;*
- *understand isomerism and know possible isomers of alkanes, alkenes and alkynes;*
- *know the major natural sources of hydrocarbons;*
- *understand the physical and chemical properties and the general methods of preparation of alkanes, alkenes, alkynes, benzene and alcohols;*
- *know the uses of organic compounds in the manufacture of plastics, beverages, pharmaceuticals, soaps and detergents, dry cleaning chemicals, fuels, pesticides, and herbicides; and*
- *demonstrate scientific inquiry skills: observing, classifying, communicating, measuring, asking questions, interpreting data, drawing conclusions, applying concepts, predicting and problem solving.*

## MAIN CONTENTS



## 1.1 INTRODUCTION

### *Competencies*

***By the end of this section, you will be able to:***

- narrate the historical development of organic compounds;
- define the term functional group;
- classify organic compounds based on their functional groups.

### Historical Notes

Friedrich Wöhler

**Friedrich Wöhler**

In 1828 German chemist, **Friedrich Wöhler** converted ammonium cyanate, an inorganic compound, into the organic substance urea. **Wöhler's** discovery revolutionized the study of chemistry by redefining the manner in which chemists distinguished between inorganic and organic compounds. He is also credited for his work in isolating the elements aluminium and beryllium.

### Activity 1.1

1. Do you agree with the notion that says: "carbon compounds can be synthesized only by animals and plants"?
2. Draw diagrams to show how carbon atoms can link to one another in different ways to form a variety of compounds by considering only four carbon atoms.

   Discuss with your group and present it to the class.

## History of Organic Chemistry

Before the beginning of the nineteenth century, chemists classified compounds into two classes; organic and inorganic. Those derived from living things (*plants* and *animals*) were classified as organic compounds, while those that came from mineral constituents of the earth or were found with non-living things are classified as inorganic compounds.

What was the basis of this classification? Early chemists believed that organic compounds differed from inorganic compounds because living things had a special 'life force' within them, which was invisible and hard to detect. According to the theory of 'life force', the only source of organic compounds was nature itself (*plants* and *animals*). It was thought impossible to synthesize them in the laboratory. This was because man could not add or create the 'life force' within them.

The belief in the 'life force' theory continued until Friedrich Wöhler synthesized urea for the first time in 1828. In attempting to prepare ammonium cyanate, $NH_4CNO$, from the reaction of silver cyanate, AgCNO, and ammonium chloride, $NH_4Cl$, he accidentally and surprisingly obtained urea, $(NH_2)_2CO$:

$$AgCNO(aq) + NH_4Cl(aq) \rightarrow AgCl(s) + NH_4CNO(aq)$$

$$NH_4CNO\ (aq) \xrightarrow{\text{evaporation}} \underset{\text{Urea}}{H_2N - \overset{\overset{\displaystyle O}{\|}}{C} - H_2N\ (s)}$$

Urea was the first organic compound synthesized in the laboratory. The synthesis of urea by Friedrich Wöhler and subsequent synthesis of other organic compounds marked the downfall of the 'life force' theory.

***How do you explain organic compounds at present and define organic chemistry?***

The common feature of organic compounds is that they all contain the element carbon. Organic compounds are the compounds of carbon found in and derived from plants and animals. They also include those substances synthesized in laboratories except the oxides of carbon, carbonates, hydrogen carbonates, cyanides and cyanates.

Besides carbon, these compounds contain a few other elements such as hydrogen, oxygen, nitrogen, sulphur, halogens and phosphorus. The branch of chemistry that studies carbon compounds is called organic chemistry. This branch of chemistry was developed, starting from the theory of 'life force' to the era in which synthetic organic compounds are used in our daily lives. The number of inorganic compounds discovered and prepared may be in the region of some hundred thousand. At present, millions of organic compounds have been discovered, synthesized, and used.

The main reason for the presence of millions of carbon compounds is the unique property of carbon called catenation. Catenation is the ability of atoms of the same element to join together forming short or long chains and rings. A few other elements like sulphur, silicon and boron show this behaviour, but to a much lesser extent.

## *Classification of Organic Compounds*

### Activity 1.2

$CH_3CH_2CHO$ and $CH_3COCH_3$ have the same chemical formula $C_3H_6O$. Write their detailed structures and observe their difference? Why do these compounds have different properties? Discuss with your group and present it to the class.

Organic compounds are generally classified based on their functional group.

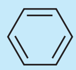
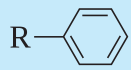
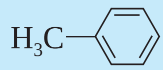
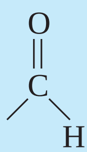
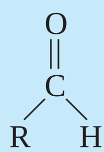
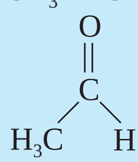
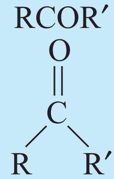
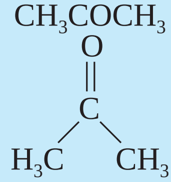
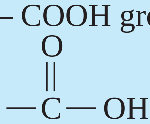
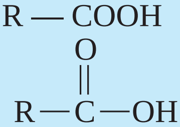
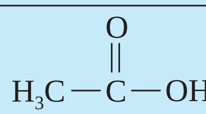
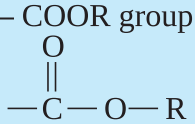
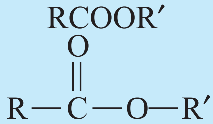
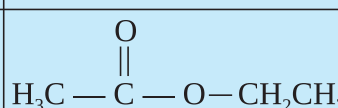
***What are functional groups and what groups of organic compounds are known on the basis of this classification?***

**The functional group** is the part of a molecule or a compound that determines the chemical properties of that molecule or compound. This group also determines some of the physical properties of a compound. Based on the functional groups they possess, the most common classification of organic compounds including alkanes, alkenes, alkynes, aromatics, alcohols, aldehydes, ketones, carboxylic acids and esters. The common functional groups of some organic compounds are given in Table 1.1.

**Table 1.1 Some classes of organic compounds, their functional groups, general structural formula with typical examples (R = alkyl or H).**

| Organic Compound | Functional Group | General Structure | Example |
|---|---|---|---|
| Alkane | $-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-$ (single bond) | $R-CH_2-CH_3$ | $H_3C-CH_2-CH_3$ Propane |
| Alkene | $>C=C<$ (double bond) | $R-CH=CH_2$ | $H_2C=CH_2$ Ethene |
| Alkyne | $-C\equiv C-$ (triple bond) | $R-C\equiv C-R$ | $H-C\equiv C-H$ Ethyne |

*Continued next page*

| Organic Compound | Functional Group | General Structure | Example |
|---|---|---|---|
| Aromatic |  (benzene ring) |  |  Toluene |
| Alcohols | — OH | R — OH | $CH_3CH_2$— OH Ethanol |
| Aldehydes | — CHO group  | R — CHO  | $CH_3$ — CHO  Ethanal |
| Ketone | — CO — group  | RCOR′  | $CH_3COCH_3$  Propanone |
| Carboxylic Acid | — COOH group  | R — COOH  |  Ethanoic acid |
| Ester | — COOR group  | RCOOR′  |  Ethyl ethanoate |

## Exercise 1.1

1. Which compounds were classified as organic compounds, according to the early chemists?
2. According to the belief of early chemists, which class of compounds has a special 'life force' within them?
3. What are the differences between organic and inorganic compounds, according to early chemists?
4. What is the main concept of the theory of 'life force'?

5. Who disproved the 'life force' theory; and how?
6. What was the first organic compound synthesized in the laboratory?
7. Identify the functional groups in each of the following compounds?
   a $CH_3CH_2COCH_2CH_2CH_3$ c $CH_3CH_2CH_2COOH$
   b $CH_3CH_2COOCH_2CH_3$ d $CH_3CH_2CH_2CH_2OH$
8. Define the following terms.
   a Organic chemistry b Catenation c Functional group
9. Why is it necessary to assign organic chemistry exclusively to the study of carbon compounds?
10. What is the basis for the classification of organic compounds?
11. Write the general structures of:
    a alkanes b alkenes c alkynes
    d aromatics e alcohols

## 1.2 SATURATED HYDROCARBONS

### *Competencies*

***At the end of this topic, you will be able to:***

- define hydrocarbons;
- define saturated hydrocarbons;
- define homologous series;
- write the general formula of alkanes;
- write the first ten members of alkanes;
- write the molecular formulas of alkanes from the given number of carbon atoms;
- explain the physical properties of alkanes;
- write the structural formulas of the first ten alkanes;
- apply IUPAC rules to name straight and branched chain alkanes;
- define isomerism as the way compounds having the same formula differ in the way their atoms are arranged;
- define structural isomerism;
- write possible structural isomers for $C_4H_{10}$, $C_5H_{12}$ and $C_6H_{14}$;
- describe the general method for the preparation of alkanes in the laboratory;

- prepare methane in a laboratory by the decarboxylation method;
- carry out a project to produce biogas from cow dung; and
- explain the chemical properties of alkanes.

## Activity 1.3

1. Draw the Lewis structure of carbon (*Z* = 6) and hydrogen (*Z* = 1) atoms. How many valence electrons are there in an atom of carbon and hydrogen respectively?
2. Consider three organic compounds containing two carbon atoms each. The two carbon atoms contributed one electron each in the first, two electrons each in the second and three electrons each in the third for the bond they form between them by sharing the electrons. The remaining valence electrons of each carbon atom in all the three compounds were used to form bonds with hydrogen atoms.
   a What type of covalent bond do the two-carbon atoms form between themselves in the first, the second and the third compound, respectively?
   b How many hydrogen atoms can form bonds with each carbon atom in the first, the second and the third compound, respectively?
   c Draw line or dot formula to show the formation of the bonds between the carbon atoms and carbon and the hydrogen atoms in the first, the second and the third compound, respectively.
   d If the three compounds mentioned above are hydrocarbons, define hydrocarbons?
   f If the first compound is a saturated hydrocarbon, the second and the third are unsaturated, what is the basis for such a classification of hydrocarbons?

   Discuss with your group and present it to the class.

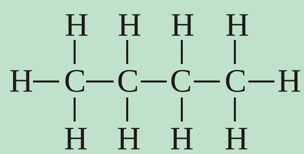
***What are hydrocarbons and on what basis do we categorize them?***

Hydrocarbons are organic compounds composed of the elements carbon and hydrogen only. Hydrocarbons are subdivided into two groups, based on the type of bonding between carbon atoms, as saturated hydrocarbons and unsaturated hydrocarbons.

Saturated Hydrocarbons are those compounds of carbon and hydrogen containing only carbon-carbon single bonds. Methane, ethane, and propane are typical examples of this group. Unsaturated Hydrocarbons are those compounds of carbon and hydrogen possessing one or more multiple bonds (*double or triple bonds*) between carbon atoms. Alkenes, alkynes and aromatic hydrocarbons are examples of unsaturated hydrocarbons.

A formula that shows all the bonds and atoms is called a detailed structure. The shorter structure is called condensed structure.

### Example

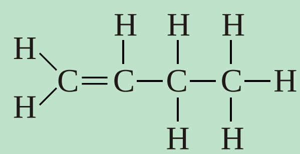


or

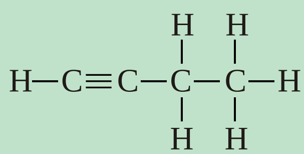
Condensed structure

$H_3C-CH_2-CH_2-CH_3$

Saturated Hydrocarbons (Detailed structure)



or $H_2C=CH-CH_2-CH_3$



or $HC\equiv C-CH_2-CH_3$

Unsaturated Hydrocarbons

## 1.2.1 Alkanes or Paraffins

**Activity 1.4**

Draw a graph using the information in Table 1.2 by plotting the number of carbon atoms of each compound on one axis, and hydrogen atoms on the other. Predict the formulas of the saturated hydrocarbons containing 8, 9 and 10 carbon atoms and complete Table 1.2. Discuss with your group and present it to the class.

Alkanes are saturated hydrocarbons. They contain chains of carbon atoms linked by single bonds only. Every carbon atom in the molecule forms four single covalent bonds with other atoms. Alkanes have the general formula $C_nH_{2n+2}$, where, $n = 1, 2, 3 \ldots$ Using this general formula, we can write the molecular formula of any alkane containing a specific number of carbon atoms. For example, the chemical formulas of alkanes containing one, two and three carbon atoms are $C_1H_{2\times1+2} = CH_4$, $C_2H_{2\times2+2} = C_2H_6$, and $C_3H_{2\times3+2} = C_3H_8$, respectively.

When we compare the formulas of $CH_4$ and $C_2H_6$ or $C_2H_6$ and $C_3H_8$, they differ by one carbon and two hydrogen atoms or $-CH_2-$ group called the methylene group. A group of compounds in which each member of the group differs from the next member by a $-CH_2$, is called a homologous series. Compounds in the same homologous series can be represented by the same general formula. The individual members of the group are called homologues.

Alkanes contain carbon-carbon single bonds (— C — C —) as their functional group. The first ten members of the homologous series of straight-chain alkanes are given in Table 1.2.

**Table 1.2 Homologous series and physical constants of the first ten straight chain alkanes**

| Name | Formula | Physical state (at room temp.) | M.P (°C) | B.P (°C) | Density at 20°C | No. of isomers |
|---|---|---|---|---|---|---|
| Methane | $CH_4$ | gas | –183 | –162 | 0.717 g/L | 1 |
| Ethane | $C_2H_6$ | gas | –172 | –89 | 1.35 g/L | 1 |
| Propane | $C_3H_8$ | gas | –187 | –42 | 2.02 g/L | 1 |
| n-Butane | $C_4H_{10}$ | gas | –135 | –0.5 | 2.48 g/L | 2 |
| n-Pentane | $C_5H_{12}$ | liquid | –130 | 36 | 0.63 g/mL | 3 |
| n-Hexane | $C_6H_{14}$ | liquid | –94 | 68 | 0.66 g/mL | 5 |
| n-Heptane | $C_7H_{16}$ | liquid | –91 | 98 | 0.68 g/mL | 9 |
| n-Octane | ? | liquid | –57 | 126 | 0.70 g/mL | 18 |
| n-Nonane | ? | liquid | –54 | 151 | 0.71 g/mL | 35 |
| n-Decane | ? | liquid | –30 | 174 | 0.73 g/mL | 75 |

## Activity 1.5

1. What happens to the percentage by mass of hydrogen and the physical state of alkanes as the number of carbon atoms increase?
2. Categorize the petroleum related products you encounter everyday as solids, liquids and gases? Discuss in your group and present it to the class.

## 1.2.2 Physical Properties of Alkanes

*Do you know which alkanes exist in the liquid, solid or gaseous state at room temperature? What types of intermolecular forces of attraction exist between the molecules of alkanes? Explain why the boiling points and melting points of alkanes increase with increasing number of carbon atoms.*

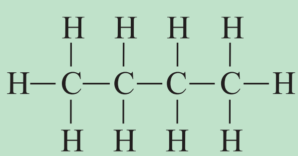
At room temperature, the first four alkanes, methane to butane, are gases; whereas pentane ($C_5H_{12}$) to heptadecane ($C_{17}H_{36}$) are liquids, and the alkanes containing eighteen and more carbon atoms are solids.

Alkanes are nonpolar organic compounds. Weak intermolecular forces called Van der Waal's forces hold their molecules together. The strength of these forces increases with the increasing surface area (*molecular mass*) of the alkanes. Since alkanes are non-polar, they are almost insoluble in polar solvents like water, but, they are soluble in non-polar solvents like benzene, toluene, ether and carbon tetrachloride.

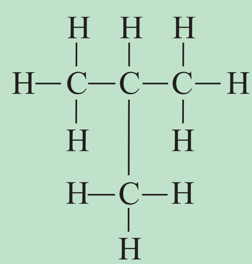
The density, melting point, and boiling point of the homologous series of alkanes increase as the carbon number increases. For alkanes of the same carbon number, branched-chain isomers have lower boiling points than the straight-chain (*normal*) alkanes. The reason is, as branching increases, there is a decrease in surface area and the strength of the intermolecular force, which, in turn, results in a decrease in boiling point; e.g., the boiling points of n-pentane, iso-pentane and neo-pentane are 36°C, 28°C and 9.5°C, respectively.

Alkanes containing all the carbon atoms in one continuous chain are called normal or straight-chain alkanes and those containing chains with branches are known as branched-chain alkanes.

**Example**

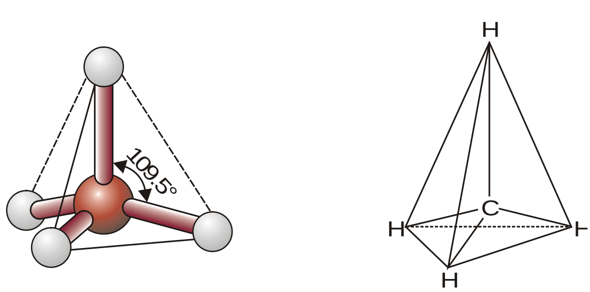


Straight-Chain Alkane



Branched-Chain Alkane

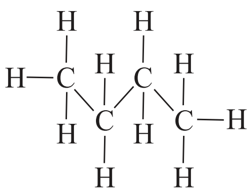
In alkanes (*branched* or *straight-chain*) each carbon atom is tetrahedrally bonded to four atoms with a bond angle of 109.5°.



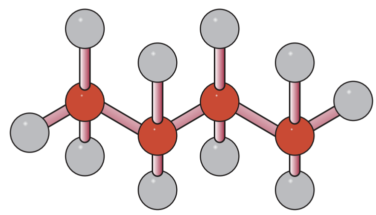

a Ball and Stick Model of Methane b Tetrahedral structure of methane

**Figure 1.1 Structure of methane.**

In alkanes containing a continuous chain of carbon atoms, the carbon atoms are not linked in straight line but in zigzag chains to keep the tetrahedral distribution of atoms.



Zigzag chain in butane



Ball and stick model of butane

**Figure 1.2 Zigzag chain and ball and stick model of butane.**

## Activity 1.6

1. Why rules are important for naming organic compounds? Discuss in your group some of the rules you know for naming organic compounds and present it to your class.
2. In mathematics, the names pentagon, hexagon, heptagon and octagon are used to describe polygons. What does each of the prefixes- pent, -hex, -hept and -oct indicate? What is the significance of these prefixes in chemistry? Discuss in groups and present it to the class.

## 1.2.3 Nomenclature (naming) of Alkanes

Organic chemistry uses a simplified and systematic way of naming organic compounds. The names of alkanes and most of the organic compounds are derived from:

*i)* a prefix- indicating the number of carbon atoms (listed in Table 1.3)and

*ii)*a -suffix indicating the type of the functional group present in the molecule.

The following table introduces the prefixes that are used to indicate the presence of one to ten carbon atoms in the longest continuous carbon chain.

**Table 1.3 Prefixes commonly used to indicate one to ten carbon atoms.**

| Prefix | Number of carbon atoms | Prefix | Number of carbon atoms |
|---|---|---|---|
| Meth- | One | Hex- | Six |
| Eth- | Two | Hept- | Seven |
| Prop- | Three | Oct- | Eight |
| But- | Four | Non- | Nine |
| Pent- | Five | Dec- | Ten |

From Table 1.2, you can note that the names of all alkanes contain the suffix '-ane', which indicates that their functional group is a carbon — carbon single bond. Thus, to name an alkane, you should use the appropriate prefix that indicates the number of carbon atoms and the suffix '-ane'. For example, to name the alkane $C_6H_{14}$, use the prefix 'Hex' that indicate the presence of six carbon atoms and add the suffix '-ane' so that the name becomes hexane.

**Activity 1.7**

Practice naming alkanes using first four prefixes mentioned in Table 1.3. In naming alkanes, why are number of carbon atoms used as prefixes? Discuss in groups.

### *Common Names of Alkanes*

Lower members of the alkane homologous series have common names. The prefixes used in the common names are *n*- (*normal*), 'iso-' and 'neo-'. The prefix *n*- is used when all the carbon atoms form a continuous chain.

**Example**

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

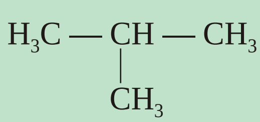
n-pentane

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

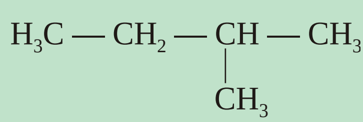
n-hexane

Iso- is used when all of the carbon atoms form a continuous chain, except for the one next to the last carbon.

**Example**



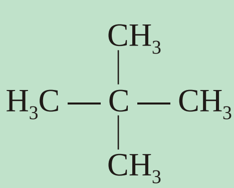
Isobutane



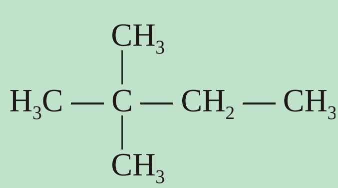
Isopentane

Neo- is used when the central carbon is bonded to four other carbon atoms.

**Example**



Neopentane



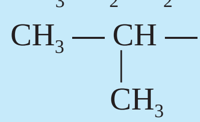
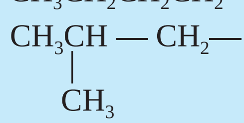
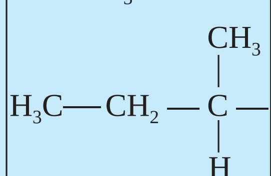
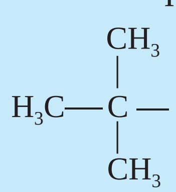
Neohexane

## *IUPAC System of Nomenclature of Alkanes*

It is difficult to have common names for the more branched and complex alkanes. In naming such alkanes, the more systematic, convenient and appropriate one is the International Union of Pure and Applied Chemistry (IUPAC) system. In order to apply this system, it is very important to know the rules to be followed, what alkyl radicals are, and how they are named.

**Alkyl radicals** are obtained by removing one hydrogen atom from the corresponding alkanes. Their general formula is $C_nH_{2n+1}$, where $n$ = 1, 2, 3 . . . . The names of alkyl radicals are derived from the names of the corresponding parent alkanes by changing the suffix -ane to -yl.

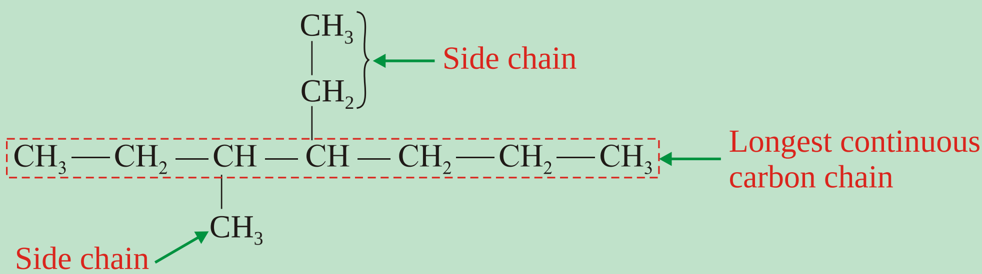
**Table 1.4 Formulas, names and structures of some alkyl groups.**

| Formula of alkane | Formula of alkyl radical | Condensed structure of alkyl radical | Common name of alkyl radical |
|---|---|---|---|
| $CH_4$ | $CH_3-$ | $CH_3-$ | Methyl |
| $C_2H_6$ | $C_2H_5-$ | $CH_3CH_2-$ | Ethyl |
| $C_3H_8$ | $C_3H_7-$ | $CH_3CH_2CH_2-$<br> | *n*-Propyl<br>Isopropyl |
| $C_4H_{10}$ | $C_4H_9-$ | $CH_3CH_2CH_2CH_2-$<br><br><br> | *n*-Butyl<br>Isobutyl<br>sec-Butyl (s-Butyl)<br>tert-Butyl (t-Butyl) |

The system of naming organic compounds is based on the recommendations of IUPAC. The following are the rules established by IUPAC to name branched-chain hydrocarbons.

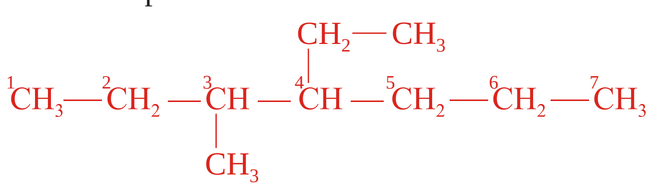
1. Select the longest continuous chain of carbon atoms in the molecule as the *parent structure*. The name of the straight-chain alkane possessing the same number of carbon atoms is used as the name of this longest chain. The groups attached to the parent structure are called side chains or substituents.

## Example 1

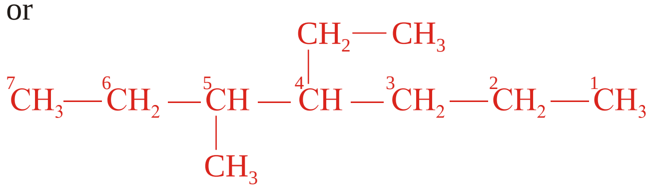



There are seven carbon atoms in the longest chain (*the parent structure*). Therefore, it gets the name "heptane".

2. Assign numbers to the carbon atoms of the longest chain starting from one end to the other so that the carbon atoms to which side chains are attached get the lowest possible number.



or



To check which direction of numbering is correct; add the locants (*numbers assigned to the carbon atoms to which substituents are attached*).

The sum of locants in the first case is $3 + 4 = 7$ and in the second case, $4 + 5 = 9$. So numbering should be done from left to right in this case. Thus, the first option is correct.

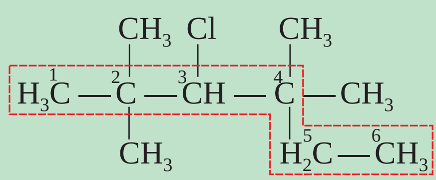
3. Indicate the position of the side chain by using the number assigned to the carbon atom to which it is attached. If the same substituents appear more than once, use the

prefix *di-*, *tri-*, *tetra-* etc. before the name of the substituent to show *two*, *three*, *four,* etc. substituents, respectively.

4. Numbers are separated from each other by commas while they are separated from substituent names by hyphens.

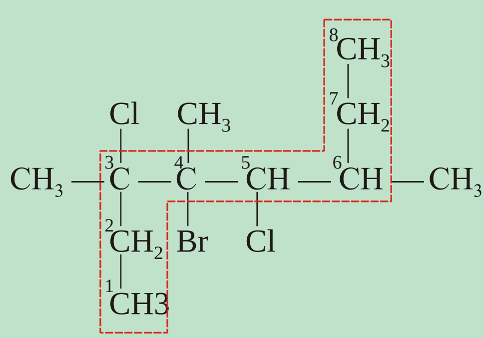
5. Arrange the names of the side chains before the parent name in alphabetical order. The complete name of the alkane given in the above example will then be 4-ethyl-3-methylheptane (substituents in *alphabetical order*).

## Example 2



The longest chain has six carbon atoms and the parent name is hexane. There are two methyl groups at carbon-2 and another two methyl groups on carbon-4 and one chlorine atom at carbon-3. Therefore, the correct name of the compound is 3-chloro-2,2,4,4-tetramethylhexane.

## Example 3

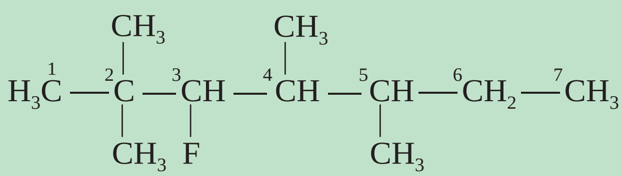


The longest chain contains eight carbon atoms. Hence, the parent name of the given molecule is octane. There are three methyl groups attached to carbon number 3, 4 and 6; one bromine atom is attached to carbon-4 and two chlorine atoms are attached to carbon-3 and carbon-5. Thus, the correct name of the compound is 4-bromo-3,5-dichloro-3,4,6-trimethyloctane.

***Note:***

When F, Cl, Br and I appear as substituents, change the names fluorine, chlorine, bromine and iodine to fluoro, chloro, bromo and iodo, respectively.

## Example 4



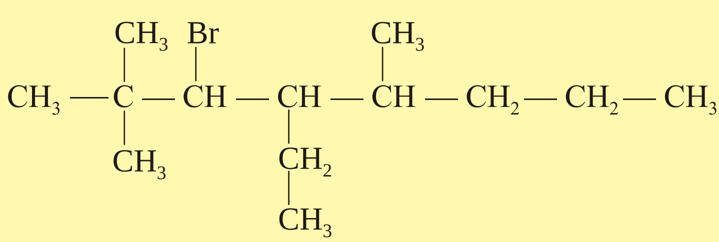
There are seven carbon atoms in the parent structure, so it takes the name heptane. There are two methyl groups at carbon-2 and two methyl groups at carbon-4 and carbon-5 and one fluorine at carbon-3. So the name of the compound is 3-fluoro-2,2,4,5-tetramethyl heptane.

## Activity 1.8

Is there any scientific background for the IUPAC rules or is it just a convention? Why IUPAC recommendations are followed throughout the world. Present your opinion to the class.

## Exercise 1.2

1. Write any three possible structures for octane, $C_8H_{18}$, and give their IUPAC names.
2. Give the IUPAC name of:

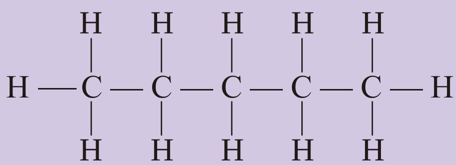


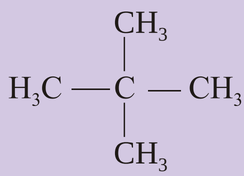
3. Write the structure of 2,2-dimethyl butane.
4. Write the structure of 2,3-dimethylpentane.
5. When F, Cl, Br and I appear as substituents in an organic compound, how are they named?

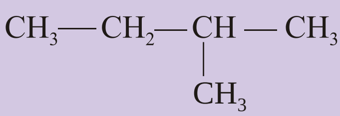
## 1.2.4 Isomerism

### Activity 1.9

1. Write the molecular formula of the following compounds?







2. Do they have the same or different molecular formula? Do they have the same or different physical and chemical properties? Why? What do we call compounds of this type? Discuss the results in your group and present it to the class.

There is only one possible structure for each of the first three alkanes, namely, methane ($CH_4$), ethane ($C_2H_6$) and propane ($C_3H_8$). Those alkanes containing four or more carbon atoms have more than one structure. The existence of two or more chemical compounds with the same molecular formula but different structures is called isomerism.

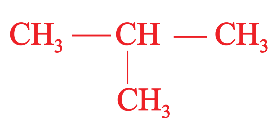
The compounds that have the same molecular formula but different structures are called isomers. Alkanes exhibit a type of structural isomerism called chain or skeletal isomerism. These structures differ in the arrangement of the carbon atoms and hydrogen atoms. To understand what isomers are, consider the isomers of butane ($C_4H_{10}$) and pentane ($C_5H_{12}$).

1. **Isomers of butane ($C_4H_{10}$)**

   Butane has two isomers:

   $CH_3 - CH_2 - CH_2 - CH_3$

   *n*-butane

   Isobutane or 2-meth 1 ro ane

2. **Isomers of pentane ($C_5H_{12}$)**

   Pentane has three isomers.

$$CH_3-CH_2-CH_2-CH_2-CH_3$$

*n*-pentane

$$\begin{array}{ccccc} & & CH_3 & & \\ & & | & & \\ H_3C & - & C & - & CH_3 \\ & & | & & \\ & & CH_3 & & \end{array}$$

Neopentane or 2, 2-dimethylpropane

$$\begin{array}{ccccccc} H_3C & - & CH & - & CH_2 & - & CH_3 \\ & & | & & & & \\ & & CH_3 & & & & \end{array}$$

Isopentane or 2-methylbutane

## Exercise 1.3

1. Which of the following statements are true about isomers:
   a They have the same molecular formula.
   b They are different compounds.
   c They have different boiling and melting points.
   d They have similar chemical properties.
2. Draw all the possible structural isomers for hexane and name them.

## 1.2.5 Preparation of Alkanes

Alkanes are the major constituents of petroleum and natural gas. They are mainly obtained by fractional distillation of petroleum. Alkanes can also be prepared in the laboratory. Some methods of their preparation are as follows:

1. Hydrogenation of alkenes with a metal catalyst.

**General Reaction:** $$\underset{\text{Alkene}}{R-CH=CH_2} + H_2 \xrightarrow[\text{heat}]{Pt} \underset{\text{Alkane}}{R-CH_2-CH_3}$$

### Example

$$\underset{\text{Ethene}}{CH_2=CH_2} + H_2 \xrightarrow[\text{heat}]{Pt} \underset{\text{Ethane}}{CH_3-CH_3}$$

2. **Wűrtz** Synthesis (*reaction*). This method involves the reaction of a halogenated alkane with sodium and the reaction is somewhat exothermic.

**General Reaction:**

$$2R-X \quad + \quad 2Na \longrightarrow R-R \quad + \quad 2NaX$$

Halogenated Alkane — Alkane — Sodium halide

**Example**

$$2CH_3I \quad + \quad 2Na \longrightarrow CH_3-CH_3 \quad + \quad 2NaI$$

Methyl iodide — Ethane — Sodium iodide

This reaction is named as Wűrtz reaction after the French chemist Charles-Adolphe Wűrtz (1817–1884).

3. Heating sodium salt of an organic acid with soda lime (*mixture of sodium hydroxide and calcium oxide*); the reaction brings about the removal of the carboxylate group from the sodium salt of the carboxylic acid. This type of reaction is called decarboxylation.

**General Reaction:**

$$RCOONa \quad + \quad 2NaOH \xrightarrow[\text{heat}]{CaO} R-H \quad + \quad Na_2CO_3(s)$$

Sodium salt of or anic acid — Alkane

**Example**

$$CH_3COONa \quad + \quad 2NaOH \xrightarrow[\text{heat}]{CaO} CH_4(g) \quad + \quad Na_2CO_3(s)$$

Sodium acetate (Sodium ethanoate) — Methane

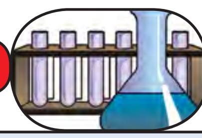
## *Methane*

Methane is the main constituent (*about 90%*) of natural gas. It is obtained during fractional distillation of petroleum. Methane is also formed by the decay and decomposition of animal and plant remains in swampy or marshy lands.

## Activity 1.10

Discuss the following points in groups, and present your ideas to the class.

1. Have you ever walked near a marshy or swampy area? Which characteristic smell do you observe?
2. In most parts of Ethiopia, the walls of houses are constructed from wood and mud. The mud for this purpose is usually prepared by mixing soil, water and hay or straw. After two or three weeks of decay and decomposition, an unusual smell is perceived. What do you think is the cause of this?
3. If Ethiopia introduces the technology of producing biogas to its residents, what benefits will be obtained by the country? What materials can be used to generate biogas? Which compound is the main constituent of biogas?



## Experiment 1.1

### *Laboratory Preparation of Methane*

**Objective:** To prepare methane and study its properties.

**Materials required:** Sodium acetate ($CH_3COONa$) and soda lime ($CaO$, $NaOH$), test tubes, delivery tube, stopper, gas jar and gas jar lid, pneumatic trough, stand, clamp, beehive shelf, Bunsen burner and balance.

***Procedure:***

Arrange the assembly as shown in Figure 1.3. Mix thoroughly 5 g powdered sodium acetate with 10 g of soda lime. Place the mixture in the test tube and heat it. Collect the gas by the downward displacement of water. Collect several jars of the gas.

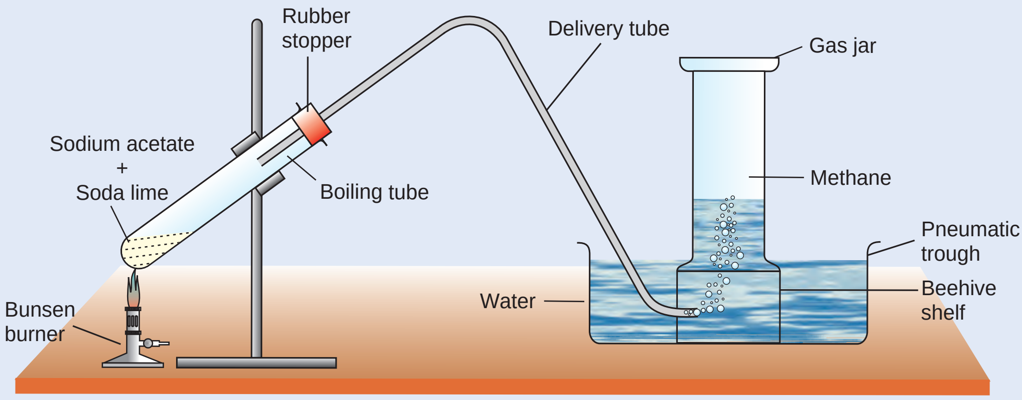



**Figure 1.3 Preparation of methane.**

*Carry out the following activities with the collected gas:*

Insert a burning splint into the jar full of the gas. Observe what happens in the jar. Add $Ca(OH)_2$ solution to the jar and observe. Add a few drops of bromine water to any one of the gas jars filled with methane. Cover the gas jar and shake well.

***Observations and analysis:***

a What is the colour of the gas? Is it soluble in water?

b Is the gas combustible? Write a balanced equation for the change.

c What change did you observe upon addition of $Ca(OH)_2$?

d Is there any change when bromine water is added?

Write a laboratory report on your observation and submit to your teacher.

Methane can be produced in a biogas plant. The biogas plant generates biogas, mainly consisting of methane by anaerobic fermentation of organic materials such as human excreta, animal dung and agricultural residue.

The conversion of organic materials into biogas involves a sequence of reactions and is graphically depicted in Figure 1.4.

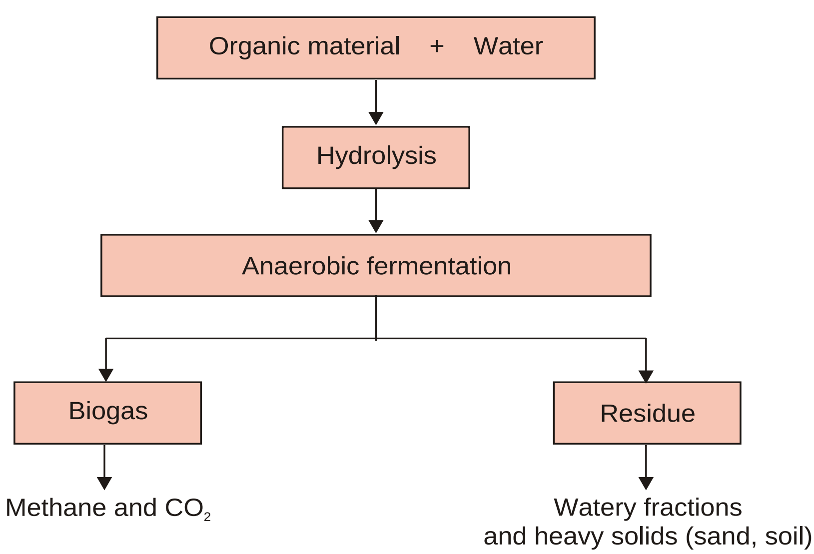



**Figure 1.4 Reactions in the production of biogas.**

The materials that can be used to produce biogas include dung from cattle, pigs, chickens, chopped green plants and plant wastes. The advantages of biogas technology include saving on fuel such as kerosene, wood and charcoal, and decrease in local deforestation. The residue obtained after preparing the biogas can be used as fertilizer.

## Experiment 1.2

### *Production of Methane from Cow Dung*

**Objective:** To prepare biogas from locally available materials.

**Materials required:** Conical flask, cow dung, water, delivery tube with tap and stopper with one hole.

***Procedure:***

1. Mix some cow dung with water and pour it in a conical flask.
2. Fit the conical flask with a stopper in which a delivery tube with a tap is inserted.
3. Cover the conical flask with a cotton wool and place it near a window and leave it there for 3 to 4 days.
4. Check the formation of methane after 4 days. (Bring a lighted splint closer to the outlet of the delivery tube and open the tap). See what happens.

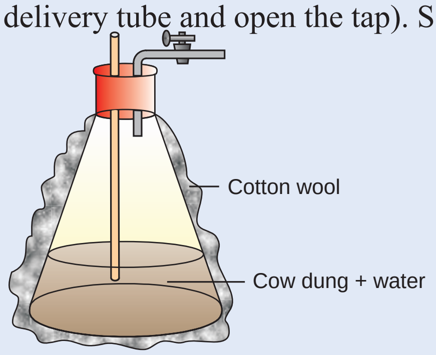



**Figure 1.5 Preparation of methane gas from cow dung.**

***Observations and analysis:***

a What is the importance of covering the conical flask with a cotton wool and placing it near the window?

b What is your observation when you bring a burning splint close to the outlet of the tube?

c What change do you think has occurred in the conical flask that leads to the formation of methane?

Write a laboratory report in group and present to the class.

## PROJECT 1.1

Organize a trip to visit a biogas plant in your Kebele or neighbouring Kebeles if any and write a report on how it operates. Construct a small scale biogas plant in groups.

## 1.2.6 Chemical Properties of Alkanes

### Activity 1.11

Discuss the following points in groups and present your opinions to the class.

1. Which chemical property of alkanes is responsible for generating electricity in diesel power stations or for moving motor vehicles? Name the major product formed when the fuel has been consumed in the diesel power station.
2. The reaction of methane with oxygen produces two different oxides of carbon, $CO_2$ and CO.

   1 What condition determines whether the product of the methane reaction is $CO_2$ or CO?

   b If a domestic heating system is fuelled by methane, what difference does it make if the combustion produces $CO_2$ or CO?

Alkanes are generally not considered to be very reactive organic compounds. The name paraffin for alkanes arose from two Latin words 'parum' meaning *little* and 'affinis' means *affinity*. Thus, paraffin means little affinity. This name was suggested because alkanes are inert towards many reagents like acids, bases, oxidizing and reducing agents. However, they undergo several reactions under suitable conditions.

***The major reactions of alkanes are the following:***

1. **Combustion Reactions:** If alkanes are burned with limited supply of oxygen, they will form water and carbon monoxide and will liberate lesser amounts of heat energy. Alkanes burn in excess oxygen to form carbon dioxide and water, liberating a greater amounts of heat. The general equation for the reaction is:

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \rightarrow nCO_2 + (n+1)\,H_2O + \text{heat}$$

where n is the number of carbon atoms in the alkane molecule.

**Example**

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O + 2299\text{ kJ}$$

The heat energy liberated is used to generate electricity, to move motor vehicles or to cook our food.

## Activity 1.12

1. Write the general equation for the combustion of alkanes in a limited supply of oxygen that forms carbon monoxide, water and energy.
2. Why is a petroleum refinery is built in the open air? Present your opinion to the class.

2. **Substitution Reaction:** This is a reaction that involves the replacement of one atom or a group of atoms by another atom or group of atoms. Halogenation of alkanes is a very good example of substitution reaction. This reaction involves reacting alkanes with chlorine and bromine. The reaction of chlorine and bromine with alkanes proceeds in presence of heat or sunlight. This type of reaction is called photochemical reaction. The reaction of alkanes with chlorine and bromine proceeds in a sequence of steps. For example, let us consider the photochemical reaction of methane with chlorine (*chlorination*):

   *i)* **Chain Initiating Step:** This step involves absorption of energy to generate reactive particles known as free radicals. A free radical is an atom or a group of atoms possessing unpaired electron. A free radical is electrically neutral. A chlorine molecule absorbs light and decomposes into two chlorine atoms:

   $$Cl - Cl \xrightarrow{\text{light}} 2\,Cl\bullet$$

   *ii)* **Chain Propagating Step:** This is a step which consumes a reactive particle (*free radical*) produced in the chain initiation step and generates another free radical.

   $$Cl\bullet + CH_4 \longrightarrow HCl + CH_3\bullet$$

   *iii)* **Chain Terminating Step:** In the chain terminating step reactive particles (*free radicals*) are consumed but not generated.

   $$CH_3\bullet + Cl\bullet \longrightarrow CH_3Cl$$

In this step, 'side reactions' that do not lead to the formation of the desired products often take place.

### Examples

$$Cl\bullet + Cl\bullet \longrightarrow Cl_2$$

$$CH_3\bullet + CH_3\bullet \longrightarrow CH_3 - CH_3$$

Such a detailed step by step description of a chemical reaction is called a reaction mechanism.

Chlorination of methane may produce different products depending on the relative amounts of methane and chlorine.

$$CH_4\,(g) + Cl_2\,(g) \rightarrow CH_3Cl\,(g) + HCl\,(g)$$

*Methyl chloride*

$$CH_3Cl\,(g) + Cl_2\,(g) \rightarrow CH_2Cl_2\,(g) + HCl\,(g)$$

*Methylene chloride* (*dichloromethane*)

$$CH_2Cl_2\,(g) + Cl_2\,(g) \rightarrow CHCl_3\,(g) + HCl$$

*Chloroform* (*trichloromethane*)

$$CHCl_3\,(g) + Cl_2\,(g) \rightarrow CCl_4\,(g) + HCl\,(g)$$

*Carbontetrachloride* (*tetrachloromethane*)

The chlorination of methane is an example of a chain reaction that involves a series of steps.

**Activity 1.13**

Alkanes do not react with chlorine and bromine in the dark but they do so in the presence of sunlight. Discuss the role of sunlight for the reaction in your group and present to the class.

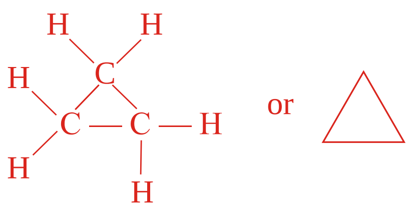
3. **Elimination reaction:** This type of reaction involves the removal of smaller molecules from a compound and leads to the formation of a compound containing a multiple bond (unsaturated compound). It can also involve the removal of hydrogen atoms from adjacent carbon atoms at relatively high temperatures.

$$\underset{\text{Ethane}}{CH_3CH_3} \xrightarrow{600\text{-}800^{\circ}C} \underset{\text{Ethene}}{CH_2{=}CH_2} + H_2$$

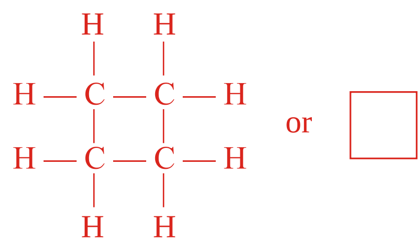
$$\underset{\text{Propane}}{CH_3CH_2{-}CH_3} \xrightarrow{400\text{-}600^{\circ}C} \underset{\text{Ethene}}{CH_2{=}CH_2} + \underset{\text{Methane}}{CH_4}$$

## *Cycloalkanes*

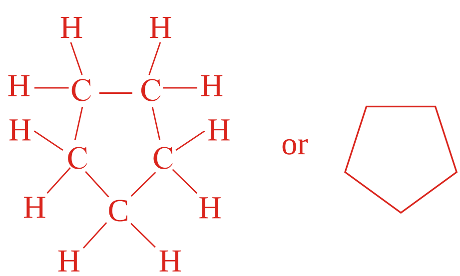
Cycloalkanes are saturated hydrocarbons in which the carbon atoms are linked in such a manner as to form closed chains or ring structures. They are represented by the general formula, $C_nH_{2n}$, where $n \geq 3$. Cycloalkanes are isomeric with open-chain alkenes. Their names are obtained by prefixing "cyclo" to the name of an alkane containing the same number of carbon atoms. The following structures represent some examples of cycloalkanes.



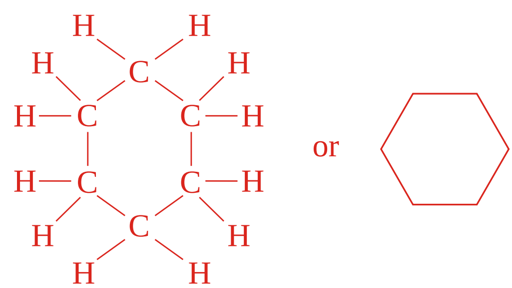

Cylopentane ($C_3H_6$)




Cylobutane ($C_4H_8$)




Cylopentane ($C_5H_{10}$)




Cyclohexane ($C_6H_{12}$)

## *Uses of Alkanes*

Alkanes are primarily used as fuels. They are also used as solvents, raw materials for making alkenes, alcohols, soaps, detergents and plastics.

## Exercise 1.4

1. Write the molecular formulas of alkanes containing the following number of carbon atoms.

   a 5    b 8    c 15

2. Define the terms

   a Homologous series    d Substitution reaction

   b Alkyl radical    e Combustion reaction

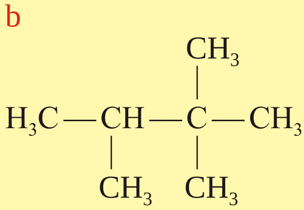
   c Isomerism    f Functional groups

3. Write the balanced equation for the complete combustion of octane.
4. How many chain isomers are there for an alkane that contains 7 carbon atoms?
5. Give IUPAC names to each of the following.

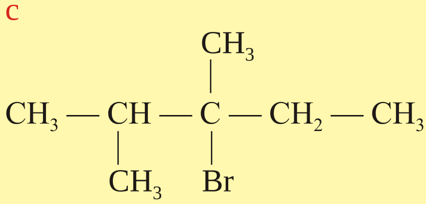
   a

$$\begin{array}{ccccccccc} CH_3 & — & CH & — & CH & — & CH_2 & — & CH_3 \\ & & | & & | & & & & \\ & & Cl & & Cl & & & & \end{array}$$

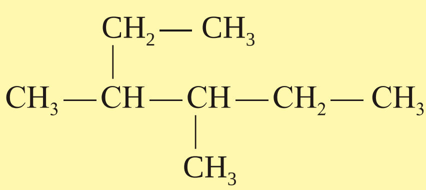
b



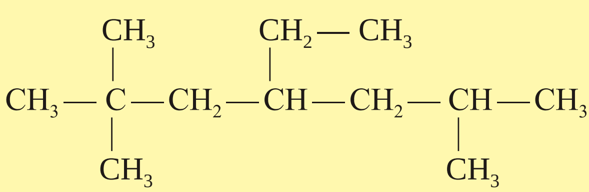
c



d



e



6. Write the structural formulas of the following compounds.
   a 2,3-dimethylbutane
   b 2-bromo-3,3,4,4-tetramethylhexane.
   c 2-chloro-4-ethyl-2,3-dimethylhexane.
7. Complete and balance the following chemical reaction:

$$C_5H_{12} \quad + \quad O_2 \xrightarrow[\text{Combustion}]{\text{Complete}}$$

## 1.3 UNSATURATED HYDROCARBONS

### *Competencies*

***By the end of this section, you will be able to:***

- define unsaturated hydrocarbons;
- define alkenes;
- write the general formula of alkenes;
- write the molecular formula for the first nine members in the homologous series of alkenes;
- define alkynes;
- write the general formula of alkynes;
- write the molecular formula for the first nine members in the homologous series of alkynes;
- write the molecular formulas of alkenes and alkynes from the given number of carbon atoms;
- describe the physical properties of alkenes and alkynes;
- apply IUPAC rules to name straight-and branched-chain alkenes and alkynes;
- write the structural formulas of alkenes and alkynes up to ten carbon atoms;
- write the possible structural isomers for $C_4H_8$ and $C_5H_{10}$;
- define geometric (cis-trans) isomerism;
- give examples of molecules that show geometric isomerism;
- construct models that show cis-trans isomerism;
- describe the general methods for the preparation of alkenes in a laboratory;
- prepare ethylene in the laboratory by the dehydration of ethanol;
- describe the general method for preparation of alkynes in a laboratory;
- prepare acetylene in the laboratory by the reaction of $CaC_2$ with water;
- test for unsaturation of ethylene and ethyne;
- explain chemical properties of alkenes;
- explain chemical properties of alkynes;
- explain the uses of ethylene and acetylene;
- compare and contrast the properties of ethane, ethene and ethyne.

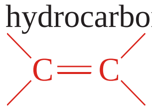
Unsaturated hydrocarbons are those compounds of carbon and hydrogen containing either double or triple bonds. These groups of hydrocarbons include alkenes and alkynes.

## 1.3.1 Alkenes or Olefins

### Activity 1.14

1. The molecular formulas for the first three members of an alkene series are $C_2H_4$, $C_3H_6$ and $C_4H_8$. Derive the general formula for alkenes and compare it with that of alkanes. Is there a difference in the number of hydrogen atoms?
2. By referring to Table 1.5, what relationship do you observe between the number of carbon atoms and melting point, boiling point and density?

   Discuss with your group and present it to the class.

Alkenes are unsaturated hydrocarbons containing a carbon-carbon double bond as their functional group: 

They are also known as olefins. They form a homologous series represented by the general formula $C_nH_{2n}$, where $n$ = 2, 3, 4….

**Table 1.5 The homologous series of alkenes and their physical constants.**

| Molecular | Condensed formula | IUPAC structure | Melting name | Boiling point (°C) | Density point (°C) |
|---|---|---|---|---|---|
| $C_2H_4$ | $CH_2=CH_2$ | Ethene | –169 | –102 | 0.61 g/L |
| $C_3H_6$ | $CH_2=CH-CH_3$ | Propene | –185 | –48 | 0.61 g/L |
| $C_4H_8$ | $CH_2=CH-CH_2-CH_3$ | 1-butene | –130 | –6.5 | 0.63 g/L |
| $C_5H_{10}$ | $CH_2=CH-(CH_2)_2-CH_3$ | 1-pentene | –130.5 | 30 | 0.64 g/L |
| $C_6H_{12}$ | $CH_2=CH-(CH_2)_3-CH_3$ | 1-hexene | –138 | 63 | 0.67 g/L |
| $C_7H_{14}$ | $CH_2=CH-(CH_2)_4-CH_3$ | 1-heptene | –119 | 93 | 0.69 g/L |
| $C_8H_{16}$ | $CH_2=CH-(CH_2)_5-CH_3$ | 1-octene | –104 | 122 | 0.72 g/L |
| $C_9H_{18}$ | $CH_2=CH-(CH_2)_6-CH_3$ | 1-nonene | –95 | 146 | 0.73 g/L |
| $C_{10}H_{20}$ | $CH_2=CH-(CH_2)_7-CH_3$ | 1-decene | –87 | 171 | 0.74 g/L |

## Physical Properties of Alkenes

### Activity 1.15

1. Why some alkenes exist in gaseous and liquid states at room temperature?
2. The melting points, boiling points and densities of alkenes increase with increasing number of carbon atoms; why?
3. Are alkenes coloured compounds? Do they have smell?

Discuss with your group and present it to the class.

At room temperature, alkenes containing two to four carbon atoms are gases. Those containing five to seventeen carbon atoms are liquids, and those containing eighteen or more carbon atoms are solids.

Alkenes are non-polar. Therefore, their molecules are held together by weak inter-molecular forces. Since they are non-polar, they are almost insoluble in polar solvents like water, but soluble in non-polar solvents like ether, benzene, toluene and carbon tetrachloride.

## Nomenclature of Alkenes

Alkenes can have common names as well as IUPAC names. The common names of alkenes are obtained by using the prefixes in Table 1.3 and adding the suffix '-ylene':

**Table 1.6 Common names of few alkenes.**

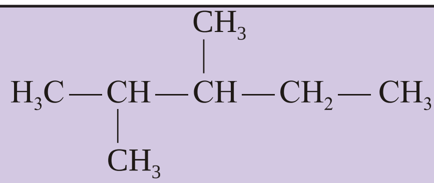
| Formula of Alkene | Condensed Structure | Common Name |
|---|---|---|
| $C_2H_4$ | $CH_2 = CH_2$ | Ethylene |
| $C_3H_6$ | $CH_2 = CH - CH_3$ | Propylene |
| $C_4H_8$ | $CH_2 = CH - CH_2 - CH_3$ | Butylene |
| . | . | . |
| . | . | . |
| . | . | . |

## IUPAC System

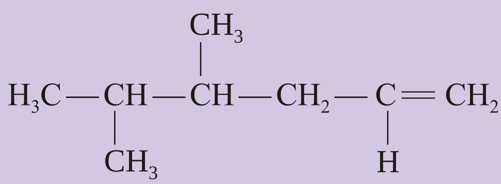
### Activity 1.16

1. What difference do you expect in the IUPAC names of alkanes and alkenes?
2. If you are asked to name the following hydrocarbons:

*i)*



*ii)*



a How many carbon atoms are there in the longest chain of each hydrocarbon?

b From which end do you start numbering the carbon atoms of the longest chain of the hydrocarbon shown in structure i?

c From which end do you start numbering the carbon atoms of the longest chain of the hydrocarbon shown in structure ii?

d Is there any difference in how you assign number to the carbon atoms of the longest chain represented by structures i and ii? If so, why?

e Which name do you think is more appropriate for the longest chain of carbon atoms in structure ii? 5-hexene or 1-hexene or hexane? Discuss these questions in your group and present to the class.

The IUPAC names of alkenes are obtained by using the prefixes listed in Table 1.3 to indicate the number of carbon atoms in the molecule and adding the suffix '-ene'. The suffix '-ene' indicates the presence of a double bond. For example, the alkene having the formula $C_8H_{16}$ is named as octene. The prefix oct- indicates that there are eight carbon atoms in the molecule and '-ene' signifies the presence of a double bond.

In the IUPAC system of naming alkenes, the rules we follow are similar to those rules we follow for naming alkanes with slight modifications. These are:

1. Select the longest continuous chain of carbon atoms in the molecule that includes the double bond as a parent structure. Its name will be the same as the alkene containing the same number of carbon atoms.

## Activity 1.17

Why should the double bond(s) in alkenes be included in the longest continuous chain? Express your opinion to the class.

2. Number the carbon atoms starting from one end to the other in such a way that the carbon atom preceding the double bond takes the lowest possible number and indicate the position of the double bond by this number in the name.

## Example 1

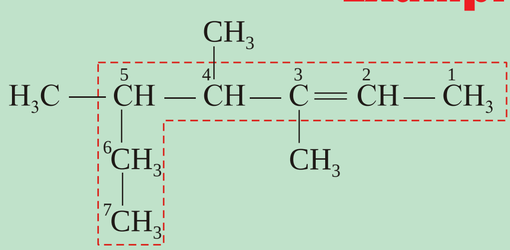
$$\underset{6}{\overset{1}{C}}H_3 - \underset{5}{\overset{2}{C}}H = \underset{4}{\overset{3}{C}}H - \underset{3}{\overset{4}{C}}H_2 - \underset{2}{\overset{5}{C}}H_2 - \underset{1}{\overset{6}{C}}H_3$$

2-hexene or hex-2-ene
but not 4-hexene

$$\underset{5}{\overset{1}{C}}H_2 = \underset{4}{\overset{2}{C}}H - \underset{3}{\overset{3}{C}}H_2 - \underset{2}{\overset{4}{C}}H_2 - \underset{1}{\overset{5}{C}}H_3$$

1-pentene or pent-1-ene
but not 4-pentene

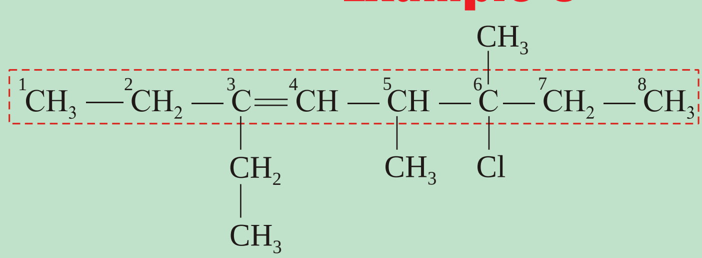
## Example 2



The longest chain contains 7 carbon atoms and a double bond between the 2nd and 3rd carbon atoms. Therefore, it takes the name 2-heptene or hept-2-ene. There are three methyl groups at carbon number 3, 4 and 5. So the complete name of the compound is:

3, 4, 5-trimethyl-2-heptene or 3, 4, 5-trimethyl hept-2-ene

## Example 3



The parent structure contains 8 carbon atoms and a double bond between $3^{rd}$ and $4^{th}$ carbon atoms. Thus, it is named as 3-octene or oct-3-ene. The side chains attached are chlorine at the $6^{th}$, two methyl groups at $5^{th}$ and $6^{th}$ and an ethyl group at carbon number 3. Therefore, the complete name of the compound is:

6-chloro-3-ethyl-5,6-dimethyl-3-octene, or
6-chloro-3-ethyl-5,6-dimethyloct-3-ene.

## Exercise 1.5

1. Write the names of the following compounds, using IUPAC rules:

   a $CH_3CH_2CH_2-C(CH_3)=C(CH_3)-CH_2CH_3$

   b $CH_3CH_2-C(=CHCH_3)-CH_2CH_3$

2. Write the structure of each of the following compounds:

   a 3-methyl-3-heptene    b 3,4-diethyl-1-hexene

## *Isomerism in Alkenes*

Alkenes containing two and three carbon atoms have only one possible structure. Alkenes containing four or more carbon atoms exhibit isomerism. Alkenes show the following three types of isomerism:

1. **Chain isomerism:** This is due to the difference in the arrangement of the carbon atoms in the longest continuous carbon chain.
2. **Position isomerism:** This is due to the difference in the position of the double bond in the carbon chain.

## Example

Consider the following compounds with the same molecular formula ($C_5H_{12}$):

a $H_2C=CH-CH_2-CH_2-CH_3$
1-pentene

b $H_3C-CH=CH-CH_2-CH_3$
2-pentene

c $H_2C=C(CH_3)-CH_2-CH_3$
2-methyl-1-butene

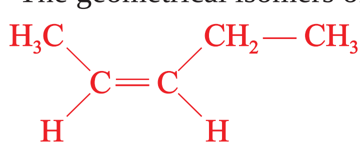
d $H_3C-C(CH_3)=CH-CH_3$
2-methyl-2-butene

e $H_2C=CH-CH(CH_3)-CH_3$
3-methyl-1-butene

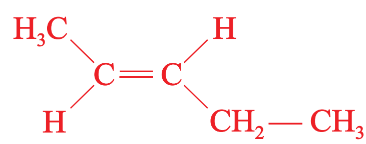
Compounds (a) and (b) represent the position isomers of pentene, (c) and (d) are position isomers of methylbutene, (a), (c) and (e) are the chain isomers, while all these compounds are the isomers of $C_5H_{12}$.

3. **Geometrical isomerism.** This results from the difference in the relative spatial arrangement of atoms or groups about the double bond. This isomerism exists because free rotation about the double bond is not possible. To differentiate geometrical isomers, we use the prefix '*cis*' if two similar groups are on the same side of the double bond and '*trans*' when the two similar groups are on opposite sides of it; '*cis*' means the same and '*trans*' means across.

The geometrical isomers of 2-pentene are:



*cis*-2-pentene or *cis*-pent-2-ene



*trans*-2-pentene or *trans*-pent-2-ene

Alkenes have more isomers than the corresponding alkanes.

## Exercise 1.6

Write three position isomers of hexene.

## PROJECT 1.2

Prepare a model from locally available materials, to show the cis-trans isomers of 2-butene.

## *Preparation of Alkenes*

Do you know the major source of alkenes and the process that leads to their formation? Alkenes are mainly obtained during fractional distillation of petroleum when the process called cracking is carried out.

***In the laboratory, alkenes can be prepared by:***

1. Dehydration of alcohols with concentrated sulphuric acid or alumina ($Al_2O_3$). Dehydration means removal of water.

**General Reaction:**

$$\underset{\text{Alcohol}}{R-CH_2-CH_2-OH} \xrightarrow[\text{heat}]{H_2SO_4} \underset{\text{Alkene}}{R-CH=CH_2} + H_2O$$

**Example**

$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} \xrightarrow[\text{heat}]{H_2SO_4} \underset{\text{Ethene}}{CH_2=CH_2} + H_2O$$

2. Dehydrohalogenation of alkyl halides with a base (KOH). Dehydrohalogenation means removal of hydrogen and a halogen atom.

   Alkyl halides are compounds of an alkyl group and a halogen such as $CH_3Cl$ and $CH_3-CH_2-Br$.

   **General reaction:**

$$\underset{\text{Alkylhalide}}{R-CH_2-CH_2-X} + KOH \longrightarrow \underset{\text{Alkene}}{R-CH=CH_2} + KX + H_2O$$

**Example**

$$\underset{\text{Ethylchloride}}{CH_3-CH_2-Cl} + KOH \longrightarrow \underset{\text{Ethene}}{CH_2=CH_2} + KCl + H_2O$$

**Activity 1.18**

In the above two methods of preparations of alkenes, (a) what difference do you observe between the structures of the major reactant and the product? (b) What is the type of reaction? Share your findings with your group.

**Exercise 1.7**

Write the complete and balanced chemical equations for each of the following reactions:

a $$CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_3 \xrightarrow[\text{heat}]{H_2SO_4}$$

b $$CH_3-\overset{\overset{\displaystyle Br}{|}}{CH}-CH_3 + KOH \longrightarrow$$

## Experiment 1.3

### *Laboratory preparation of Ethene*

**Objective:** To prepare ethene and study some of its properties

**Materials required:** Ethanol, concentrated $H_2SO_4$, water, bromine water, basic $KMnO_4$. Round-bottomed flask, stopper, delivery tube, gas jar, pneumatic trough, thermometer, tripod, Bunsen burner, stand and clamp, beehive shelf and wire gauze.

***Procedure:***

1. Arrange the set-up as shown in Figure 1.6
2. Take ethanol in the flask and add concentrated $H_2SO_4$ through the thistle funnel; heat carefully until the temperature reaches about 170°C. Discard the initially formed gas as it might contain air; collect the ethene gas in three gas jars by downward displacement of water; perform the following activities.
   - a Insert a lighted splint into the jar containing the gas and see what happens.
   - b Add two drops of bromine water to the other gas jar, cover the jar and shake well.

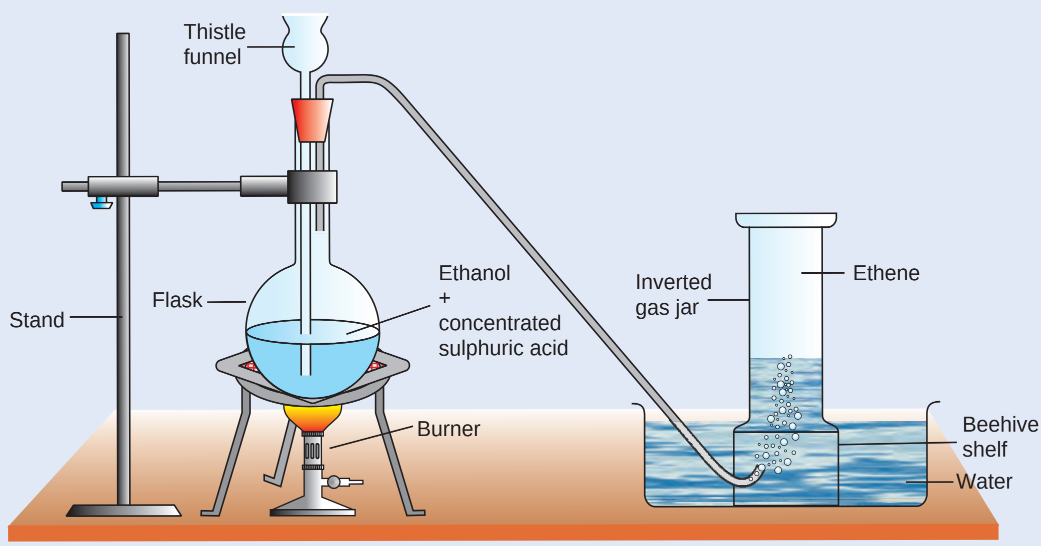



**Figure 1.6 Preparation of Ethene.**

c Add a few drops of alkaline $KMnO_4$ solution to another jar containing the gas and observe what happens.

***Observations and analysis:***

a What is the colour and odour of the gas?

b What is the substance left after combustion of the gas in the jar?

c What change is observed when the gas is shaken with bromine water or alkaline potassium permanganate? Write equations for the reactions?

d Name the dehydrating agent used in the experiment?

e Which method of preparation of an alkene is used in this experiment?

Write a laboratory report about the experiment and submit to your teacher.

## *Chemical properties of Alkenes*

Alkenes are unsaturated hydrocarbons containing double bond (a strong bond and a weak bond) between the two carbon atoms. They are more reactive than alkanes, because the weak bond can be used for further reaction. They undergo several types of reactions.

1. **Combustion reaction.** Alkenes burn in oxygen with a luminous flame to form carbon dioxide and water.

**General reaction:** $$C_nH_{2n} + \left(\frac{3n}{2}\right) O_2 \rightarrow nCO_2 + nH_2O + \text{heat}$$

**Example**

$$C_4H_8(g) + 6O_2(g) \rightarrow 4CO_2(g) + 4H_2O(g) + \text{heat}$$

2. **Addition reaction.** Alkenes undergo mainly addition reactions. The addition occurs at the carbon-carbon double bond.

a **Addition of halogens (halogenation):** When a halogen molecule, $X_2$, (where, $X_2 = Cl_2$ or $Br_2$) is added to alkenes, the product is a dihaloalkane.

**General reaction:**

$$\underset{\text{Alkene}}{R{-}CH{=}CH_2} + \underset{\text{Halogen}}{X_2} \longrightarrow \underset{\text{Dihaloalkane}}{R{-}\underset{X}{\underset{|}{C}H}{-}\underset{X}{\underset{|}{C}H_2}}; \quad (X_2 = Cl_2, Br_2)$$

**Example**

$$\begin{array}{l} CH_3-CH=CH_2 \;+\; Cl_2 \longrightarrow \end{array} \begin{array}{ccccc} CH_3 & - & CH & - & CH_2 \\ | & & | & & \\ Cl & & Cl & & \end{array}$$

Propene 1,2-dichloropropane

If bromine water (bromine in $CCl_4$) is added to alkenes, the reddish brown colour of $Br_2$ in $CCl_4$ will disappear. This is due to the addition of bromine ($Br_2$) across the double bond. So, $Br_2$ in $CCl_4$ is used to detect unsaturation (presence of multiple bond) in a compound.

b **Addition of hydrogen (Hydrogenation):** Addition of hydrogen molecule to alkenes in the presence of a nickel or platinum catalyst yields alkanes.

**General reaction:** $\underset{\text{Alkene}}{R-CH=CH_2} + H_2 \xrightarrow{Pt} \underset{\text{Alkane}}{R-CH_2-CH_3}$

**Example**

$$\underset{\text{Ethene}}{CH_2=CH_2} + H_2 \xrightarrow{Pt} \underset{\text{Ethane}}{CH_3-CH_3}$$

c **Addition of hydrogen halides, HX (hydrohalogenation):** Addition of hydrogen halide (HCl, HBr or HI) to alkenes leads to the formation of alkyl halides. The product of the reaction can be predicted by Markovnikov's rule; which states that "when an alkene reacts with a hydrogen halide to give an alkyl halide, the hydrogen adds to the carbon atom of the double bond that has the greater number of hydrogen atoms, and the halogen to the carbon that has the fewer number of hydrogen atoms".

The same is true when an alkene reacts with water in an addition reaction to form an alcohol.

**General reaction:**

$$\underset{\text{Alkene}}{R-CH=CH_2} \;+\; HX \longrightarrow \underset{\text{Alkyl halide}}{\begin{array}{ccccccc} & & & & H & & \\ & & & & | & & \\ R & - & CH & - & C & - & H \\ & & | & & | & & \\ & & X & & H & & \end{array}}$$

**Example**

$$CH_3-CH=CH_2 + HBr \longrightarrow CH_3-CH(Br)-CH_3$$

Propene 2-bromopropane

*Have you noticed the location where H and Br have formed bonds?*

d **Addition of water (hydration):** When alkenes are hydrated in the presence of an acid catalyst, they produce alcohols, in accordance with Markovnikov's rule.

**General reaction:**

$$R-CH=CH_2 + HOH \xrightarrow{H^+} R-CH(OH)-C(H)(H)-H$$

Alkene Alcohol

**Example**

$$CH_3-CH=CH_2 + HOH \xrightarrow{H^+} CH_3-CH(OH)-CH_3$$

Propene 2-propanol

e **Oxidation of alkenes:** Oxidation of alkenes with cold alkaline potassium permanganate solution ($KMnO_4$) forms diols (compounds containing two hydroxyl groups).

**General reaction:**

$$R-CH=CH_2 \xrightarrow[KMnO_4]{Alkaline} R-CH(HO)-CH_2(OH)$$

Alkene Diol

**Example**

$$CH_2=CH_2 \xrightarrow[KMnO_4]{Alkaline} H_2C(HO)-CH_2(OH)$$

Ethene 1,2-ethanediol

Alkaline $KMnO_4$ solution is also used as a qualitative test for the identification of unsaturation in a compound. The solution is called Baeyer's reagent. In the presence of unsaturated hydrocarbons, the purple colour of alkaline $KMnO_4$ solution fades and a brown precipitate is formed.

f **Polymerization (self-addition) of alkenes:** Polymerization is the union of small molecules called monomers to form a large molecule called a polymer.

**Example**

$$n(CH_2{=}CH_2) \xrightarrow[O_2\ (\text{Catalyst})]{1000\ \text{atm},\ 473\text{K}} (-CH_2-CH_2-)_n$$

Ethene Polyethene

## *Uses of Ethene (Ethylene)*

Ethene is used in the production of ethanol, and polymers such as polyethene, polyvinylchloride (PVC), polystyrene and teflon. It is also used in the production of 1,2-ethanediol, which is used as an antifreeze material; and for the preservation as well as artificial ripening of fruits.

**Activity 1.19**

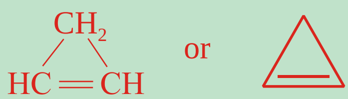
Take some green tomatoes in first basket and put a ripe banana in between them. In a second basket put only green tomatoes (but not a banana). Compare the tomatoes in the two baskets. Do the tomatoes ripen at the same rate in both baskets; if not, why? Share your opinion with your classmates.

## *Cycloalkenes*

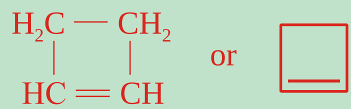
Cycloalkenes are unsaturated cyclic hydrocarbons. The carbon atoms are linked in such a manner as to form a closed chain or a ring structure. They contain a double bond between carbon atoms and are represented by the general formula $C_nH_{2n-2}$, where $n$ should be equal to or greater than 3. They are isomeric with alkynes. They are named by prefixing "cyclo" to the name of alkenes containing the same number of carbon atoms. The given structures show some examples of cycloalkenes.

The IUPAC names for alkynes are obtained by using the prefixes listed in Table 1.3. The suffix '-yne' is added to the prefixes, which indicates the presence of a triple bond between a pair of adjacent carbon atoms. Alkynes are named in the same way as alkenes.

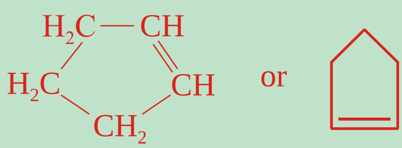
## Examples



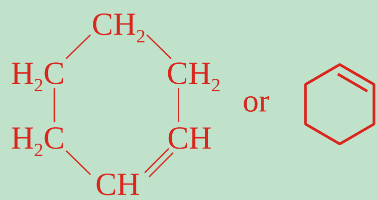
Cyclopropene



Cyclobutene



Cyclopentene



Cyclohexene

## Exercise 1.8

Complete each of the following equations and name the products:

a $CH_3CH_2CH{=}CH_2 + HCl \rightarrow$

b $CH_3CH_2CH{=}CH_2 + Br_2 \rightarrow$

c $CH_3CH_2CH{=}CH_2 + H_2O \xrightarrow{H^+}$

d $CH_3CH_2CH{=}CH_2 \xrightarrow[\text{KMnO}_4]{\text{Alkaline}}$

## 1.3.2 Alkynes

Alkynes are another group of unsaturated hydrocarbons possessing a triple bond as their functional group. The homologous series of alkynes is represented by the general formula $C_nH_{2n-2}$, where $n \geq 2$. The first member of the group is commonly known as acetylene. The homologous series of alkynes is also called acetylene series.

**Table 1.7 Homologous series of alkynes and their physical constants.**

| Formula of Alkyne | Condensed Structure | IUPAC Name | Melting Point (°C) | Boiling Point (°C) |
|---|---|---|---|---|
| $C_2H_2$ | $CH \equiv CH$ | Ethyne | – 82 | –75 |
| $C_3H_4$ | $CH \equiv C - CH_3$ | Propyne | –101.5 | –23 |
| $C_4H_6$ | $CH \equiv C - CH_2$ | 1 - butyne | –122 | 9 |

*Continued next page*

| Formula of Alkyne | Condensed Structure | IUPAC Name | Melting Point (°C) | Boiling Point (°C) |
|---|---|---|---|---|
| $C_5H_8$ | $CH \equiv C-(CH_2)_2-CH_3$ | 1 - pentyne | –98 | 40 |
| $C_6H_{10}$ | $CH \equiv C-(CH_2)_3-CH_3$ | 1 - hexyne | –124 | 72 |
| $C_7H_{12}$ | $CH \equiv C-(CH_2)_4-CH_3$ | 1 - heptyne | –80 | 100 |
| $C_8H_{14}$ | $CH \equiv C-(CH_2)_5-CH_3$ | 1 - octyne | –70 | 126 |
| | | 1- nonyne | –65 | 151 |
| | | 1- decyne | –36 | 182 |

## *Physical Properties of Alkynes*

Alkynes are non-polar compounds whose molecules are held together by weak intermolecular forces. The strength of the intermolecular forces increases with increasing molecular size. The physical properties of alkynes are almost similar to those of alkenes.

### Activity 1.20

1. By looking at the trends for alkynes in **Table 1.7**, write the molecular formula and and the structures of the alkynes containing 9 and 10 carbon atoms.
2. Compare the physical state, melting points and boiling points of alkynes with alkenes and alkanes, as the number of carbon atoms increases. Discuss with your group and present to the class.

## *Nomenclature of Alkynes*

Alkynes are commonly named as a derivative of acetylene.

**Example**

| $CH \equiv CH$ | $CH \equiv C - CH_3$ | $CH \equiv C - CH_2 - CH_3$ |
|---|---|---|
| acetylene | methyl acetylene | ethyl acetylene |

**IUPAC System:** The IUPAC names for alkynes are obtained by using the prefixes listed in Table 1.3. The suffix '-yne' is added to the prefixes. '-yne' indicate the presence of a triple bond between a pair of adjacent carbon atoms. Alkynes are named in the same way as alkenes.

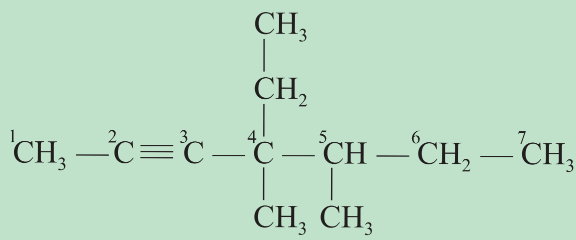
## Example

$^{1}CH \equiv {}^{2}C - {}^{3}CH_2 - {}^{4}CH_2 - {}^{5}CH_3$

1-pentyne or pent-1-yne

$^{1}CH_3 - {}^{2}C \equiv {}^{3}C - {}^{4}CH_2 - {}^{5}CH_3$

2-pentyne or pent-2-yne



4-ethyl-4,5-dimethyl-2-heptyne or 4-ethyl-4,5-dimethyl-hept-2-yne

### *Isomerism in Alkynes*

Alkynes show both chain and position isomerism, but not geometrical isomerism.

## Example

Isomers of butyne, $C_4H_6$

$HC \equiv C - CH_2 - CH_3$

1-butyne or but-1-yne

$H_3C - C \equiv C - CH_3$

2-butyne or but-2-yne

1-Butyne and 2-butyne are position isomers.

## Activity 1.21

Write the structural formulas for pentane, pentene, and pentyne. Why are not these three hydrocarbons considered as isomers? Tell your idea to the class.

## Exercise 1.9

1. Write the possible isomers of 1-pentyne and identify which isomers are:
   a chain isomers? b position isomers?
2. Write the structures of all isomers of 1-pentyne ($C_5H_8$) and name them.
3. How many isomers are possible for 1-hexyne?

## *Preparation of Alkynes*

Alkynes can be prepared by several methods. Some of the general methods of preparation of alkynes are:

1. Dehydrohalogenation of vicinal (adjacent) dihalides with a base NaOH or KOH or $NaNH_2$.

   **General reaction:**

   $$\underset{\text{Vicinal dihalide}}{R-\underset{|\atop X}{CH}-\underset{|\atop X}{CH_2}} + 2NaOH \longrightarrow \underset{\text{Alkyne}}{R-C\equiv CH} + 2NaX + 2H_2O$$

**Example**

$$\underset{\text{1, 2-dibromoethane}}{\underset{|\atop Br}{CH_2}-\underset{|\atop Br}{CH_2}} + 2NaOH \longrightarrow \underset{\text{Ethyne}}{CH\equiv CH} + 2NaBr + 2H_2O$$

2. Alkylation of sodium acetylide (dicarbide) with a primary alkyl halide.

   **General reaction:**

   $$\underset{\text{Sodium carbide}}{HC\equiv C^{-}Na^{+}} + \underset{\text{Primary Alkyl halide}}{R-X} \longrightarrow \underset{\text{Alkyne}}{HC\equiv C-R} + NaX$$

**Example**

$$\underset{\text{Sodium carbide}}{HC\equiv C^{-}Na^{+}} + \underset{\text{Ethyl bromide}}{CH_3CH_2Br} \longrightarrow \underset{\text{But-1-yne (1-butyne)}}{HC\equiv C-CH_2-CH_3} + NaBr$$

**Exercise 1.10**

Write the major product of the following reactions:

a $CH_3-\overset{H}{\underset{Br}{\overset{|}{\underset{|}{C}}}}-\overset{H}{\underset{Br}{\overset{|}{\underset{|}{C}}}}-H + 2KOH \longrightarrow$

b $H-C\equiv C^{-}Na^{+} + CH_3Br \longrightarrow$

## Experiment 1.4

### *Laboratory Preparation of Ethyne*

**Objective:** To prepare ethyne from calcium carbide and water.

**Materials required:** $CaC_2$, $H_2O$, bromine water, round-bottomed flask, separating funnel, delivery tube, trough, beehive shelf and gas jar.

***Procedure:***

1. Arrange the set up as shown in Figure 1.7. Put a layer of sand in a conical flask and place calcium carbide on the sand.
2. Add water drop by drop from the separating funnel onto the calcium carbide. Watch carefully and record your observation. Touch the flask with the tip of your finger.
3. Collect several jars of the gas over water and carry out the following tests:
   a Burn the gas as you did with methane and ethene.
   b Add a few drops of bromine water to another jar filled with ethyne and note the changes.

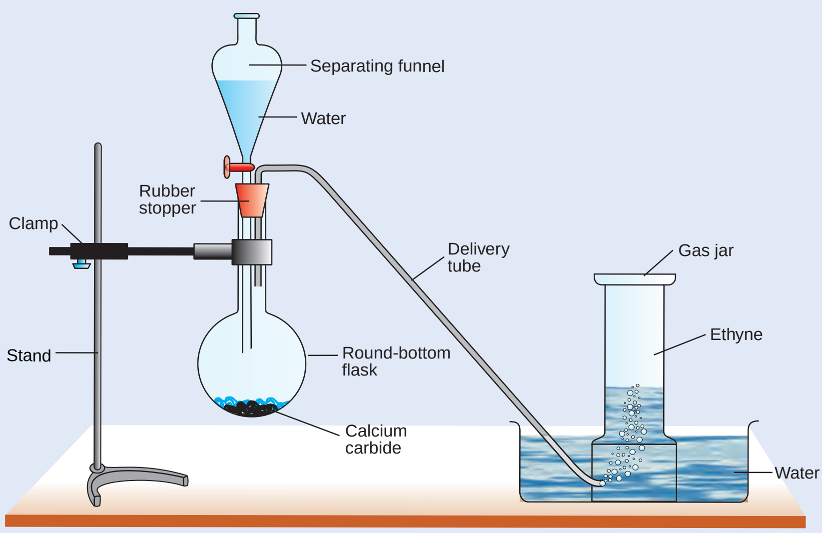



**Figure 1.7 Laboratory Preparation of Ethyne.**

***Observations and analysis:***

a What do you feel when you touch the flask? Is the reaction exothermic or endothermic?

b How do you compare the colour of the flame produced with that of methane and ethene?

Write a complete laboratory report and submit to your teacher.

## *Chemical Properties of Alkynes*

***Alkynes are more reactive than alkanes and alkenes. Why?***

Alkynes are more unsaturated than alkanes and alkenes due to the presence of a carbon-carbon triple bond. They can undergo combustion and addition reactions.

***Some of the common reactions of alkynes are:***

1. **Combustion reaction:** Alkynes burn with a smoky luminous flame, forming $CO_2$ and water. Smoky luminous flames result from the combustion of alkynes due to their high carbon content.

**General reaction:** $C_nH_{2n-2} + \frac{3-1}{2}O_2 \rightarrow nCO_2 + (n-1)H_2O$

**Example**

$$C_3H_4 + 4O_2 \rightarrow 3CO_2 + 2H_2O + \text{heat}$$

2. **Addtion reaction:** Alkynes undergo addition reaction at the carbon-carbon triple bond. Some of the addition reactions of alkynes are the following:

   a **Addition of hydrogen (hydrogenation):** In the presence of nickel or palladium catalyst, alkynes produce alkanes.

   **General relation:**

$$\underset{\text{Alkyne}}{C_nH_{2n-2}} + H_2 \xrightarrow[\text{heat}]{\text{Ni}} \underset{\text{Alkene}}{C_nH_{2n}} \xrightarrow[\text{Ni/heat}]{H_2} \underset{\text{Alkane}}{C_nH_{2n+2}}$$

**Example**

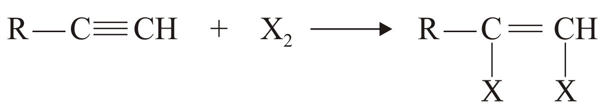
$$\underset{\text{Ethyne}}{CH \equiv CH} + H_2 \xrightarrow[\text{heat}]{\text{Ni}} \underset{\text{Ethene}}{CH_2 = CH_2} \xrightarrow[\text{Ni/heat}]{H_2} \underset{\text{Ethane}}{CH_3 - CH_3}$$

Partial hydrogenation of alkynes in the presence of Lindlar's catalyst gives alkenes. Lindlar's catalyst is powdered palladium partially deactivated with lead acetate.

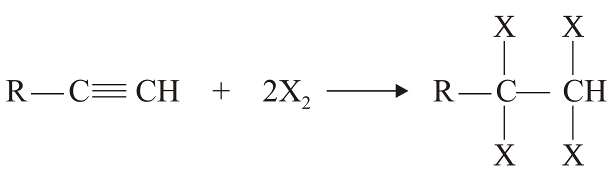
$$\underset{\text{2- butyne}}{CH_3 - C \equiv C - CH_3} + H_2 \xrightarrow[\text{Catalyst}]{\text{Lindlar's}} \underset{\text{2- butene}}{CH_3 - CH = CH - CH_3}$$

b **Addition of halogens:** When molecule of an alkyne reacts with one and two molecules of halogens, it gives a dihaloalkene and a tetrahaloalkane, respectively.

**General Reaction:**

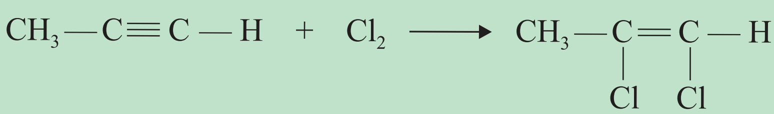


Alkyne Dihaloalkene

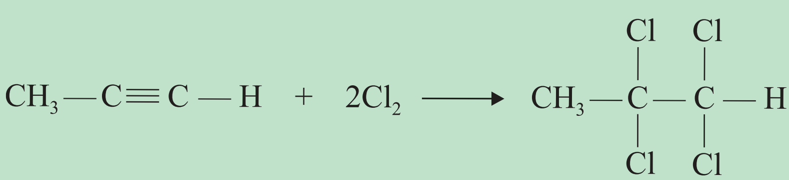


Alkyne Tetrahaloalkane

## Example



Propyne 1,2-dichloropropene



Propyne 1,1,2,2-tetrachloropropane

## Activity 1.22

1. Do you expect alkynes to decolorize bromine water; if so why?
2. Write the balanced chemical equation for the reaction between $C_2H_2$ and $2Br_2$.

c **Addition of Hydrogen Halides:** Alkynes react with hydrogen halides to form a monohaloalkene and a dihaloalkane. The addition reaction occurs according to Markovnikov's rule.

**General Reaction:**

$$R-C\equiv CH \xrightarrow{HX} R-\underset{\substack{|\\X}}{C}=CH_2 \xrightarrow{HX} R-\underset{\substack{|\\X}}{\overset{\substack{X\\|}}{C}}-CH_3$$

Alkyne  Monohaloalkene  Dihaloalkane

## Example

$$CH_3-C\equiv CH \xrightarrow{HBr} CH_3-\underset{\substack{|\\Br}}{C}=CH_2 \xrightarrow{HBr} CH_3-\underset{\substack{|\\Br}}{\overset{\substack{Br\\|}}{C}}-CH_3$$

Propyne  2-Bromopropene  2, 2-Dibromopropane

## Activity 1.23

1. Is Markonikov's rule applied in the reaction between propyne and hydrobromic acid? How?
2. The addition reaction of alkynes proceeds in two steps. Explain what changes occur during the first and the second steps.
3. Compare the reaction products when 1-butyne and 2-butyne react with HBr.

3. **Trimerization of Acetylene:** Acetylene, on prolonged heating at 600 – 700ºC, yields benzene.

$$3\ CH\equiv CH \xrightarrow{600°C\text{-}700°C}$$ 

Acetylene  Benzene

## 1.3.3 Properties and uses of Acetylene or Ethyne

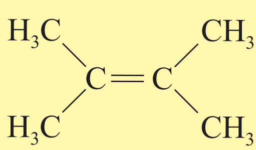
Acetylene is a colourless, sweet-smelling gas in pure form and is insoluble in water. It is usually stored as a solution of acetone in steel cylinders. Combustion of acetylene with oxygen produces an intensely hot flame of about 3000ºC. Thus, a large quantity of acetylene is used as a fuel in oxy-acetylene torches for cutting and welding metals. Acetylene is also used to prepare acrylonitrile which is a starting material for producing polyacrylonitrile, a raw material for textile fibre. It is also used for making vinyl chloride which polymerizes to give polyvinyl chloride (PVC) commonly used for making floor tiles, electrical insulators, shoe soles, water pipes etc. Acetylene is used to produce 1,1,2,2-tetrachloroethane that serves as a solvent for wax, grease, rubber etc.

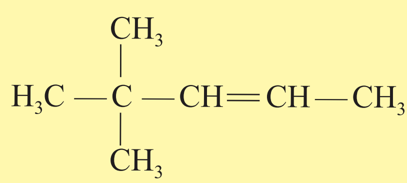
**Table 1.8 Comparison of some properties of Ethane, Ethene and Ethyne**

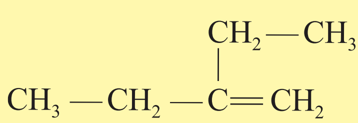
| Property | Ethane | Ethene | Ethyne |
|---|---|---|---|
| Nature of flame | Non-luminous | Luminous | Smoky luminous |
| Effect on colour of $Br_2$ in $CCl_4$ | No effect | Decolorizes | Decolorizes |
| Effect on colour of alkaline $KMnO_4$ | No effect | Decolorizes | Decolorizes |

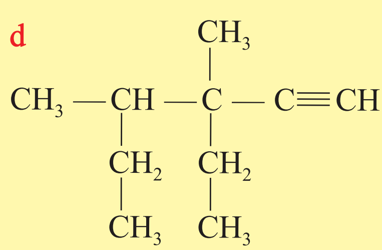
## Exercise 1.11

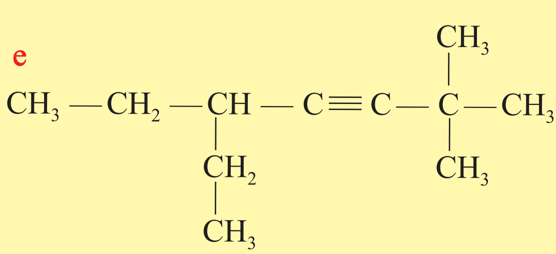
1. What reagents can be used to test for unsaturation of hydrocarbons?
2. Name the following hydrocarbons.

a


b


c


d


e


3. Which of the following hydrocarbons exhibit geometrical isomerism?
   a 1-butene
   b 2-butene
   c 1-pentene
   d 3-hexene
4. Complete the following reactions and name the main products:
   a $CH_3CH_2CH_2Cl + KOH \xrightarrow{\text{Heat}}$
   b $CH_3 - CH = CH - CH_3 + Cl_2 \rightarrow$

c $CH_3 - CH_2 - CH = CH_2 + HCl \rightarrow$

d $CH_3 - CH = CH_2 + H_2O \xrightarrow{H^+}$

e $CaC_2 + 2H_2O \rightarrow$

f $CH_3 - C \equiv CNa + CH_3CH_2Br \rightarrow$

g $CH_3 - C \equiv CH + 2H_2 \xrightarrow[Heat]{Ni}$

h $CH_3 - CH_2 - C \equiv CH + 2HBr \rightarrow$

i $H - C \equiv C - H + Br_2 \rightarrow$

j $H - C \equiv C - H + 2Br_2 \rightarrow$

## 1.4 AROMATIC HYDROCARBONS

### *Competencies*

***At the end of this section you will be able to:***

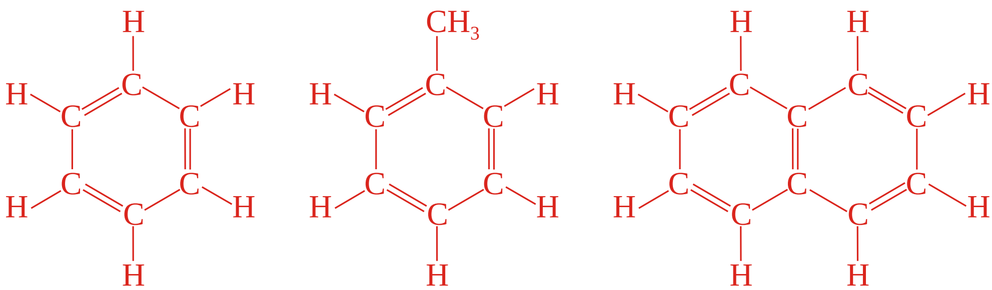
- define the term aromatic hydrocarbons;
- draw the structure of benzene;
- describe the main physical properties of benzene;
- explain the chemical reactions of benzene;
- carry out test-tube reactions with $Br_2$ in $CCl_4$, $KMnO_4$, concentrated $H_2SO_4$.

**Activity 1.24**

Discuss the following in your group and present it to the class:

1. What comes to your mind when you hear the word "benzene"?
2. What is the word "aroma" mean? Which substances have an aroma smell?
3. Are aromatic hydrocarbons unsaturated as alkenes? Why?

The term aromatic is derived from the word 'aroma' meaning pleasant smell, which was originally used to describe naturally occurring compounds with pleasant smells. At present, the term is used without its original significance. Aromatic hydrocarbons are generally obtained from petroleum and coal tar. They are a group of hydrocarbons characterized by the presence of a benzene ring or related structures. Some examples of aromatic hydrocarbon structures are given below:



Benzene    Methyl benzene (Toluene)    Naphthalene

**Figure 1.9 Structures of some Aromatic Hydrocarbons.**

## 1.4.1 Benzene

Benzene is the simplest aromatic hydrocarbon. Its molecular formula is $C_6H_6$. Friedrich A. Kekule, in 1865, suggested that the six carbon atoms of benzene are arranged in the shape of a hexagon. He also suggested a resonance hybrid structure. He represented benzene by the resonance structures (Figure 1.10) in which the two structures shown make equal contribution for the resonance hybrid or actual structure.

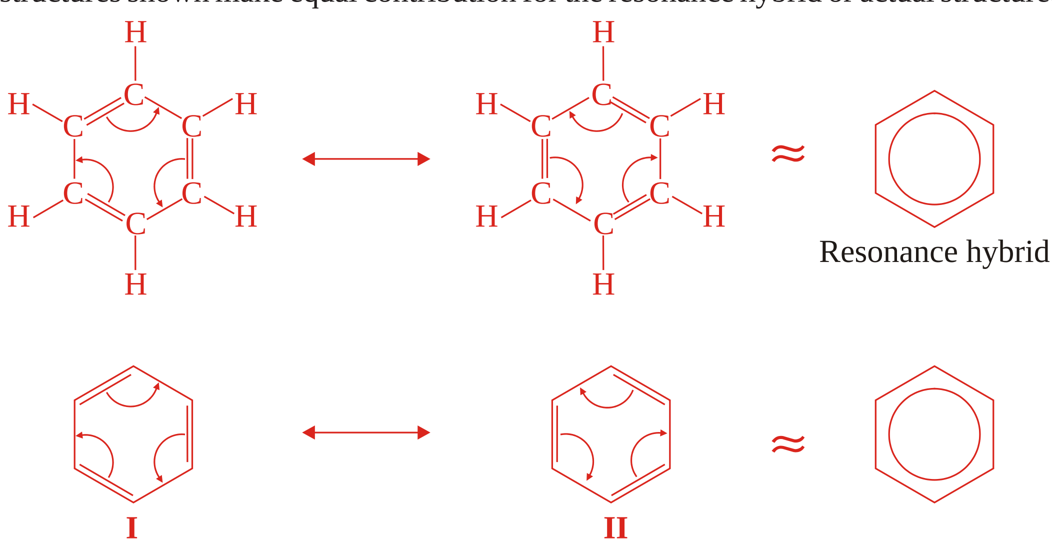
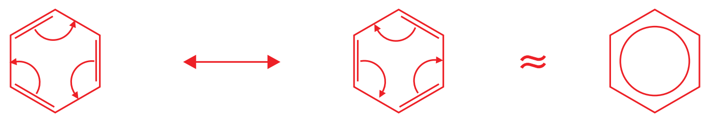



**Figure 1.10 Resonance structures of benzene.**

The bonds in benzene are neither single nor double but have an intermediate character between those of single and double bonds. All the carbon-carbon bonds in the molecule are same in length and nature. Since structure I or II given above are not the true structures of the benzene molecule, the benzene ring is written, in most cases, in its resonance hybrid form as follows:



I  II

The six electrons in the hexagonal ring are delocalized.

From structures I and II in Figure 1.10, one may think that benzene has three double bonds and has the same chemistry as that of alkenes. But, this is not true. Benzene and other aromatic hydrocarbons are not as unsaturated as alkenes because the three double bonds in benzene are delocalized due to resonance. They are more stable than alkenes. They undergo substitution reactions to a far greater extent than addition reactions, which is a different characteristic compared to alkenes.

## *Physical Properties of Benzene*

Benzene is a flammable, colourless, and volatile liquid with a characteristic smell. It is nonpolar and immiscible with water but miscible with non-polar solvents like ether and carbon tetrachloride. It freezes at 5.4°C and boils at 80.4°C. It is a carcinogenic (*cancer causing*) substance. Benzene is a good solvent for fats, gums, rubber etc., and is used in the manufacture of dyes, drugs and explosives.

## *Chemical Properties of Benzene*

Benzene and other aromatic hydrocarbons are more stable than alkenes and alkynes due to the stability of the aromatic ring. It neither decolorizes bromine water ($Br_2$ in $CCl_4$) nor is reactive towards cold potassium permanganate solution. However, benzene undergoes the following reactions:

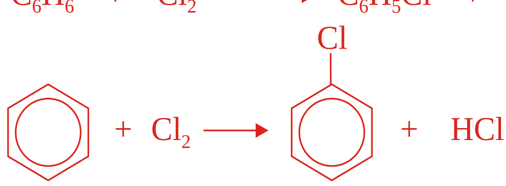
1. **Combustion reaction:** Benzene is highly inflammable. It burns with a smoky luminous flame to form $CO_2$ and $H_2O$.

   $$2C_6H_6 + 15O_2 \rightarrow 12CO_2 + 6H_2O + \text{Heat}$$

2. **Substitution reaction:** The reactions of benzene are chiefly substitution but not addition reactions. In this reaction, hydrogen atom from the benzene ring is replaced by another atom or group.

   a **Halogenation:** Benzene reacts with bromine and chlorine in the presence of iron (III) chloride or aluminium chloride catalyst to form substitution products.

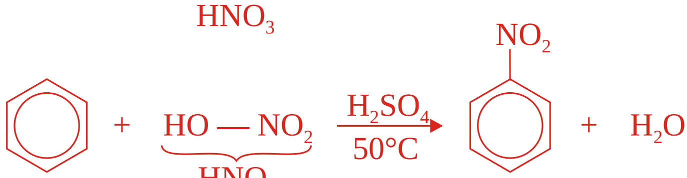
   $$C_6H_6 + Cl_2 \xrightarrow{AlCl_3} C_6H_5Cl + HCl$$




Benzene  Chlorobenzene

b **Nitration:** Concentrated nitric acid mixed with some concentrated sulphuric acid reacts with benzene at moderate temperatures to form nitrobenzene.

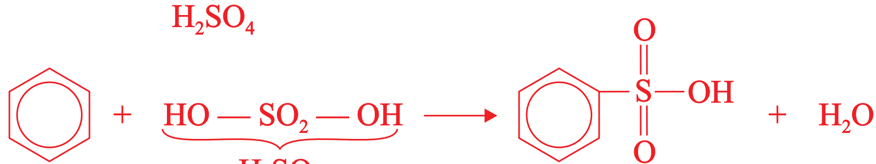
$$C_6H_6 + \underbrace{HO - NO_2}_{HNO_3} \xrightarrow[50°C]{H_2SO_4} C_6H_5NO_2 + H_2O$$



Nitrobenzene

c **Sulphonation:** Benzene reacts with concentrated sulphuric acid, $H_2SO_4$, at room temperature to form benzenesulphonic acid.

$$C_6H_6 + \underbrace{HO - SO_2OH}_{H_2SO_4} \longrightarrow C_6H_5SO_2OH + H_2O$$



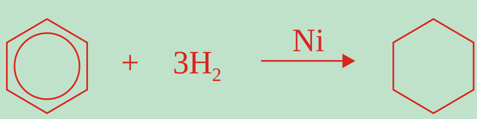
Benzene　　　　Benzenesulphonic acid

3. **Addition reaction:** Benzene undergoes addition reactions under special conditions.

## Example

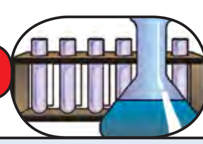
When a mixture of benzene vapour and hydrogen is passed over finely divided nickel catalyst at 200°C, cyclohexane is formed.

$$C_6H_6 + 3H_2 \xrightarrow[200°C]{Ni} C_6H_{12}$$



Cyclohexane

## Experiment 1.5



### *Chemical Reaction of Toluene*

**Objective:** To distinguish aromatic hydrocarbons from other unsaturated hydrocarbons

**Materials required:** Toluene, $Br_2$ in $CCl_4$, $KMnO_4$, concentrated $H_2SO_4$, test tubes, test tube rack, test tube holder, measuring cylinder, Bunsen burner and dropper.

***Procedure:***

1. Take three test tubes and place them in the test tube rack.
2. Add 5 mL of toluene (*methylbenzene*) to each of the three test tubes.
3. Add one or two drops of $Br_2$ in $CCl_4$ in the first test tube and add the same amount of cold $KMnO_4$ solution in the second test tube and observe the changes.
4. Add a few drops of concentrated sulphuric acid to the third test tube and, if necessary, heat it gently, holding it with a test tube holder.

***Observations and analysis:***

In which test tube does a reaction occur?

Write a complete report of your observations and submit to your teacher.

## Exercise 1.12

1. What is an aromatic hydrocarbon?
2. Are aromatic hydrocarbons saturated or unsaturated?
3. What is the name of the simplest aromatic hydrocarbon?
4. Describe the main reactions of benzene?
5. Benzene does not change the colour of $Br_2$ in $CCl_4$ or that of $KMnO_4$ solution; why?
6. How do you prepare the following compounds from benzene?

   a Chlorobenzene    b Nitrobenzene    c Benzene sulphonic acid.

## 1.5 NATURAL SOURCES OF HYDROCARBONS

### *Competencies*

***After completing this subunit, you will be able to:***

- list the major natural sources of hydrocarbons;
- describe natural gas;
- define crude oil;
- explain the fractional distillation of crude oil;
- mention the products of the fractional distillation of crude oil;
- tell the uses of petroleum products;
- describe the composition of coal;
- explain the destructive distillation of coal.

## Activity 1.25

Discuss the following in your group and present it to the class:

1. What do you think is the major component of natural gas?
2. How can petroleum be separated into different fractions?
3. How are natural gas, petroleum and coal formed in nature? Can they be recycled?

## A. Natural Gas

The principal sources of hydrocarbons are natural gas, crude oil and coal. Natural gas is found in association with petroleum or alone. It is found in underground deposits several hundreds or thousands of metres below the earth's surface, where it originated from the decay and decomposition of animal and plant remains millions of years ago. Natural gas mainly contains methane (more than 90%), ethane, propane, butane and small quantities of higher alkanes. Other gases such as, $CO_2$, $N_2$, $O_2$ and $H_2S$, may also be present in natural gas. The composition of natural gas varies, depending on its place of origin. Natural gas is widely used as a fuel. It is advantageous over liquid and solid fuels and also other gases, except $H_2$, due to its very high heat of combustion.

## B. Petroleum

The word petroleum is derived from two Latin words, '*petra*' meaning rock, and '*oleum*' meaning oil. Thus, petroleum means rock oil. The term petroleum refers to a broad range of fossil hydrocarbons that are found as gases, liquids or solids beneath the surface of the earth. The crude oil is generally found along with natural gas in the form of a dark-coloured viscous liquid, which is a complex mixture of hydrocarbons. Its composition varies according to its place of origin. However, crude oil mainly contains alkanes, cycloalkanes and aromatic hydrocarbons. It also contains organic compounds consisting of nitrogen, sulphur and oxygen in small amounts.

### *Refining of Crude Oil*

Crude oil or petroleum is obtained by drilling wells until the oil-bearing region is reached. After the crude oil is brought to the surface of the earth, it must be refined before it can be used.

Crude oil is refined or separated into several components by fractional distillation based on the differences in boiling ranges of its fractions. (Figure 1.11).

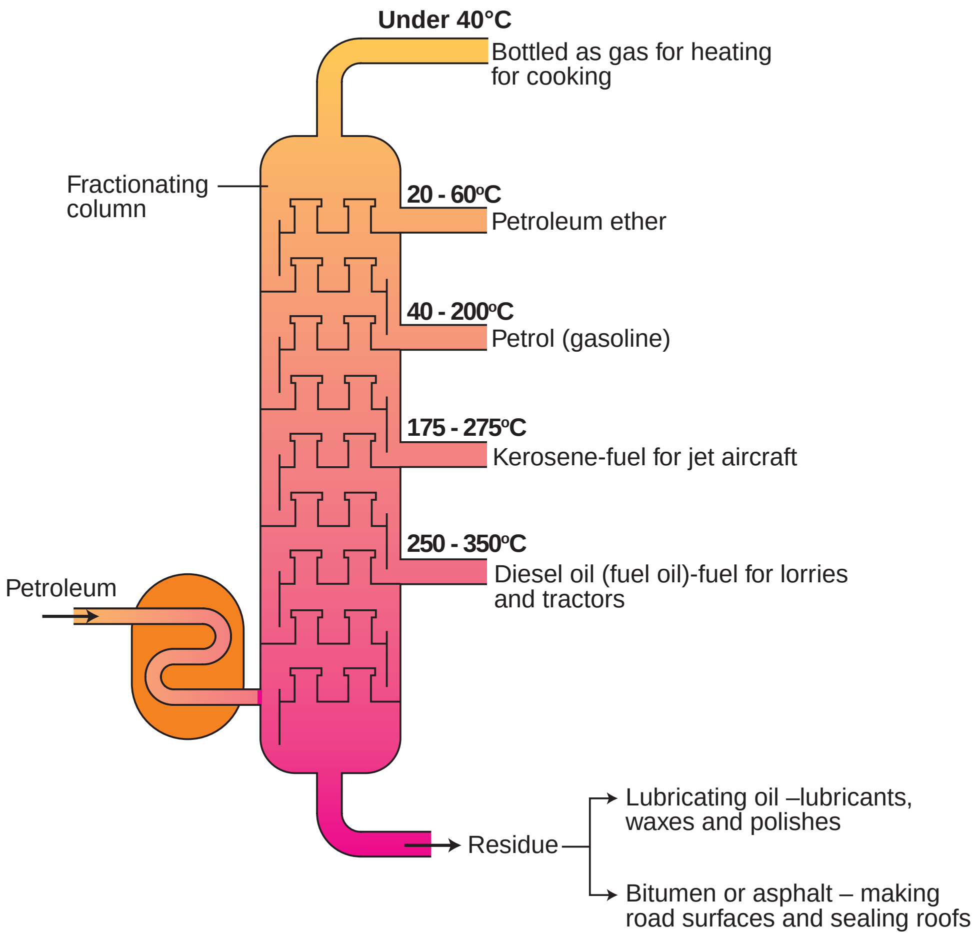



**Figure 1.11 Fractional Distillation of Petroleum.**

The major products (*fractions*) obtained from fractional distillation of petroleum and their uses are given in Table 1.9.

**Table 1.9 Common petroleum products.**

| Fractions | Approximate composition (carbon number) | Boiling point range (°C) | Uses |
|---|---|---|---|
| Gases | $C_1 \rightarrow C_4$ | below 20 | – As fuel in the form of bottled gas. |
| Petroleum ether | $C_5 \rightarrow C_7$ | $20 \rightarrow 60$ | – As solvent, in dry cleaning. |
| Gasoline (petrol) | $C_5 \rightarrow C_{10}$ | $40 \rightarrow 200$ | – Motor fuel for internal combustion engines. |
| Kerosene | $C_{10} \rightarrow C_{16}$ | $175 \rightarrow 275$ | – Jet engine fuel,<br>– household fuel. |

*Continued next page*

| | | | |
|---|---|---|---|
| Fuel oil (diesel oil) | $C_{15} \rightarrow C_{18}$ | $250 \rightarrow 350$ | – Furnace fuel, diesel engine fuel. |
| Lubricating oils<br>Greases<br>Petroleum jelly | $> C_{19}$ | Non-volatile liquids | – Lubrication. |
| Paraffin wax<br>Asphalt (bitumen)<br>Coke | $> C_{20}$ | Non-volatile solids | – Candles, polishes.<br>– Roofing and road construction.<br>– Electrodes, fuel for power stations. |

Most hydrocarbons present in petroleum are long-chain hydrocarbons. However, there is a very high demand for petrol or gasoline, which contains hydrocarbons, composed of five to ten carbon atoms. Therefore, the amount of petrol obtained by fractional distillation of crude oil does not satisfy the demand for it. To satisfy the demand and maximize the output of petrol or gasoline, the process called cracking is carried out during fractional distillation.

*What does cracking mean?* Cracking is the decomposition of large hydrocarbon molecules into smaller ones by the application of heat (*thermal cracking* or *pyrolysis*) or in the presence of catalysts (*catalytic cracking*).

**Example**

$$\underset{\text{Hexadecane}}{C_{16}H_{34}} \xrightarrow{\text{heat}} \underset{\text{Octane}}{C_8H_{18}} + \underset{\text{Octene}}{C_8H_{16}}$$

Hydrogen gas can be added during cracking to saturate the alkenes formed in the process.

## C. Coal

Coal is formed naturally by the decomposition of plant matter over several millions of years. It is not a pure form of carbon. It is an important source of aromatic hydrocarbons. Heating mineral coal in the absence of air, or oxygen is called destructive distillation of coal or coking of coal. When coal is heated in the absence of air it gives volatile products and coke. The volatile products separate into coal gas and a liquid, called coal tar when cooled. Aromatic hydrocarbons and many other substances are isolated from coal tar by fractional distillation.

Coke, which is a solid and relatively pure form of carbon, is used as a fuel in the blast furnace during the extraction of iron. It is also used to produce gaseous fuels, such as water gas (mixture of $H_2$ and CO) and producer gas (mixture of $N_2$ and CO).

## Exercise 1.13

1. What are the major natural sources of hydrocarbons?
2. Which hydrocarbons are the main constituents of petroleum?
3. What is destructive distillation?
4. Describe how we can obtain aromatic hydrocarbons from coal.
5. Which fraction of petroleum is in very high demand?
6. What process should be carried out during fractional distillation of crude oil to maximize the output of petrol or gasoline?
7. Describe the main uses of

   a petroleum ether; b kerosene; c gasoline;

   d diesel oil; e refinery gases.

### *Research and writing*

Consult reference materials in the library and read about products made from hydrocarbons. Make a list of petroleum-related products you use almost daily.

## 1.6 ALCOHOLS

### *Competencies*

***After completing this section, you will be able to:***

- *define alcohols;*
- *tell the functional group of alcohols;*
- *classify alcohols based on the number of hydroxyl groups;*
- *write the general formulas of monohydric alcohols;*
- *write the molecular formulas and the names of the first six members of the monohydric alcohols;*
- *give the IUPAC names for the given alcohols;*
- *classify monohydric alcohols based on the number of alkyl groups attached to the carbon atom carrying the hydroxyl group;*
- *give some examples for primary, secondary and tertiary alcohols;*
- *describe the physical properties of alcohols;*
- *explain general methods of preparation of alcohols;*
- *explain the industrial preparation of ethanol;*
- *perform an experiment to prepare ethanol from sugar;*

- *explain the chemical reactions of alcohols such as oxidation, reaction with active metals, esterification and dehydration;*
- *carry out an activity to show chemical reactions of alcohols with active metals;*
- *write the general structural formula of aldehydes;*
- *write the molecular formulas and names of simple aldehydes;*
- *write the general structural formula of ketones;*
- *write the molecular formulas and names of simple ketones;*
- *write the general structural formula of carboxylic acids;*
- *write the molecular formulas and names of simple carboxylic acids;*
- *write the general structural formula of esters;*
- *write the molecular formulas and names of simple esters.*

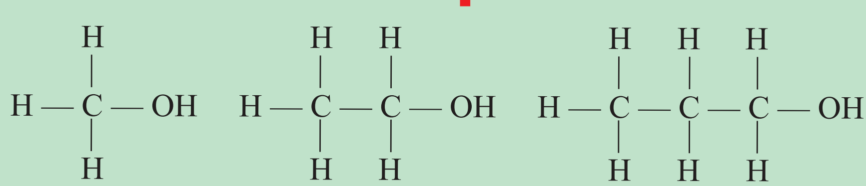
## Activity 1.26

1. List some alcohols you know? Name the alcohol used in alcoholic beverages? What are the uses of alcohols in industry?
2. Ethiopia uses an alcohol blended with benzene to drive cars. What is the name of the alcohol? What is the source of this alcohol?

What do you think when you hear the word "alcohol"? Can you define alcohol? Give a few examples of the uses of alcohols. Most people think of two common alcohols- the substance that intoxicates people and the one used in clinics and hospitals. However, there are many types of alcohol. The only alcohol present in all alcoholic beverages is called ethanol. Other alcohols are used for different purposes.

Alcohols are hydroxyl derivatives of hydrocarbons that can be obtained by replacing one or more hydrogen atom(s) of a hydrocarbon with the hydroxyl (–OH) group. The hydroxyl group is the functional group of alcohols.

### Examples



Methanol Ethanol 1-propanol

## 1.6.1 Classification of Alcohols

Alcohols are generally classified as monohydric, dihydric and trihydric depending on the number of hydroxyl (–OH) groups they contain in their molecular structure.

**Monohydric alcohols** are alcohols containing only one hydroxyl group.

**Examples**

$CH_3—CH_2—OH$ $CH_3—CH_2—CH_2—OH$

Ethanol 1-propanol

**Dihydric alcohols** are those containing two hydroxyl groups per molecule. They are also named **glycols** or **diols**.

**Example**

$$\begin{array}{ccc} H_2C & — & CH_2 \\ | & & | \\ HO & & OH \end{array}$$

Ethane-1,2-diol (Ethylene glycol)

**Trihydric alcohols** are those containing three hydroxyl groups in their molecular structure.

**Polyhydric alcohols** are those containing three or more hydroxyl groups in their molecular structure. Trihydric alcohols are also considered as polyhydric alcohols.

**Example**

$$\begin{array}{ccccc} H_2C & — & CH & — & CH_2 \\ | & & | & & | \\ OH & & OH & & OH \end{array}$$

Propane-1,2,3-triol or Glycerine or glycerol

## 1.6.2 Nomenclature of Alcohols

An alcohol can be considered to be derived from a hydrocarbon by the replacement of at least one H atom by hydroxyl group. Hence, alcohols can be systematically named by using the suffix *-ol* to replace the terminal *-e* in the corresponding alkane name.

**Table 1.10 IUPAC Names, Condensed Structure and Physical Constants of the First Six Monohydric Alcohol.**

| Structure of monohydric alcohol | IUPAC name | Melting point (°C) | Boiling point (°C) | Density g/mL |
|---|---|---|---|---|
| $CH_3OH$ | Methanol | →97 | 64.7 | 0.792 |
| $CH_3CH_2OH$ | Ethanol | →117 | 78.3 | 0.789 |
| $CH_3CH_2CH_2OH$ | 1-Propanol | →126 | 97.2 | 0.804 |
| $CH_3(CH_2)_2CH_2OH$ | 1-Butanol | →90 | 117.7 | 0.810 |
| $CH_3(CH_2)_3CH_2OH$ | 1-Pentanol | →78.5 | 138 | 0.817 |
| $CH_3(CH_2)_4CH_2OH$ | 1-Hexanol | →52 | 156.5 | 0.819 |

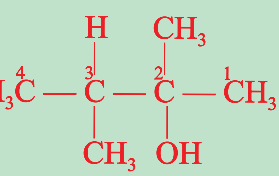
## Activity 1.27

Based on the structural formulas given in table 1.10, derive the general formula for the homologous series of monohydric alcohols. Discuss in your group and present to the class.

In the IUPAC system of nomenclature of alcohols containing side chains or –OH groups in different positions, the longest chain to which the –OH group is attached, is chosen as a parent structure. The chain is then numbered, starting from the end closer to the carbon atom to which the –OH group is bonded. The other rules are similar to the nomenclature of hydrocarbons.

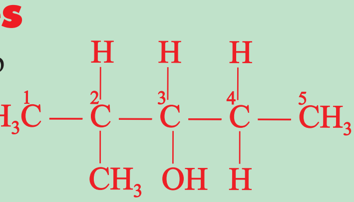
### Examples

a



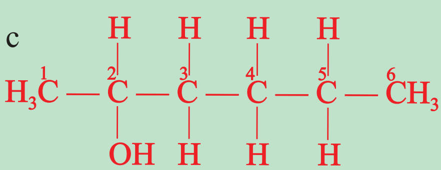
2,3-dimethyl-2-butanol

b



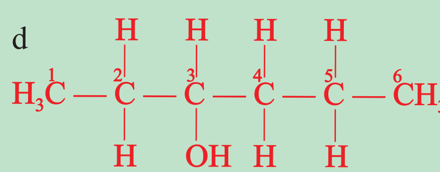
2-methyl-3-pentanol

c



2-hexanol

d

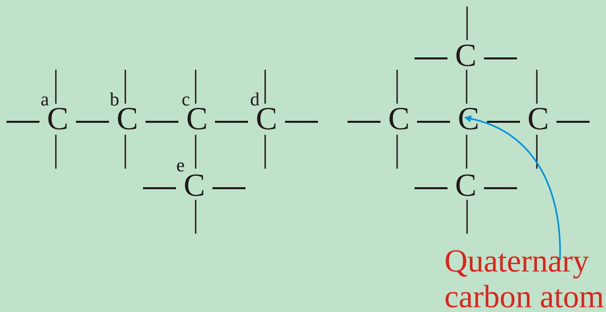


3-hexanol

## *Classification of Monohydric Alcohols*

Carbon atoms can be classified as primary (1°), secondary (2°), tertiary (3°) and quaternary (4°) if they are bonded to one, two, three and four carbon atoms, respectively.

## Example

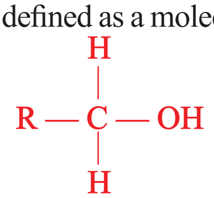



Carbon atoms indicated by letters *a*, *d*, and *e*, are primary. The carbon atom indicated by letter *b* is secondary, and the one indicated by letter *c* is tertiary.

Monohydric alcohols can be classified as primary (1°), secondary (2°) and tertiary (3°) alcohols, depending on the number of hydrocarbon groups (*alkyl groups*) attached to the carbon atom to which the hydroxyl group is bonded.

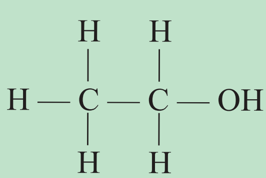
**Primary alcohols** are those alcohols which have the hydroxyl group connected to a primary carbon. They can also be defined as a molecule containing a "–$CH_2OH$" group.

**General Structure:**

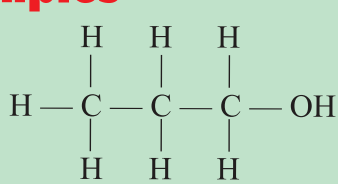


Primary (1°) alcohol

## Examples

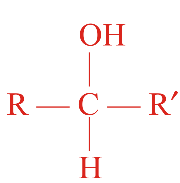


Ethanol

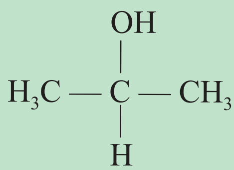


1-propanol

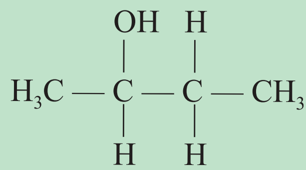
**Secondary alcohols** are those in which the carbon atom bonded to the hydroxyl group is attached to two alkyl groups or contains an –OH group bonded to a secondary carbon atom.

**General structure:**  where R and R′ may be same or different

**Examples**



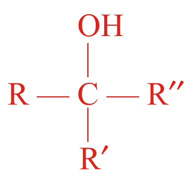
2-propanol



2-butanol

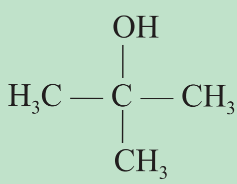
**Tertiary alcohols** are those in which the carbon atom bonded to the hydroxyl group is attached to three hydrocarbon (*alkyl*) groups or contain –OH group attached to a tertiary carbon atom.

**General Structure:**



where R, R′ and R′′ may be same or different

**Example**



2-methyl-2-propanol

**Exercise 1.14**

1. Classify the following alcohols as monohydric, dihydric and trihydric alcohols.
   a 2-propanol b 1,3-propanediol c 1,2,3-butanetriol
2. Classify the following monohydric alcohols as primary, secondary or tertiary alcohols.
   a 1-pentanol b 2-pentanol c 2-methyl-2-butanol

## 1.6.3 Physical Properties of Alcohols

**Activity 1.28**

1. Why do alcohols have higher boiling points than the corresponding hydrocarbons?
2. Why boiling points of dihydric and trihydric alcohols are higher than those of monohydric alcohols of comparable molecular size?

3. Lower alcohols, like methanol and ethanol, are miscible with water in all proportions, while lower hydrocarbons are not so. Explain.
4. Based on the boiling point of water, $H_2O$, and methanol, $CH_3OH$, in which one would you expect to observe a greater degree of hydrogen bonding? Explain. Discuss with your group and present to the class.

The hydroxyl group in an alcohol is polar due to the high electronegativity of oxygen. As a result, there is significant hydrogen bonding in alcohols.

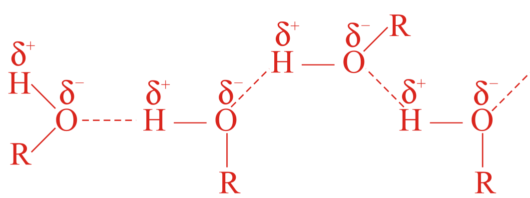


**Figure 1.12 Hydrogen bonding between molecules of an alcohol.**

Due to the hydrogen bonding in alcohols, they have higher melting and boiling points than hydrocarbons of comparable molecular size (*mass*). Hydrogen bonding is also the cause for even lower members to be liquids at room temperature. The boiling point of more branched isomer is lower than that of its isomeric straight-chain alcohol.

**For Example:** $CH_3CH_2CH_2CH_2OH$, boils at 117.7°C, while $H_3C-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH$ boils at 82.5°C. Dihydric and the trihydric alcohols have higher boiling points than monohydric alcohols of similar molecular size (*mass*). Ethane-1,2-diol (*dihydric alcohol, molecular mass* = 62), boils at 197°C, while 1-propanol (*monohydric, molecular mass* = *60*) boils at 97.2°C.

The first three alcohols, methanol, ethanol and 1-propanol are miscible with water in all proportions, while the solubility in water decreases with increasing carbon number. The water solubilities of dihydric and trihydric alcohols are higher than those of monohydric alcohols of similar molecular mass.

## 1.6.4 Preparation of Alcohols

The general laboratory methods of preparation of alcohols are:

a **Acid-catalyzed hydration of alkenes:**

**General Reaction:**

$$R-CH=CH_2 \quad + \quad H_2O \xrightarrow{H^+} R-\begin{array}{c} H \\ | \\ C \\ | \\ OH \end{array}-CH_3$$

Alkene Alcohol

**Example**

$$CH_3-CH_2-CH=CH_2 \quad + \quad H_2O \xrightarrow{H^+} CH_3-CH_2-\begin{array}{c} H \\ | \\ C \\ | \\ OH \end{array}-CH_3$$

1-butene 2-butanol

b **Hydrolysis of alkyl halides:**

Warming alkyl halides with sodium hydroxide forms alcohols.

**General Reaction:**

$$R-CH_2X \quad + \quad NaOH \xrightarrow{heat} R-CH_2OH \quad + \quad NaX$$

Alkyl halide
(where X = Cl, Br or I)

Alcohol

**Example**

$$CH_3-CH_2Cl \quad + \quad NaOH \xrightarrow{heat} CH_3-CH_2OH \quad + \quad NaCl$$

Ethyl chloride Ethanol

c **Hydrolysis of Esters:**

Heating esters with potassium hydroxide produce alcohols.

**General Reaction:**

$$RCOOR' \quad + \quad KOH \xrightarrow{heat} RCOOK \quad + \quad R'OH$$

Ester Alcohol

**Example**

$$CH_3COOCH_2CH_3 \quad + \quad KOH \xrightarrow{heat} CH_3COOK \quad + \quad CH_3CH_2OH$$

Ethyl acetate Ethanol

The two methods, b and c, involve the replacement of other groups by the –OH group. Hence, they are examples of substitution reactions.

## *Ethanol (Ethyl Alcohol)*, $CH_3CH_2OH$

**Activity 1.29**

1 How do the local people in Ethiopia prepare alcoholic beverages like "Tella", "Tej" and "Katikalla"? What raw materials and apparatus do they use?

2 Which industrial method of production of ethanol is more or less similar to the method followed by the local people? Share your ideas with your class.

Ethanol is the second member of the homologous series of monohydric alcohols. It is one of the constituents of all alcoholic beverages. 'Tella', 'Tej', beer, wine, 'Katikalla', ouzo, gin and whisky contain ethanol. There are a number of methods for preparing ethanol using different materials.

### *Industrial preparation of Ethanol*

Ethanol is manufactured industrially by:

1. **Fermentation of carbohydrates such as sugar:** Fermentation is the slow decomposition of carbohydrates such as sucrose, starch and cellulose in the presence of suitable enzyme, that results in the formation of ethanol and carbon dioxide:

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \longrightarrow \underset{\text{Ethanol}}{2CH_3CH_2OH} + 2CO_2$$

Fermentation can produce an alcoholic beverage whose ethanol content is 12 – 15% only. The alcohol kills the yeast and inhibits its activity when the percentage is higher. To produce beverages of higher ethanol content, distillation of the aqueous solution is required.

Most liquor factories in Ethiopia use molasses, a by-product of sugar industries, as a raw material to produce ethanol. In the brewing industry, germinated barley called malt (*in Amharic, 'Bikil'*) is used as the starting material. The whole process taking place in breweries is summarized as follows:

$$\underset{\text{Starch}}{2\,(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}} \xrightarrow[\text{Maltase}]{nH_2O} \underset{\text{Glucose}}{2nC_6H_{12}O_6}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethanol}}{CH_3CH_2OH} + CO_2$$

2. **Catalytic Hydration of Ethene:** Most ethanol is manufactured at present by this method. In this process, ethene is treated with steam at 573 K and 60 atm pressures in the presence of phosphoric acid, $H_3PO_4$, catalyst.

$$\underset{\text{Ethene}}{CH_2{=}CH_2\,(g)} + H_2O\,(g) \xrightarrow[\text{573 k/60 atm}]{H_3PO_4} \underset{\text{Ethanol}}{CH_3CH_2OH\,(g)}$$

## Experiment 1.6

### *Preparation of Ethanol by Fermentation*

**Objective:** To prepare ethanol from sugar.

**Materials required:** Conical flask, glass rod, distillation flask, condenser, spatula, thermometer, watch glass, Bunsen burner, beaker, stopper and delivery tube. Sugar, ammonium phosphate or ammonium sulphate, yeast, $Ca(OH)_2$.

***Procedure:***

1. Take 50 mL of distilled water in a conical flask, add 15 g of sugar to it and stir. Add about 1 gram of yeast and a small amount of ammonium phosphate or ammonium sulphate to the solution. Arrange the set up, as shown below, and let the flask stand for three days at a warm place.

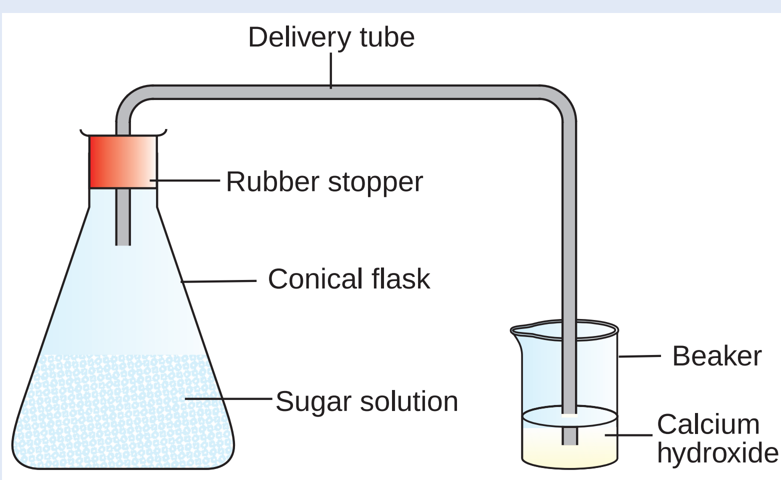



**Figure 1.13 The Fermentation of Sugar.**

***Observations and analysis:***

a What is the purpose of adding yeast to the solution?

b Why do we add ammonium phosphate or ammonium sulphate to the sugar solution?

c What happened to the calcium hydroxide solution at the end of the first or second day? Which gas is produced?

d What is the smell of the solution in the flask after three days?

e What has happened in the flask containing the sugar solution as it stood for three days?

2. After three days, filter the solution, and arrange the set up as in Figure 1.14. Pour 20 mL of the filtrate in a distilling flask, heat the solution, and collect the liquid in a receiver.

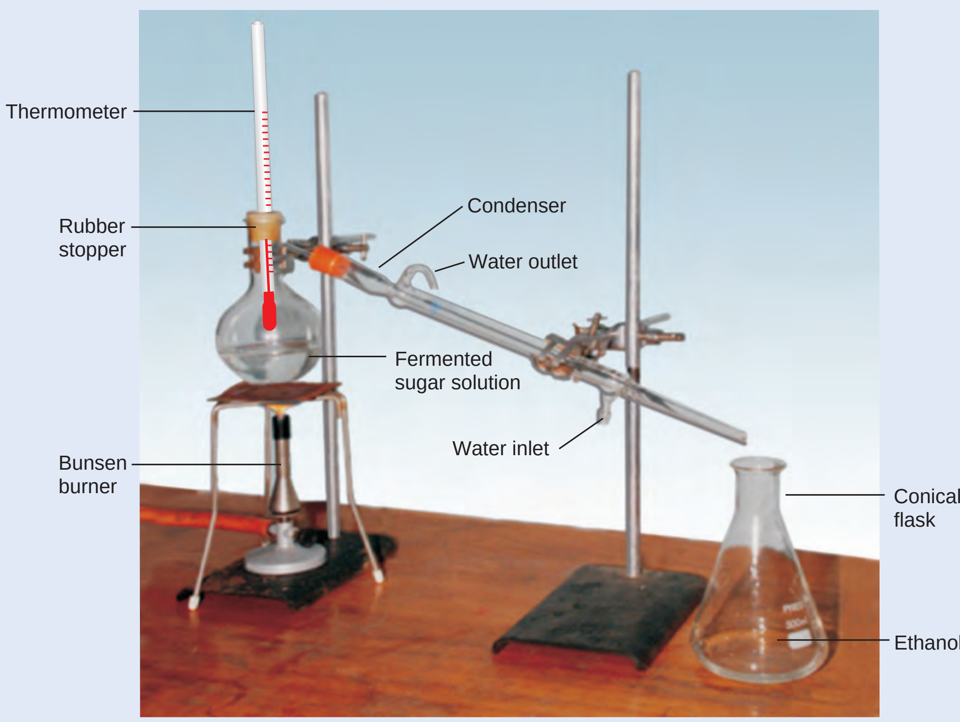



**Figure 1.14 Separation of ethanol by distillation.**

***Points to observe:***

a Observe the colour and identify the smell of the distillate.

b Pour a small amount of the distillate on a watch glass, strike a match and bring the flame close to the distillate. Does it catch fire?

Write complete laboratory report on this experiment and submit to your teacher.

### *Properties and Uses of Ethanol*

Ethanol is a colourless liquid with a pleasant smell and a burning taste. It boils at 78.3°C and freezes at –117°C. It is inflammable and burns with a blue flame. It is miscible with water in all proportions, non-poisonous and has an intoxicating effect. It is a hypnotic (*sleep producer*).

Ethanol is a constituent of all alcoholic beverages. It is a good solvent for many organic compounds that are insoluble in water, such as paints, dyes, perfumes etc. It is also used as a fuel for cars and spirit lamps, and to make denatured alcohol which is a mixture of ethanol and other poisonous substance that has been added to make the alcohol unfit for drinking. For example, methylated spirit is a mixture of 95% ethanol and 5% methanol.

- Currently, Ethiopia uses 5% ethanol with 95% benzene as fuel for cars.

## 1.6.5 Chemical Properties of Alcohols

**Activity 1.30**

Why alcoholic beverages such as "Tela", "Tej", beer and wine turn sour if they are not properly stored? Which reaction of alcohols is responsible for this phenomenon? Write a chemical equation to support your answer. Discuss with your group and present it to the class.

What types of reactions do alcohols undergo? Alcohols contain a hydrocarbon group and a functional group (–OH). Which part of alcohols is responsible for most of their chemical reactions?

Reactions of alcohols may involve the cleavage of the oxygen hydrogen bond (—O—H) or the carbon-oxygen bond (—C—O).

**The reactions of alcohols involving the –O–H bond cleavage are:**

a Alcohols react with strongly electropositive metals like Na, K and Ca to form alkoxides and liberating $H_2$ gas.

**General reaction:**

$$\underset{\text{Alcohol}}{2R-CH_2-O-H} + 2Na \longrightarrow \underset{\text{Sodium ethoxide}}{2R-CH_2-O^-Na^+} + H_2$$

**Example**

$$\underset{\text{Ethanol}}{2CH_3-CH_2-O-H} + 2Na \longrightarrow \underset{\text{Sodium ethoxide}}{2CH_3CH_2-O^-Na^+} + H_2$$

## Experiment 1.7

### *Reactions of Alcohols with Active Metals*

**Objective:** To observe the reaction of alcohols with sodium and magnesium.

**Materials required:** Ethanol, sodium and magnesium metal. Test tubes, test tube holder, test tube rack, measuring cylinder, Bunsen burner, scissors or knife.

***Procedure:***

Take two test tubes and add 2-5 mL of ethanol to each of the test tubes. Cut a very small piece of sodium with a knife and drop it into the first test tube. Take magnesium ribbon and drop it in the second test tube.

***Observations and analysis:***

1. What do you observe:
   a in the 1st test tube? b in the 2nd test tube?
2. Is there an evolution of gas? What do you think this gas is?
3. If no reaction occurs in any of the test tubes, heat the mixture gently using a Bunsen burner and write your observation.
4. Which bond of the alcohol is broken in the reaction?
5. Write a general reaction for such reactions?
6. What type of metals react in this manner?

b **Oxidation of alcohols:** The oxidation products of alcohols depend on the type of alcohol and the nature of oxidizing agents. Oxidation of alcohols is a very important method for the production of other oxygen-containing compounds of hydrocarbons, such as aldehydes, ketones and carboxylic acids.

*i*) Oxidation of primary alcohols in the presence of mild oxidizing agents yields aldehydes.

**General reaction:**

$$\underset{\text{Primary alcohol}}{R-CH_2OH} \xrightarrow[360^\circ C]{Cu} \underset{\text{Aldehyde}}{RCHO}$$

## Example

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[360^\circ C]{Cu} \underset{\text{Ethanal}}{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-H}$$

Strong oxidizing agents, such as acidified $KMnO_4$ or $K_2Cr_2O_7$ and $CrO_3$ in $H_2SO_4$, oxidize primary alcohol first to aldehydes and then to carboxylic acids. It is difficult to stop the reaction at the aldehyde stage.

$$\underset{\text{Primary alcohol}}{R-CH_2OH} \xrightarrow{H^+/KMnO_4} \underset{\text{Aldehyde}}{RCHO} \xrightarrow{H^+/KMnO_4} \underset{\text{Carboxylic acid}}{R-COOH}$$

**Example**

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{H^+/KMnO_4} \underset{\text{Ethanal}}{CH_3CHO} \xrightarrow{H^+/KMnO_4} \underset{\text{Ethanoic acid}}{CH_3COOH}$$

Note that aldehydes are represented by the general structural formula $R-\overset{\overset{\large O}{\|}}{C}-H$ or RCHO, where R is an alkyl group. In the case of methanal R = H. For naming aldehydes, use the suffix *-al* to replace the terminal *-e* in the corresponding alkane name. The suffix "-al" indicates the functional group –CHO. The names and condensed structures of the first six aldehydes are given in Table 1.11.

**Table 1.11 Condensed structures and IUPAC names of some aldehydes.**

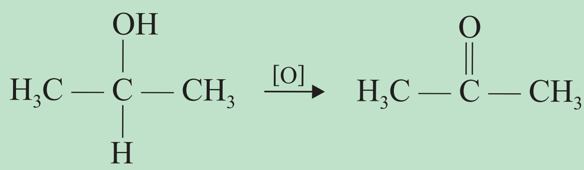
| Molecular formula of aldehyde | Structure of aldehyde | IUPAC name |
|---|---|---|
| $CH_2O$ | HCHO | Methanal |
| $C_2H_4O$ | $CH_3CHO$ | Ethanal |
| $C_3H_6O$ | $CH_3CH_2CHO$ | Propanal |
| $C_4H_8O$ | $CH_3(CH_2)_2CHO$ | Butanal |
| $C_5H_{10}O$ | $CH_3(CH_2)_3CHO$ | Pentanal |
| $C_6H_{12}O$ | $CH_3(CH_2)_4CHO$ | Hexanal |

*ii)* Oxidation of secondary alcohols yields ketones.

**General reaction:**

$$\underset{\text{Secondary alcohol}}{R-\overset{\overset{\large OH}{|}}{\underset{\underset{\large H}{|}}{C}}-R'} \xrightarrow{[O]} \underset{\text{Ketone}}{R-\overset{\overset{\large O}{\|}}{C}-R'}$$

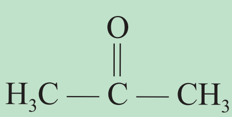
**Example**



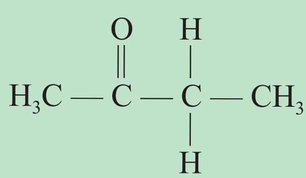
2-propanol Propanone

The general structural formula of ketones is: $R-\overset{\overset{\displaystyle O}{\|}}{C}-R'$ or RCOR' where R and R' may be same or different. The IUPAC names of ketones are obtained by using the suffix *-one* to replace the terminal *-e* in the corresponding alkane name. The suffix '*-one*' indicates the functional group. Unlike aldehydes, the position of the functional group must be indicated in the name of higher ketones. To do so, the longest chain containing the functional group is chosen as a parent structure and then the carbon atoms of the chain are numbered starting from the end closer to the carbonyl group.

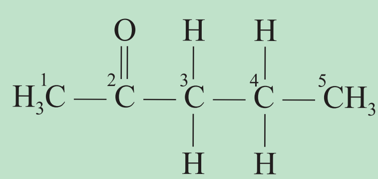
**Examples**



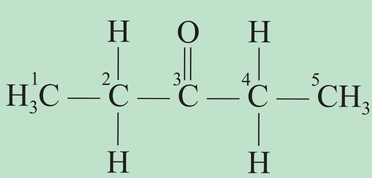
Propanone



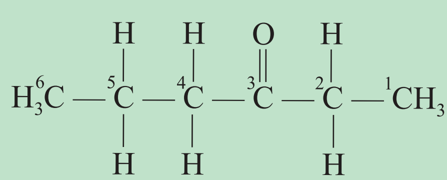
Butanone



2-pentanone or pent-2-one



3-pentanone or pent-3-one



3-hexanone or hexan-3-one

*iii)* Tertiary alcohols and ketones are generally resistant to oxidation. However, they can undergo oxidation under drastic conditions to form a mixture of carboxylic acids.

## Examples

$$\begin{array}{c} CH_3 \\ | \\ H_3C - C - OH \\ | \\ CH_3 \end{array} \xrightarrow{[O]} H_3CCOOH \quad + \quad 2HCOOH$$

3°alcohol — Ethanoic acid — Methanoic acid

$$\begin{array}{c} O \\ \| \\ H_3C - C - CH_3 \end{array} \xrightarrow{[O]} CH_3COOH \quad + \quad HCOOH$$

Propanone (ketone) — Ethanoic acid — Methanoic acid

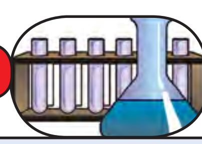
The general structural formula of carboxylic acids is $\left[\begin{array}{c} O \\ \| \\ R - C - OH \end{array}\right]$ or simply R– COOH where R – is an alkyl group or hydrogen in case of the first member of the carboxylic acid homologous series. The IUPAC names of carboxylic acids are derived by replacing the final *-e* of the corresponding alkane with *-oic acid*. The suffix '-oic acid' representing the functional group –COOH. The molecular formulas, condensed structure and IUPAC names of the first six carboxylic acids are shown in the Table 1.12.

**Table 1.12 IUPAC names, formulas and condensed structure of some carboxylic acids.**

| Formula of carboxylic acid | Condensed structure | IUPAC name of the acid |
|---|---|---|
| HCOOH | HCOOH | Methanoic acid |
| $CH_3COOH$ | $CH_3COOH$ | Ethanoic acid |
| $C_2H_5COOH$ | $CH_3CH_2COOH$ | Propanoic acid |
| $C_3H_7COOH$ | $CH_3 \to (CH_2)_2$ COOH | Butanoic acid |
| $C_4H_9COOH$ | $CH_3 \to (CH_2)_3 \to$ COOH | Pentanoic acid |
| $C_5H_{11}COOH$ | $CH_3 \to (CH_2)_4 \to$ COOH | Hexanoic acid |

c  Esterification: Carboxylic acids react with alcohols to form esters. This reaction is known as esterification.

## Experiment 1.8



### *The reaction of alcohols and organic acids*

**Objective:** To investigate the reaction of ethanol and ethanoic acid.

**Material required:** Ethanol, ethanoic acid, concentrated sulphuric acid, test tube, test tube holder, Bunsen burner, beaker, water and glass rod.

***Procedure:***

1. Pour 2 mL of ethanol and 4 mL of acetic acid in a test tube. Add a few drops of concentrated suphuric acid to the mixture of the alcohol and acid.
2. Hold the test tube containing the mixture with a test tube holder and heat it gently from three to five minutes. Allow the contents to cool, add it to a beaker half-filled with water. Stir the mixture and smell the product.

***Observations and analysis:***

1. What smell did you recognize? What do you think is the origin of this smell?
2. Write a balanced chemical equation to show what has happened on heating the mixture of ethanol and ethanioic acid?
3. What is the purpose of adding few drops of concentrated sulphuric acid to the mixture of the alcohol and acid ?
   Write a laboratory report in groups and present to the class.

**General reaction:**

$$\mathrm{R-\overset{\displaystyle O}{\overset{\|}{C}}-OH + H O-R' \longrightarrow R-\overset{\displaystyle O}{\overset{\|}{C}}-OR' + H_2O}$$

Carboxylic Acid    Alcohol    Ester

**Example**

$$\mathrm{H_3C-\overset{\displaystyle O}{\overset{\|}{C}}-OH + HO-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-CH_3 \longrightarrow H_3C-\overset{\displaystyle O}{\overset{\|}{C}}-OCH_2CH_3 + H_2O}$$

Ethanoic acid    Ethanol    Ethyl ethanoate

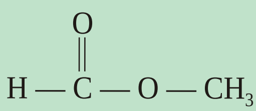
The general structural formula of esters is: $\mathrm{R-\overset{\displaystyle O}{\overset{\|}{C}}-OR'}$ or simply RCOOR′ where R and R′ are alkyl groups. In some cases, R can be a hydrogen atom. In the nomenclature of esters they are considered as derivatives of both carboxylic acids and alcohols.

$$\boxed{\mathrm{R-\overset{\displaystyle O}{\overset{\|}{C}}-}}\boxed{\mathrm{O-R}}$$

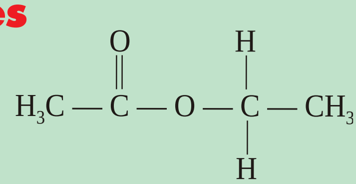
Acid portion    Alcohol portion

Esters are named first by naming the alkyl group derived from the alcohol followed by the name of the acid changing the suffix "-*ic* acid" to "-*ate*".

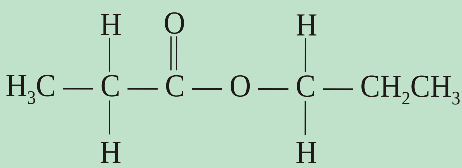
## Examples



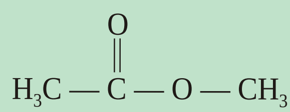
Methyl methanoate



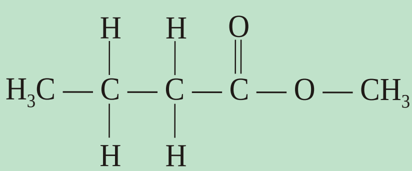
Ethyl ethanoate



*n*-propyl propanoate



Methyl ethanoate

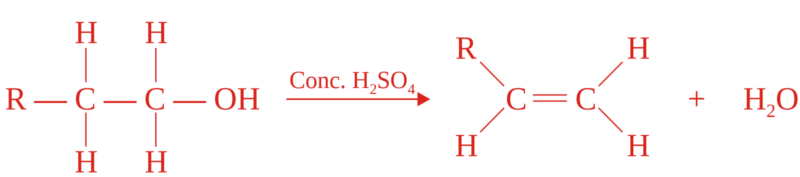


Methyl butanoate

The reactions of alcohols involving the – C – O bond cleavage include:

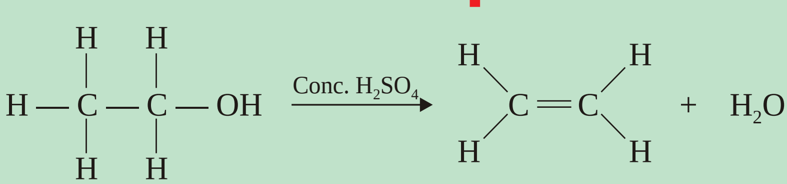
a **Dehydration of alcohols:** Heating alcohols in the presence of dehydrating agents, like concentrated $H_2SO_4$, yield alkenes.

**General reaction:**



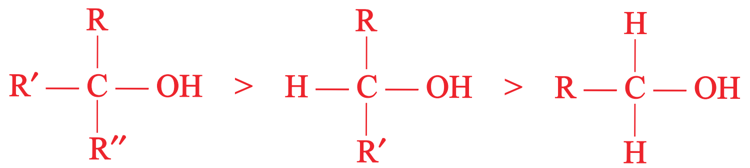
Alcohol Alkene

## Example



Ethanol Ethene

The overall tendency of alcohols to undergo dehydration is in the following order:



Tertiary alcohol Secondary alcohol Primary alcohol

b **Reactions of alcohols with hydrogen halides produce alkyl halides:**

**General reaction:**

$$\underset{\text{Alcohol}}{R-CH_2-OH} + HX \longrightarrow \underset{\substack{(X = Cl,\ Br,\ I) \\ \text{Alkyl halide}}}{R-CH_2-X} + H_2O$$

## Example

$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} + HCl \longrightarrow \underset{\substack{\text{Ethyl chloride} \\ \text{(1-chloroethane)}}}{CH_3-CH_2Cl} + H_2O$$

## Activity 1.31

1. Write the general structural formulas for aldehydes and ketones.
2. What structural difference do you see between aldehydes and ketones?
3. Write the general structural formulas for carboxylic acids and esters.

Discuss with your group and present it to the class.

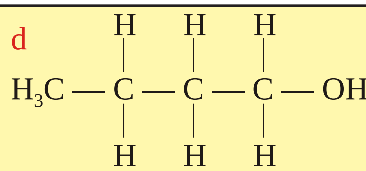
## Exercise 1.15

1. Which functional group characterizes alcohols?
2. What is the basis for the classification of alcohols?
3. What is the general formula of alcohols?
4. Classify the following alcohols as primary, secondary and tertiary alcohols:

a

$CH_3CH_2OH$

d



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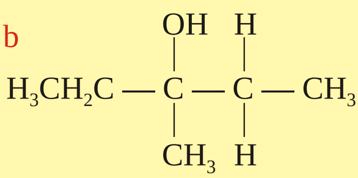
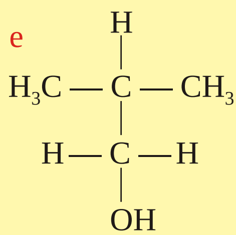


e



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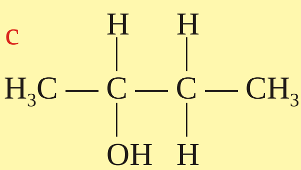

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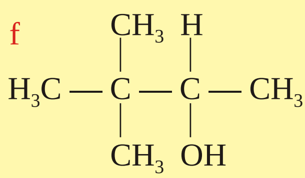
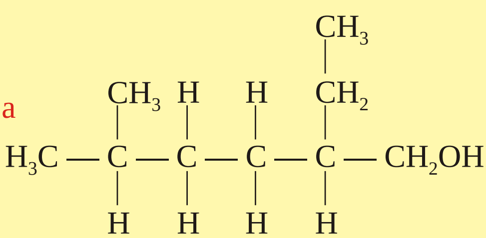
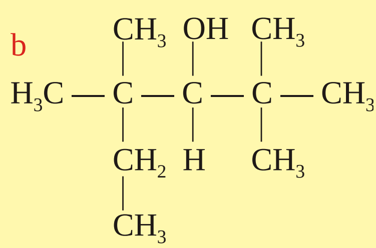


5. Write IUPAC name for each of the following alcohols:

a



b



6. What causes the boiling points of alcohols to be higher than hydrocarbons of similar molecular mass?

7. Complete the following chemical reactions:

   a $CH_3I + NaOH \rightarrow$

   b $CH_3CH_2COOCH_2CH_3 + KOH \rightarrow$

8. What is the functional group of aldehydes?

9. What is the functional group of ketones?

10. What suffixes are used in their IUPAC names to indicate the functional group of aldehydes and ketones respectively?

11 What functional group characterizes carboxylic acids?

12 Complete the following chemical reactions:

a

$$CH_3CH_2CH_2OH \xrightarrow{[O]}$$

b

$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H_3C & — & C & — & C & — & CH_3 \\ & & | & & | & & \\ & & H & & OH & & \end{array} \xrightarrow{[O]}$$

c

$$CH_3CH_2COOH \ + \ CH_3CH_2OH \xrightarrow{H^+}$$

## 1.7 INDUSTRIAL AND AGRICULTURAL APPLICATIONS OF ORGANIC COMPOUNDS

### *Competencies*

***After completing the section, you will be able to:***

- discuss the uses of organic compounds in the manufacture of beverages;
- discuss the uses of organic compounds in the manufacture of pharmaceuticals;
- discuss the uses of organic compounds in the manufacture of soaps and detergents;
- discuss the uses of organic compounds in the manufacture of dry cleaning agents;
- discuss the uses of organic compounds in the manufacture of fuels;
- conduct an experiment to prepare soap from naturally existing esters;
- discuss the uses of organic chemicals in the manufacture of pesticides and herbicides;
- discuss the importance and manufacture of urea.

**Activity 1.32**

1. What are the major application areas of organic compounds?
2. Do you know substances that are used in the preparation of soaps and detergents? If yes name them?
3. Do you know substances (*chemicals*) that are used in dry cleaning?
4. What agricultural applications of organic compounds do you know?

Share your ideas with your group.

## *Industrial application*

Organic chemicals are used for the manufacturing of a large number of industrial products that have a variety of uses. Some of these products include alcoholic beverages, pharmaceuticals, soaps and detergents etc.

### A. Alcoholic beverages

All alcoholic beverages commonly contain the alcohol known as ethanol. The ethanol content of all alcoholic beverages is not the same. Some beverages contain small concentrations of ethanol while others contain higher concentrations. These alcoholic beverages can be either undistilled or distilled. The undistilled alcoholic beverages include beer, wine, "Tella", 'Tej' etc while ouzo, gin, brandy, whisky, 'Katikalla', and vodka are among the distilled alcoholic beverages.

**Beer:** Beer is one of the alcoholic beverages widely manufactured and consumed in most parts of the world. The common raw materials for its production are barley and hops. Although the types of beer produced in the world are very many, the average beer has alcohol content between 3-6 percent by volume.

**Wine:** Wine is another undistilled alcoholic beverage. The most common raw material for producing wine are grapes. In the production process, grapes are first crushed and then steamed. The liquid derived from crushing is called must. It then goes to a fermentation tank where fermentation takes place. Then it passes to a settling tank, where sediments are allowed to settle, and it proceeds from there to a filter. The clear liquid is cooled in a refrigerator and is pasteurized as it passes through a flash pasteurizer. Most wines have an alcohol content varying from 10-15% by volume.

**Liquor:** Compared with beer and wine, liquor contains higher concentrations of ethanol. It is not possible to obtain an alcoholic beverage of more than 15% alcohol by volume through fermentations. This is because the yeast cells are not able to stay alive in alcohol of higher concentration. To get alcoholic beverages with higher percentages of alcohol, the alcohol must be separated from the solution by distillation.

The alcoholic beverages like ouzo, gin, cognac, whisky etc, are made by distillation. Different types of liquors have different alcohol concentrations. In most distilled alcoholic beverages the percentage ranges between 30-45% alcohol by volume. However, some alcoholic beverages like Araki are expected to have a higher percentage of ethanol.

### B. Pharmaceuticals

Organic chemicals are used to manufacture drugs and medicines for various uses. These drugs and medicines are collectively known as pharmaceuticals. Some of the pharmaceuticals are:

**Analgesics:** These are substances that reduce pain. For example: aspirin and paracetamol.

**Antiseptics:** These are substances that help to prevent infections in wounds by killing bacteria; for example, acriflavine.

**Sedatives:** These are drugs that make a person go to sleep or make them feel calm and relaxed. Examples of such type of medicines are the barbiturates, which include several important drugs.

**Disinfectants:** These are substances used to disinfect something or to kill bacteria; for example, Dettol.

**Sulphonamides:** These are medicines used as antibiotics. For example: penicillin.

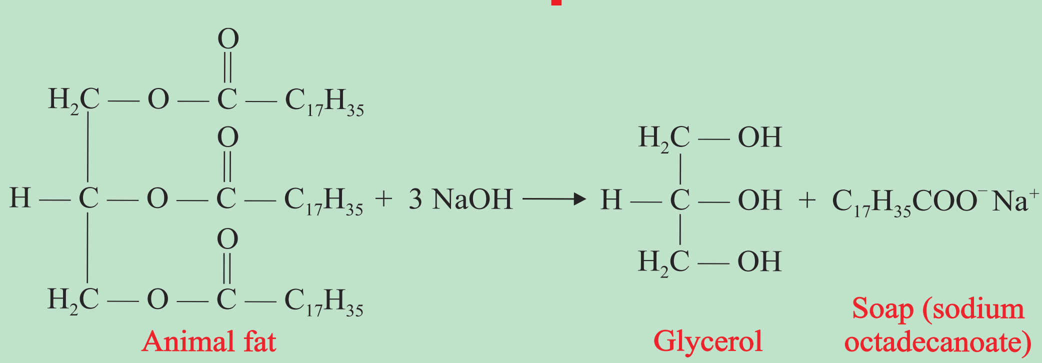
## C. Soaps and Detergents

Organic chemicals are used for the synthesis of soaps and detergents. For example, animal fat and vegetable oils are used for manufacturing soap. Fats and oils are naturally occurring esters of glycerol and the higher fatty acids. Long open-chain alcohols and alkyl benzene sulphonic acid can be used for the production of detergents.

Soaps and detergents are substances used to remove dirt. They are also called surfactants or surface active agents. This is because they reduce the surface tension of water and change the surface properties.

Soaps are either sodium or potassium salts of higher (*long-chain*) carboxylic acids. Soaps that are sodium salts are called hard soaps and those that are potassium salts are soft soaps. Soaps are prepared by boiling animal fat or vegetable oil with a base. The reaction that produces soap is called saponification.

**Example**



Detergents contain either a sulfate or a sulphonate group. One example of detergents is sodium lauryl sulfate, $C_{12}H_{25}—O—SO_2—ONa$. It is prepared first by reacting dodecyl (lauryl) alcohol with sulphuric acid followed by reaction with sodium hydroxide.

The reaction equation is:

$$\underset{\text{Dodecyl alcohol (lauryl alcohol)}}{C_{12}H_{25}—OH} + \underbrace{HO—SO_2—OH}_{H_2SO_4} \longrightarrow \underset{\text{Lauryl hydrogen sulphate}}{C_{12}H_{25}—O—SO_2—OH} + H_2O$$

$$C_{12}H_{25}—O—SO_2—OH + NaOH \longrightarrow \underset{\text{Sodium lauryl sulphate}}{C_{12}H_{25}—O—SO_2—ONa} + H_2O$$

## Experiment 1.9

### *Preparation of Soap*

**Objective:** To prepare soap from animal fat or vegetable oil.

**Materials required:** Animal fat or vegetable oil, NaOH, NaCl, measuring cylinder, beaker, glass rod, Bunsen burner, filter paper, funnel, conical flask, and test tube.

***Procedure:***

Measure 3 mL vegetable oil or 3 g animal fat and place it in a 100 mL beaker; add 3 mL of ethanol and 3 mL of 5M NaOH. Stir the mixture vigorously with a glass rod and gently heat over a flame for 15 minutes or until it turns in to a paste. When the paste begins to form, stir very carefully to prevent frothing. After all the paste has formed, set the beaker on the bench to cool. Add about 15 mL of saturated NaCl solution to the paste mixture and stir thoroughly. This process is called salting out the soap. Filter off the soap mixture by suction filtration and wash the collected soap precipitate with 15 mL of ice water.

***Observations and analysis:***

a Why do we add ethanol during the preparation?

b What is the purpose of adding saturated NaCl solution to the paste mixture?

Write a laboratory report and present to the class.

## D. Dry Cleaning

The qualities of some clothes decrease when they are washed with water using ordinary soap. In order to avoid this, other chemicals are used for washing purposes that remove dirt in the same manner as soaps. Dry cleaning refers to the use of different chemicals that are capable of dissolving grease and other dirt stains in a similar manner as soaps without the use of water. The most commonly used chemicals in dry cleaning are organic chemicals such as tetrachloromethane, $CCl_4$; tetrachloroethylene, $Cl_2C = CCl_2$; benzene and gasoline.

## E. Fuels

The term fuel refers to any material that is capable of burning to produce energy, heat and light. Most fuels occurring in nature are organic compounds. However, some inorganic substances like hydrogen, producer gas and water gas are also used as gaseous fuels. But, the most widely used fuels at present are of organic origin. This includes petroleum which chiefly contains alkanes. Natural gas which is used as a fuel for stoves contains mainly methane. Gasoline which is used as a fuel for internal combustion engines also contains alkanes. Paraffin wax which is used to make candles is another fuel to get light energy and it is a mixture of alkanes containing more than twenty carbon atoms. Besides its use as a constituent of all alcoholic beverages, ethanol can also be used as a fuel for internal combustion engines. At present, it is one of the substances that we can rely on for use as a fuel for automobiles. The use of ethanol as a fuel is now practiced in our country by mixing it with petrol. Ethanol and other plant seed oils can be classified as bio fuels.

### *Agricultural Applications*

Organic compounds also play an important role in agriculture, specially to increase crop productivity by controlling the damages caused by insects, rodents, fungi, birds and weeds. So, organic chemicals can be used in the manufacture of pesticides and herbicides.

***What is the distinction between herbicides and pesticides?***

**Pesticides** are the chemicals used for controlling the damage that can be caused by fungi, insects and other pests that attack crops. Among the pesticides, Bordeaux mixture is used as fungicide. Other chemicals like DDT, aldrine, dieldrine, malathion are used as insecticides.

**Herbicides** are the chemicals that are applied on agricultural lands to remove unwanted plants or weeds. Some examples of compounds that are used as herbicides include paraquat, diquat, ammonium sulphamate, ammonium glyphosinate, sodium chlorate etc.

**Fertilizers:** In order to increase crop productivity we use either synthetic or natural fertilizers. Synthetic fertilizers are grouped into three classes as nitrogen, potash and phosphate fertilizers. Nitrogen is one of the essential plant nutrients. It is absorbed by plants in the form of nitrate ion, $NO_3^-$. Nitrogen enables green plants to synthesize amino acids and proteins, and it is also a constituent of DNA molecules. To provide nitrogen for plants, nitrogen-containing fertilizers are usually added to the soil. These include, ammonium salts like $NH_4Cl$, $(NH_4)_2SO_4$; nitrates like $KNO_3$ and urea. Urea is one of the most important nitrogen fertilizers. It is a component of urine. On an industrial scale, urea is manufactured by the dehydration of ammonium carbamate:

$$H_2N—COO^-NH_4^+ (s) \longrightarrow H_2NCONH_2 (s) + H_2O (g)$$

It can also be prepared by direct combination of ammonia and carbon dioxide at 180℃ and pressure of about 140 atm.

$$2NH_3 (g) + CO_2 (g) \longrightarrow \underset{\text{Urea}}{NH_2CONH_2 (s)} + H_2O (g)$$

## Check list

### *Key terms of the unit*

- addition reaction
- alcohol
- aldehyde
- alkane
- alkene
- alkyl halide
- alkyl radicals
- alkynes
- benzene
- biogas
- carboxylic acid
- chain isomerism
- cracking
- crude oil
- cycloalkanes
- cycloalkene
- decarboxylation
- dehydrohalogenation
- destructive distillation
- detergents
- elimination reaction
- ester
- fermentation
- fertilizer
- functional group
- geometrical isomerism
- halogenation
- hedrohalogenation
- herbicide
- homologous series
- hydrogenation
- inorganic compound
- isomers
- ketone
- lifeforce theory
- Markovnikov's rule
- natural gas
- nitration
- organic compound
- pesticide
- petroleum
- pharmaceuticals
- polymerization
- position isomerism
- resonance structure
- saturated hydrocarbons
- soaps
- substitution reaction
- sulphonation
- unsaturated hydrocarbons
- Wurtz reaction

## Unit Summary

- *The "life force" theory states that living organisms (plants and animals) have a special life force which helps them to synthesize organic compounds and that organic compounds cannot be synthesized artificially by man in the laboratory.*
- *Organic chemistry is the study of carbon compounds including natural and synthetic ones.*
- *Organic compounds are classified based on the functional group they contain in their molecules.*
- *The functional group is a part of a molecule that determines the chemical and physical properties of a compound.*
- *Hydrocarbons are compounds composed of carbon and hydrogen atoms only.*
- *Saturated hydrocarbons contain only single bonds between carbon atoms*
- *Unsaturated hydrocarbons are those containing one or more double or triple bonds between carbon atoms.*
- *A homologous series is a group of compounds in which each member of the group differs from the next member by* $–CH_2–$ *group.*
- *Alkanes are saturated hydrocarbons represented by the general formula* $C_nH_{2n+2}$. *Alkanes are named by using prefixes that indicate the number of carbon atoms and the suffix '-ane'.*
- *Isomerism is the existence of two or more compounds with the same molecular formula but different structures. These compounds are called isomers.*
- *Alkenes are unsaturated hydrocarbons containing a carbon-carbon double bond as their functional group. Their general formula is* $C_nH_{2n}$. *The suffix '-ene' in their names indicates the presence of a carbon-carbon double bond.*
- *Alkynes are unsaturated hydrocarbons containing a carbon - carbon triple bond as their functional group. They are represented by the general formula* $C_nH_{2n-2}$. *The suffix '-yne' indicates the carbon-carbon triple bond.*
- *Alkenes and alkynes undergo mainly addition reactions while alkanes undergo substitution reactions.*
- *Aromatic hydrocarbons are compounds containing benzene rings. Benzene is the simplest aromatic hydrocarbon.*
- *Benzene mainly undergoes substitution reactions.*
- *The natural sources of hydrocarbons are crude oil, natural gas and coal.*

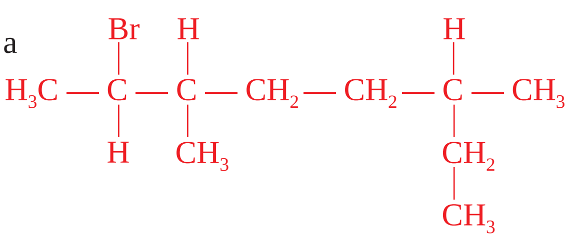
- *Crude oil is a complex mixture of hydrocarbons, mainly alkanes, and also contain cycloalkanes and aromatics.*
- *Crude oil is separated into a number of useful fractions by fractional distillation.*
- *Alcohols are compounds containing the hydroxyl* (–*OH*) *group as their functional group and represented by the general formula* $C_nH_{2n+1}OH$.
- *Alcohols are classified depending on the number of hydroxyl groups they contain as monohydric, dihydric and trihydric alcohols.*
- *Monohydric alcohols are classified as primary* (1°), *secondary* (2°) *and tertiary alcohols* (3°).
- *The names of alcohols contain the suffix '-ol' which indicates the presence of –OH group in the molecule.*
- *Primary alcohols oxidize to give aldehydes and then carboxylic acids, and secondary alcohols yield ketones on oxidation.*
- *Organic chemicals have industrial applications such as in the production of alcoholic beverages and pharmaceuticals.*
- *Organic chemicals are also used in the production of fertilizers, pesticides and weed killers for agricultural uses.*
- *Organic chemicals are also used as fuels, and to produce soaps and detergents and also for dry cleaning.*

## REVIEW EXERCISE ON UNIT 1

### Part I: Nomenclature based problems

1. Give the IUPAC names of the following compounds:

a



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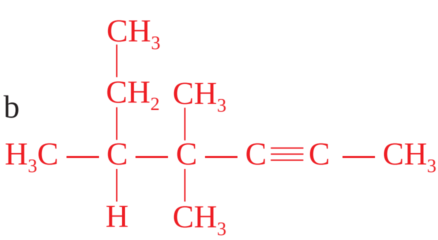

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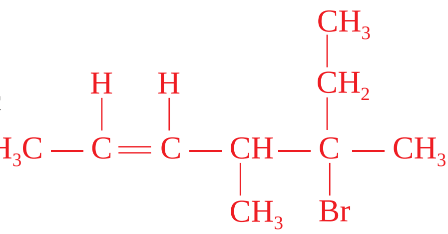

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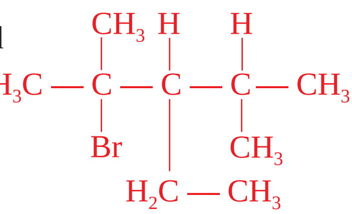

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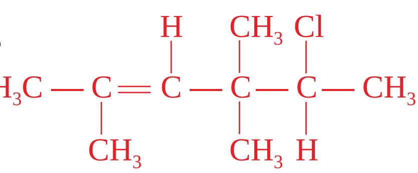

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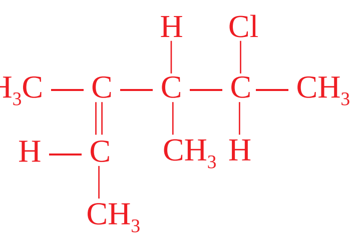

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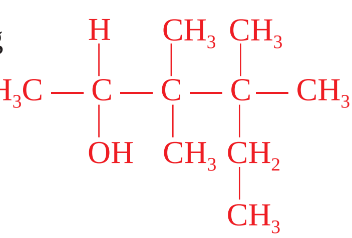

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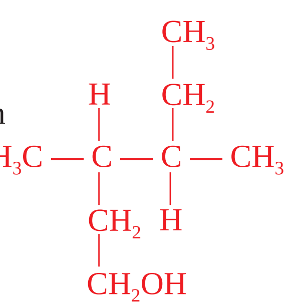


2. Write the structural formulas of the following compounds:

   a 3-bromo-2-chlorohex-1-ene

b 4-ethyl-2,2,3-trimethylhexane

c 2-methyl-2-butanol

3. Complete the following chemical equations:

a $CH_2{=}CH_2 + H_2 \xrightarrow[\text{Heat}]{\text{Ni}}$

b $CH_3COONa + NaOH \xrightarrow{\text{CaO, heat}}$

c $2CH_3-CH_2Br + 2Na \longrightarrow$

d $$\begin{array}{l} CH_3-\underset{\displaystyle |\atop\displaystyle Br}{CH}-\underset{\displaystyle |\atop\displaystyle Br}{CH_2} + 2KOH \longrightarrow \end{array}$$

e $CH_3CH_2CH_2OH \xrightarrow[\text{Heat}]{H_2SO_4}$

f $CH_3CH_2CH_2Cl + KOH \xrightarrow[\text{Heat}]{}$

g $HC{\equiv}CNa + CH_3CH_2Br \longrightarrow$

h $CH_3COOCH_2CH_3 + KOH \longrightarrow$

4. Complete the following reaction equations:

a $CH_3-CH{=}CH_2 + HBr \longrightarrow$

b $HC{\equiv}C-CH_2-CH_3 + 2HCl \longrightarrow$

c $CH_3-CH_2-CH{=}CH_2 + H_2O \xrightarrow{H^+}$

d $$H_3C-\overset{\displaystyle H\atop\displaystyle |}{\underset{\displaystyle |\atop\displaystyle H}{C}}-\overset{\displaystyle H\atop\displaystyle |}{\underset{\displaystyle |\atop\displaystyle OH}{C}}-CH_3 \xrightarrow{[O]}$$

e $CH_3-CH_2-CH{=}CH_2 + H_2O \xrightarrow[KMnO_4]{\text{Alkaline}}$

f $CH_3-CH_2-CH_2OH \xrightarrow{[O]}$

g $CH_3CH_2CH_2COOH + CH_3-CH_2-CH_2OH \longrightarrow$

h $C_6H_6 + Cl_2 \xrightarrow{FeCl_3}$

## Part II: Multiple choice Type Questions

5. Which of the following hydrocarbons does not belong to the homologous series of alkanes?

   a $C_3H_8$  b $C_8H_{18}$  c $C_6H_{10}$  d $C_{10}H_{22}$

6. Which of the following alkanes is a liquid at room temperature?

   a $CH_4$  b $C_{10}H_{22}$  c $C_4H_{10}$  d $C_3H_8$

7. The hydrocarbon used as a fuel in an oxyacetylene torch is:

   a $C_2H_2$  b $C_2H_4$  c $C_4H_{10}$  d $CH_4$

8. The general formula that represents the olefin homologous series is:

   a $C_nH_{2n+1}$  b $C_nH_{2n+2}$  c $C_nH_{2n-2}$  d $C_nH_{2n}$

9. The most common reaction that alkenes undergo is:

   a elimination  b substitution  c addition  d decomposition

10. Benzene is an unsaturated hydrocarbon; it mainly undergoes:

    a addition  b elimination  c polymerization d substitution

11. Which of the following compounds is an alkene?

    a $H_3C — CH_2 — CH_3$  b $H_2C = CH — CH_3$

    c $HC \equiv C — CH_3$  d $CH_3 — CH_2 — CH_2 — OH$

12. Which of the following compounds is a ketone?

    a $\begin{array}{l} H_3C — C = O \\ \qquad\quad\; | \\ \qquad\quad\; H \end{array}$  b $\begin{array}{l} H_3C — C = O \\ \qquad\quad\; | \\ \qquad\quad\; OH \end{array}$

    c $\begin{array}{l} H_3C — C = O \\ \qquad\quad\; | \\ \qquad\quad\; CH \end{array}$  d $\begin{array}{l} H_3C — C = O \\ \qquad\quad\; | \\ \qquad\quad\; OCH \end{array}$

13. Which of the following classes of hydrocarbons is the most reactive?

    a Alkynes  b Alkanes

    c Alkenes  d Aromatic hydrocarbons

14. The compounds $CH_3OH$ and $CH_3COOH$ react in the presence of an acid catalyst to form:

    a a carboxylic acid  b an aldehyde

    c a ketone  d an ester

15. Which hydrocarbon is the main constituent of natural gas and biogas?

    a $C_4H_{10}$  b $CH_4$

    c $C_2H_6$  d $C_6H_{14}$

16. During the fractional distillation of crude oil, the process of cracking is carried out to:

a separate the crude oil into different fractions

b vaporize the liquid components

c maximize the output of petrol or gasoline

d separate alkanes from alkenes

17. Ethyne decolorizes $Br_2$ in $CCl_4$. This is due to the formation of:

a 1,1-dibromoethane

b 1,1,2,2-dibromoethene

c 1,2-dibromoethane

d 1,1,2,2-dibromoethane

18. The following reaction can be classified as:

$$CH_4 + Br_2 \rightarrow CH_3Br + HBr$$

a an addition reaction

b an elimination reaction

c a substitution reaction

d a saponification reaction

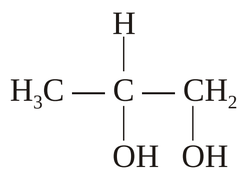
19. Which one of the following substance is not used in dry cleaning?

a $CCl_4$

b $Cl_2C == CCl_2$

c $C_6H_6$

d $CH_3COOH$

20. The compound with the structure  is a:

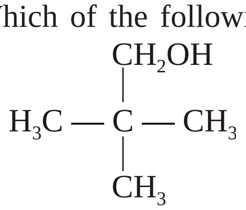
a secondary alcohol

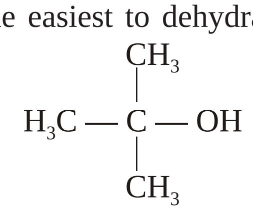
b trihydric alcohol

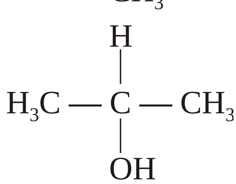
c carboxylic acid

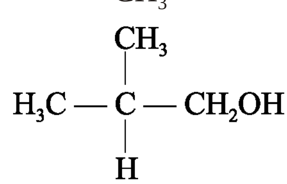
d dihydric alcohol

21. Which of the following alcohols is the easiest to dehydrate?

a 

b 

c 

d 

22. Alcohols that yield ketones on oxidation are classified as:
   a primary alcohols
   b secondary alcohols
   c dihydric alcohols
   d trihydric alcohols
23. The first organic compound was synthesized in the laboratory by:
   a Friedrich Wohler
   b A. Kekule
   c John Dalton
   d Wurtz

## Part III: Which of the following statements are true?

24. a A weed killer is a pesticide.
   b Carbon tetrachloride is used in dry cleaning.
   c Antiseptics are sleep inducing drugs.
   d 'Tella' is a distilled alcoholic beverage.
   e Soaps and detergents are surfactants.
   f Alkanes easily undergo addition reactions.
   g Benzene burns with a sooty flame.
   h Biogas mainly contains n-butane.