13.   HYDROCARBONS

A: ANALYSIS OF ORGANIC COMPOUNDS

INTRODUCTION

Carbon is unique in the ability of its atoms to link up with each other, forming straight-chain, branched-chain and cyclic compounds. In addition, carbon atoms form bonds with atoms of many other elements, including oxygen, hydrogen, nitrogen, sulphur, the halogens, and even metals. The result is that there are so many compounds of carbon, that a branch of chemistry is devoted to their study.

The study of this branch of chemistry, called Organic Chemistry, is interesting, not just because of the number of compounds involved, but also because many of these compounds are very important in industry, in our homes, and in medicine. Structural modifications made to obtain certain desired properties add new findings to the list of organic compounds every year.

13.1 Composition of Organic Compounds.

When a chemist isolates a new compound, one of the first things he wants to find out about it, is its composition. So, he determines its structure and properties. It is from the properties that he can find uses for the compound. But how does a chemist determine the composition and structure of organic compounds?

First, the chemist needs to know what elements are present in the compound, their proportions, the relative molecular mass of the compound, and finally the arrangement of the atoms in its molecule.

All organic compounds burn in air or oxygen, producing carbon(IV) oxide and water. The detection of these products is evidence for the presence of carbon and hydrogen.

Experiment 13.1: Detection of carbon and hydrogen.

Mix about 1 g of an organic compound such as starch with about 2g of copper(II) oxide in a boiling tube. Fit a cork bearing a delivery tube to the tube. Clamp the tube horizontally, then heat the mixture strongly. Pass any gas evolved into lime water for a minute. Record your observation.

Remove the delivery tube and test the liquid which condenses near the cork, with white anhydrous copper(II) tetraoxosulphate(VI). Record your observation.

The turning of the lime water milky confirms the evolution of carbon(IV) oxide, and hence the presence of carbon. The turning of the white anhydrous copper(II) tetraoxosulphate(VI) to blue, indicates the presence of water, and hence of hydrogen.

$$C(s) + 2CuO(s) \rightarrow CO_2(g) + 2Cu(s)$$
$$CO_2(g) + Ca(OH)_2(aq) \rightarrow CaCO_3 + H_2O$$
$$\text{milky solution}$$
$$H_2(g) + CuO(s) \rightarrow H_2O(l) + Cu(s)$$
$$5H_2O(g) + CuSO_4(s) \rightarrow CuSO_4.5H_2O(s)$$
$$\text{(white)} \qquad \text{(blue)}$$
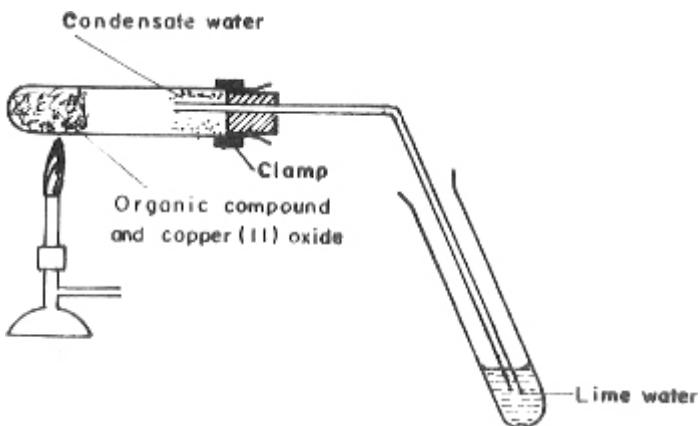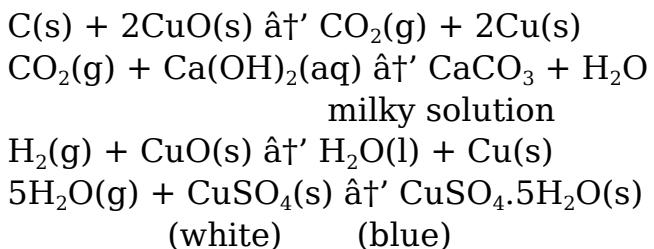
Figure 13.1 Detection of carbon and hydrogen

Why should the boiling tube be placed horizontally?

The result of Experiment 13.1 indicates that a given organic compound contains carbon and hydrogen. It does not tell whether other elements are also present or not. If we carry out the experiment quantitatively, more information can be obtained. The quantitative experiment involves determining how much carbon(IV) oxide and water are formed from a known mass of organic compound. The steps are:

1. Weigh the given organic compound into a combustion tube.
2. Burn it in a stream of oxygen.
3. Absorb the water produced in a weighed drying agent, and the carbon(IV) oxide produced in a weighed reagent that absorbs the gas, like potassium hydroxide.

If an organic compound contains nitrogen, sulphur, and the halogens, the elements form volatile products which escape during burning. Thus, no residue is usually left. An organic compound which

contains a metallic element, however, leaves a residue. This is usually an oxide of the metal, which can be analysed to identify the particular metal.

Experiment 13.2: Investigating the presence of a metal in an organic compound

Heat a little sample of the organic compond in a crucible lid until combustion is complete. Observe for residue formation.

If a residue is left, the organic compound must contain a metallic element. Dissolve the residue in trioxonitrate(V) acid and carry out a qualitative analysis for the metallic element present.
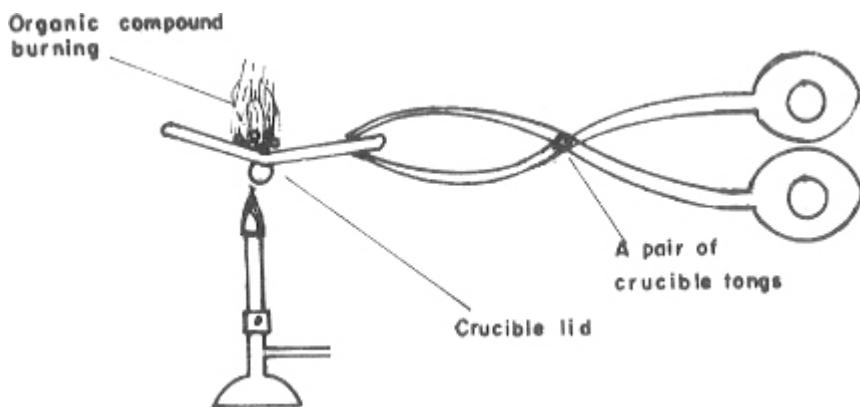

Figure 13.2 Burning an organic compound in a crucible lid
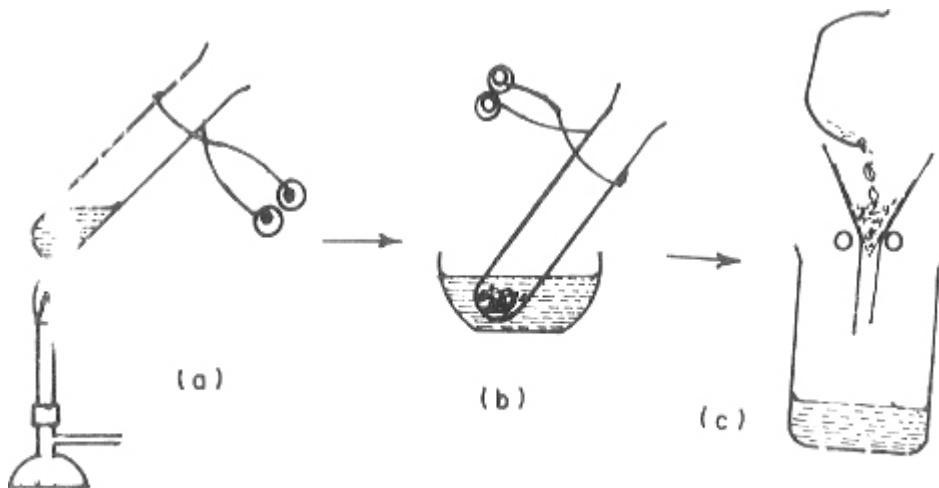
Can nitrogen, sulphur, and the halogens be detected in the vapours from the burning organic compound? Although this is possible, it is easier to fuse the organic compound with sodium metal. During this process, nitrogen forms sodium cyanide, sulphur is converted to sodium sulphide, and any halogen present is converted to the sodium halide. The fusion mixture is dissolved in water and the CN^-, S^{2-} or halide ion, if present, will also be dissolved. These ions can be identified by the appropriate wet tests.

Experiment 13.3: Detection of nitrogen, sulphur and halogens in an organic compound

Cut a piece of sodium the size of a groundnut seed. Dry it between filter papers, then drop it into a micro test-tube. Cover the sodium with a spatulafull of the organic compound (if liquid, use about $1cm^3$).

Heat the micro test-tube on a bunsen flame, slowly at first, then more strongly, till red-hot. If the vapours of the burning mixture catch fire while you are heating, cover the mouth of the micro test-tube with wire gauze to put out the flame. When the tube is red-hot and all the sodium and volatile compounds have been burnt or evaporated, plunge the tube into about $5cm^3$ of distilled water in a mortar. Cover it immediately till all reactions have subsided.

Crush the micro test-tube and stir the fused products in water. Filter off any undissolved solid and use the filtrate for the following tests.

(a) Heating organic compound and sodium in a micro test-tube.
(b) Red-hot tube plunged into cold water, and crushed.
(c) Filtration of product of fluid after stirring with water.

Figure 13.3 Preparation of the filtrate for the sodium fusion test

1. Test for CN⁻ (and hence nitrogen)

To 1cm^3 of the filtrate in a test-tube add iron(II) tetraoxosulphate(VI) solution, then dilute tetraoxosulphate(VI) acid. Leave for a few minutes.

The formation of a blue precipitate or colouration indicates the presence of CN⁻ ion, and hence of nitrogen in the original organic compound.
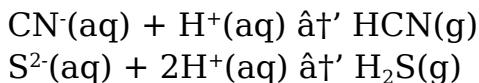
2. Test for S²⁻ (and hence sulphur)

Acidify another 1cm^3 sample of the filtrate with dilute ethanoic acid, then add lead ethanoate solution dropwise till in excess.

A black precipitate of lead sulphide indicates the presence of S^{2-} ion, and hence of sulphur in the organic compound.

3. Test for halogens

Boil 2cm^3 of another sample of the filtrate with 2cm^3 dilute trioxonitrate(V) acid till half the volume evaporates. Any CN⁻ or S²⁻present in the filtrate is then expelled as HCN or H_2S.

$$CN^-(aq) + H^+(aq) \rightarrow HCN(g)$$
$$S^{2-}(aq) + 2H^+(aq) \rightarrow H_2S(g)$$

Cool, then dilute with an equal volume of distilled water. Add silver trioxonitrate(V) solution.

A white or yellow precipitate that darkens on standing, indicates the

presence of a halogen. Add dilute ammonia solution to the precipitate and shake. If the precipitate dissolves readily, chloride ion is present and the organic compound contains chlorine. If the precipitate is pale yellow and sparingly soluble, bromide ion is present and hence the compound contains bromine. But if the precipitate is yellow and insoluble in ammonia solution, iodide ion is present, and hence iodine is present.

The quantitative determination of nitrogen, sulphur or halogen is outside the scope of this text. However, from data on percentage compositions of elements (including these elements) in organic compounds, we can calculate empirical and molecular formulae, and from information about the chemical behaviour of the compounds the structural formulae can be determined.

Experiment 13.4: Determination of the composition of a hydrocarbon.

Weigh about 0.3g of a given hydrocarbon accurately in a porcelain boat. Put the boat into a combustion tube. Weigh a U-tube containing fused calcium chloride, and two conical flasks containing potassium hydroxide solution. Set up the apparatus as shown in Figure 13.4.
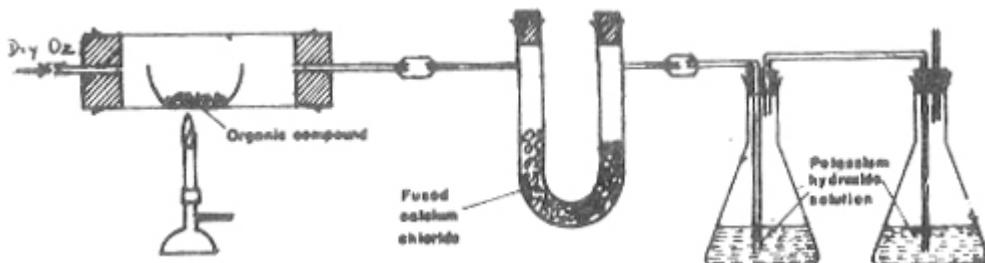

Figure 13.4 Determination of the composition of a hydrocarbon

Heat the combustion tube while passing dry oxygen through it. When the hydrocarbon is completely burnt, allow the apparatus to cool. Weigh the U-tube and conical flasks, and hence determine the mass of water and carbon(IV) oxide formed. These are equal to the increase in the masses of the U-tube and conical flasks respectively. From these, calculate the percentage of hydrogen and of carbon in the organic compound. If they sum up to 100% of the mass of the organic compound, then the compound is a hydrocarbon. That is, it contains carbon and hydrogen only.

SPECIMEN RESULTS AND CALCULATION

Mass of hydrocarbon	= 0.38g.
Mass of water formed	= 0.54g.
Mass of carbon(IV) oxide formed	= 1.17g.
Mass of carbon in 1.17g carbon(IV) oxide	

$$= \frac{12}{44} \times 1.17g \doteq 0.32g.$$

Mass of hydrogen in 0.54g of water

$$= \frac{2}{18} \times 0.54g = 0.06g$$

The sum of the masses of oxygen and hydrogen present in the organic compound is 0.38g. This is equal to the mass of the organic compound oxidized. Therefore, the compound is a hydrocarbon.

$$\therefore \quad \% \text{ of carbon} = \frac{0.32}{0.38} \times 100 = 84.2\%$$

$$\therefore \quad \% \text{ of hydrogen} = \frac{0.06}{0.38} \times 100 = 15.8\%$$

13.2 Calculation of Empirical Formula of an Organic Compound

From the result of the analysis of the organic compound to determine its composition and the masses of the components, we can calculate its empirical formula. Empirical formula is the formula that shows the ratio of the atoms in a compound.

In Experiment 13.4, we found that the mass of carbon in 0.38g of the hydrocarbon = 0.32g. Relative atomic mass of carbon = 12

$$\therefore \text{ Number of mole of carbon} = \frac{0.32}{12}$$

Mass of hydrogen in 0.38g of hydrocarbon = 0.06g

Relative atomic mass of hydrogen = 1

$$\therefore \text{ Number of mole of hydrogen} = \frac{0.06}{1}$$

$\therefore$ Mole ratio C:H

$$= \frac{0.32}{12} : \frac{0.06}{1}$$

$$= 0.0267 : 0.06$$

$$= \frac{0.0267}{0.0267} : \frac{0.06}{0.0267}$$

$$= 1 : 2.25$$

$$\text{or} \quad 4 : 9$$

â^´ Empirical formula = C_4H_9

13.3 Calculation of the Molecular

Formula

Since the empirical formula gives only the relative number of atoms of the elements in a molecule of a compound, the formula of the compound in Experiment 13.4 may be C_4H_9, C_8H_{18} or $C_{12}H_{27}$, i.e. any integral multiple of C_4H_9 units. Suppose there are n units of C_4H_9 in a molecule of the compound, then we need to know the relative molecular mass of the compound to be able to determine the value of **n**.

Many methods are available for determining relative molecular masses. The one that is often used for volatile organic compounds is by vapour density determination. This applies the relationship:

$2 \times$ Vapour density = Relative molecular mass.

If the vapour density of the hydrocarbon in our experiment is found to be 114, then its relative molecular mass is 228. Adding up the relative atomic masses, we have:

$$n(C_4H_9) = 228$$
i.e. $n(4 \times 12) + n(9 \times 1) = 228$
$\therefore 48n + 9n = 228$
$\therefore 57n = 228$
$\therefore n = 4$

$\therefore$ The molecular formula of the hydrocarbon is $C_{16}H_{36}$
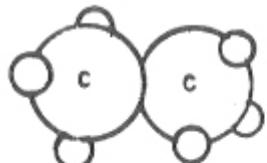
EXERCISE 13B

Calculate the molecular formula of the hydrocarbon with empirical formula CH_3, and relative molecular mass 30. Answer is C_2H_6.
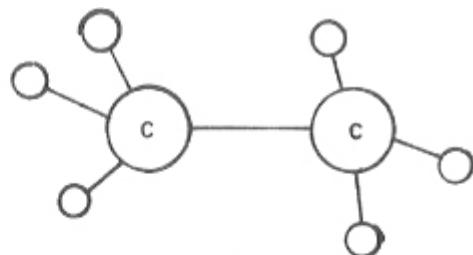
13.4 Structural Formula

The structural formula of a compound is the formula which shows how the atoms are bonded to each other in the molecule. In ethane, C_2H_6, the only possible arrangement is for the two atoms of carbon to be linked, and for each carbon atom to be additionally linked to three hydrogen atoms. Each carbon atom exhibits its tetravalence, and each hydrogen atom its univalence. Various ways of representing this arrangement are shown in Figure 13.5. The last, (c), is the structural formula of ethane.
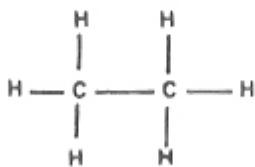
Formula of ethane

(a)   (b)
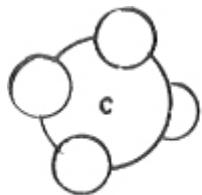
(c)
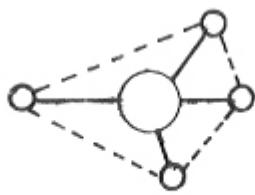
Structural formula

Figure 13.5 Structures of ethane
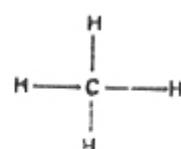
In methane, molecular formula CH_4, each of the hydrogen atoms is covalently linked to the carbon atom. Since the hydrogen atoms must be equally spaced out, the molecule has the structures indicated in Figure 13.6.

(a)   (b)   (c)

Figure 13.6 Structures of methane.

A ball-and-spoke model of it is represented in Figure 13.6 (b). Since both Figure 13.6 (a) and (b) are difficult to draw, (c) is used to represent the structure of methane. It is thus the structural formula of methane.

The structures of propane, C_3H_8, are represented in Figure 13.7

(a)

(b)

$$H—C—C—C—H$$

(c)
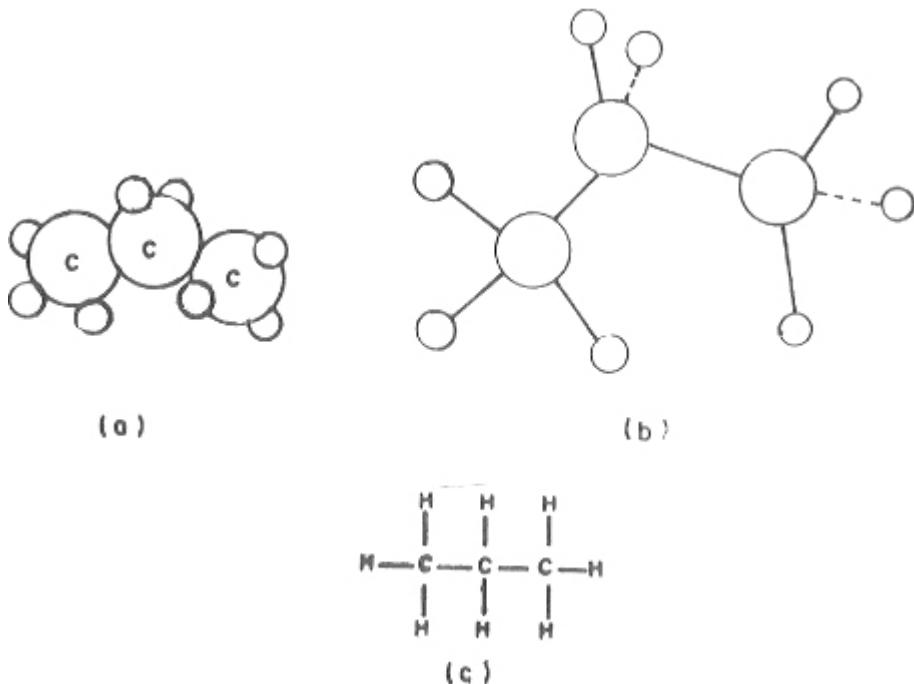
Figure 13.7 Structures of propane

WORKED EXAMPLE

A pungent-smelling organic compound is found to contain 30.6% of carbon, 3.8% of hydrogen, 43.3% of chlorine by mass, the rest being oxygen. What is its empirical formula? If its relative molecular mass is 78.5, what is its molecular formula?

SOLUTION

(a) **Calculation of empirical formula.**

Mass of elements in l00g of compound:

	C	H	O	Cl
	30.6g	3.8g	22.3	43.3g
Mole ratios	30.6:	3.8:	22.3:	43.3
	= 2.55 :	3.8 :	1.4 :	1.2

Divide by the least

$$\begin{array}{cccc} 2.55: & 3.8: & 1.4: & 1.2 \\ 1.2 & 1.2 & 1.2 & 1.2 \\ = 2: & 3: & 1: & 1 \end{array}$$

That is, the empirical formula is C_2H_3OCl.

(b) **Calculation of molecular formula**
   If there are n units of empirical formula in one molecule of the compound, then

$n[(12 \times 2) + (3 \times 1) + (16 \times 1) + (35.5 \times 1)] = 78.5$

$\therefore n \times 78.5 \qquad\qquad\qquad = 78.5$

$\therefore n \qquad\qquad\qquad\qquad = 1$

$\therefore$ Molecular formula is C_2H_3OCl

We do not have further information to consider writing the structural formula of the compound.

EXERCISE 13C

A liquid organic compound is found to contain 52.18% of carbon, 13.04% of hydrogen by mass, the rest being oxygen. What is its empirical formula? If its vapour density is 23, what is its molecular formula?

Answer:
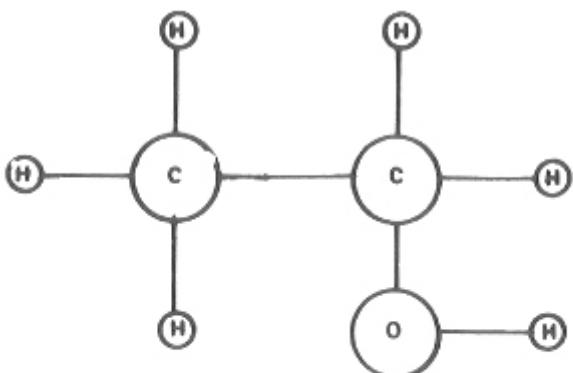
Empirical formula: C_2H_6O

Molecular formula: C_2H_6O.
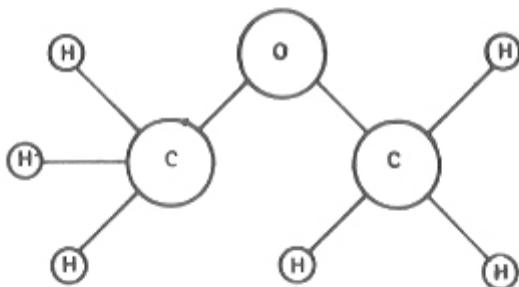
The determination of the molecular structure of a compound is like a detective story. The physical and chemical properties of the compound furnish clues to the solution of the problem.

Activity 13.1: Making Models of the Structure of C_2H_6O.

Try to link up two black balls with four holes in each (representing carbon atoms), six white balls with one hole in each (representing hydrogen atoms), and one red ball with two holes in it (representing oxygen atom) using short spokes. The number of holes in each ball is the valence, or combining power of the atom it represents. If you do it properly, two different arrangements emerge, (Figure 13.8).

(a)

(b)
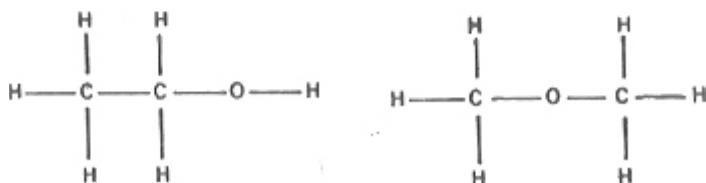
Figure 13.8 Possible structures of C_2H_6O

The two arrangements represent two different compounds whose molecular structures are the same. Such compounds are called **isomers**.

> **Isomerism is the existence of two or more compounds with the same molecular formula but different structural formulae.**

Isomerism is a widespread phenomenon in organic chemistry. It shows that molecular formula alone does not completely identify a compound.

But which of the two arrangements is the structure of ethanol?

Evidence from chemical reactions: The structural formula of an organic compound can be deduced from its chemical reactions. The presence of some type of bonding between the atoms in an organic compound will cause it to possess certain characteristic properties.

These properties can be used for ascertaining the structural formulae of such compounds. Experiment 13.5 illustrates this.

Experiment 13.5: Investigating the action of sodium on ethanol.

Drop a small pellet of sodium into 1cm³ of ethanol in an evaporating basin. A vigorous reaction similar to the action of sodium on water ensures. When the reaction subsides and evolution of hydrogen ceases, evaporate the resultant solution to dryness. A white solid remains.

Add 1cm³ of water to it. It dissolves readily. Test the solution with red litmus, and observe that the litmus paper turns blue. The solid residue resembles the sodium hydroxide formed by the action of sodium on water.

$$2Na(s) + 2C_2H_5OH(aq) → 2C_2H_5ONa(s) + H_2(g)$$
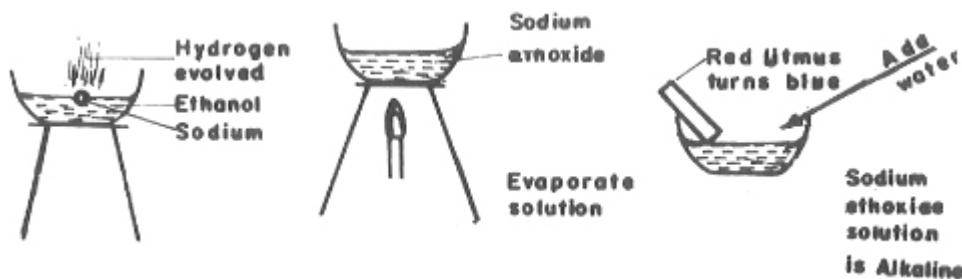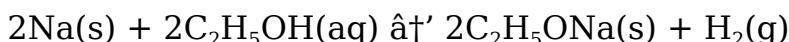
Figure 13.9 Action of sodium on ethanol

The clue from this demonstration is that ethanol behaves like water towards sodium. Then ethanol must have a structural similarity to water. Water has two hydrogen atoms attached to oxygen. There should, therefore, be at least one hydrogen attached to the oxygen in ethanol. This points to structure (a) in Figure 13.8.

Other chemical evidence in support of structure (a) will become obvious when we have studied the reactions of alkanols.

Evidence from physical properties: Determination of some physical properties of the sample and comparison with corresponding properties of compounds with known structure can give some clues.

Experiment 13.6: Determining the Boiling point of Ethanol.

Set up a distillation apparatus as shown in Figure 13.10. Put about 10cm³ of the given ethanol into the distillation flask. Insert a cork carrying a thermometer and a condenser. Heat the flask and record the steady temperature of ethanol vapours as boiling proceeds.
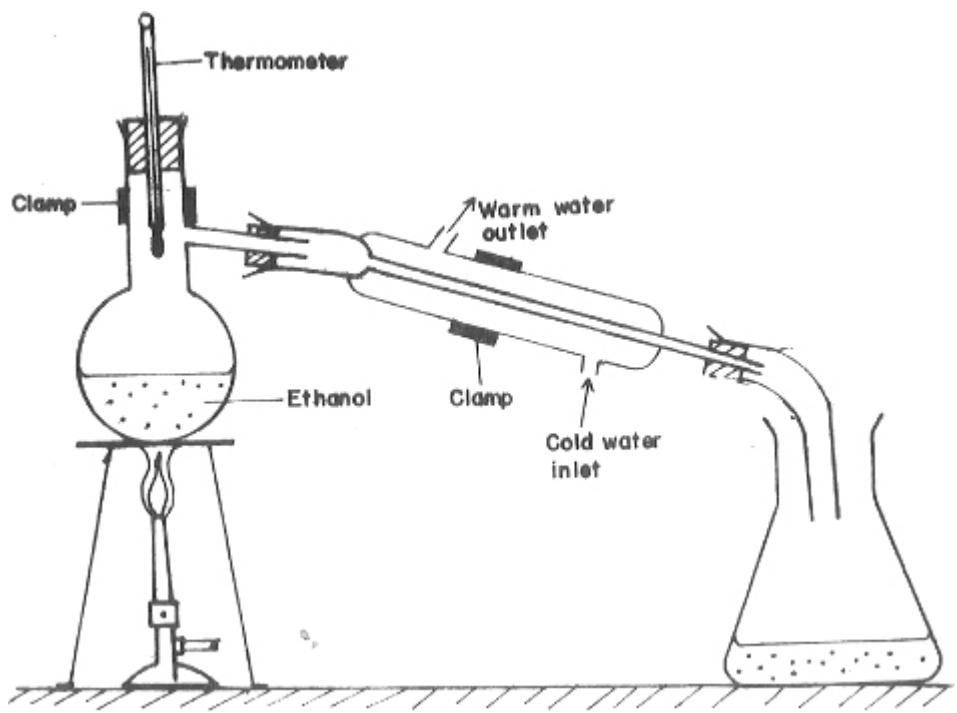
Figure 13.10 Determining the boiling point of ethanol

The boiling point of ethanol is 78°C at atmospheric pressure. Comparing with that of ethane, (– 172°C), and that of water, 100°C, we see again that ethanol is more like water in nature than like ethane. This again points to structure (a) for ethanol. Other physical properties which can be determined and compared with those of compounds of known structures include melting point (for solids), solubility, X-ray diffraction pattern, etc.

13.5 Functional Groups

The study of organic compounds is simplified by grouping them into families, called homologous series. Members of a homologous series have similar structures. They therefore react alike. **The reactive group present in every member of a homologous series, and which gives them their characteristic behaviour, is known as a functional group**. The following are the characteristics of members of a homologous series.

1.   They react alike.
2.   They show a gradation in physical properties.
3.   Adjacent members differ by CH_2, (or 14 atomic mass units).
4.   They can be represented by a general formula.
5.   They have the same general methods of preparation.
6.   They are often known by a general group name, and each member's systematic name is derived from the number of consecutively joined carbon atoms, plus a suffix, or prefix

group-name.

Table 13.1 lists the names and functional groups of common homologous series.

TABLE 13.1 COMMON HOMOLOGOUS SERIES

Homologous Series	Functional Group	Group Name	Example Structure	Name
Alkane	R-C-H	Suffix: -ane	CH_3CH_3	Ethane
Alkene	R-C=C-	'' -ene	$H_2C=CH_2$	Ethene
Alkyne	R-C≡C-	'' -yne	H-C≡C-H	Ethyne
Alkanol	R-OH	'' -ol	CH_3CH_2OH	Ethanol
Halogeno-alkane	R-X (X=Cl, Br,I)	Prefix: Halogeno-	CH_3CH_2Cl	Chloro-ethane
Alkanal	R-CHO	Suffix: -al	CH_3CHO	Ethanal
Alkanone	R-CO-R	'' -one	CH_3COCH_3	Propanone
Alkanoic acid	R-COOH	'' -oic acid	CH_3COOH	Ethanoic acid
Amine	$R-NH_2$	Prefix: Amino-	$CH_3CH_2NH_2$	Amino-ethane

★ R is either an alkyl group, or in some cases, a hydrogen atom.

Other homologous series not listed will be included in due course. The system of nomenclature will become clearer as you study each homologous series.

13.6 Sources of Hydrocarbons

The simplest of the numerous compounds of carbon are the hydrocarbons. These are compounds which contain carbon and hydrogen only.

Most organic compounds have their origin from substances that were part of living organisms.

Hydrocarbons are obtained from the following sources:

1. **Coal:** Coal tar, one of the fractions of the destructive distillation of coal, is a complex mixture. Over 200 compounds have been separated from it. Some of these are hydrocarbons. These include benzene, methylbenzene (toluene), and naphthalene. Some other hydrocarbons are made from coke, the residue from the distillation of coal.

2. **Petroleum:** Petroleum is also a complex mixture. Its constituents

are essentially saturated hydrocarbons. They are separated by fractional distillation.

3. **Natural gas:** The difference between petroleum and natural gas is the state of the components, due to the sizes of the molecules. Natural gas consists of low molar mass hydrocarbons which exist in the gaseous state, whereas most of the hydrocarbons in petroleum are of higher molar mass and exist in the liquid state. Natural gas is used as fuel for both domestic and industrial purposes. The common cooking gas which is supplied in steel cylinders is mainly butane.

B: ALKANES

The alkanes are saturated hydrocarbons. All bonds in their molecules, whether they are between carbon and hydrogen, or between two carbon atoms, are single bonds. Alkanes have the general formula, C_nH_{2n+2}. It is from the general formula that we can write the formulae of the other members (Table 13.2)

When there are many carbon atoms in an alkane molecule, three possible arrangements arise:

1. The carbon atoms could be consecutively linked. These are called straight-chain alkanes.

2. The carbon atoms may form branches. These are branched-chain alkanes.

3. The carbon atoms may form a ring as in cyclic alkanes. Examples are shown in Figure 13.11.

(1) Pentane

(a) (b) (c)

(2) 2-Methyl butane

(a) (b) (c)

(3) Cyclopentane

(a) (b) (c)
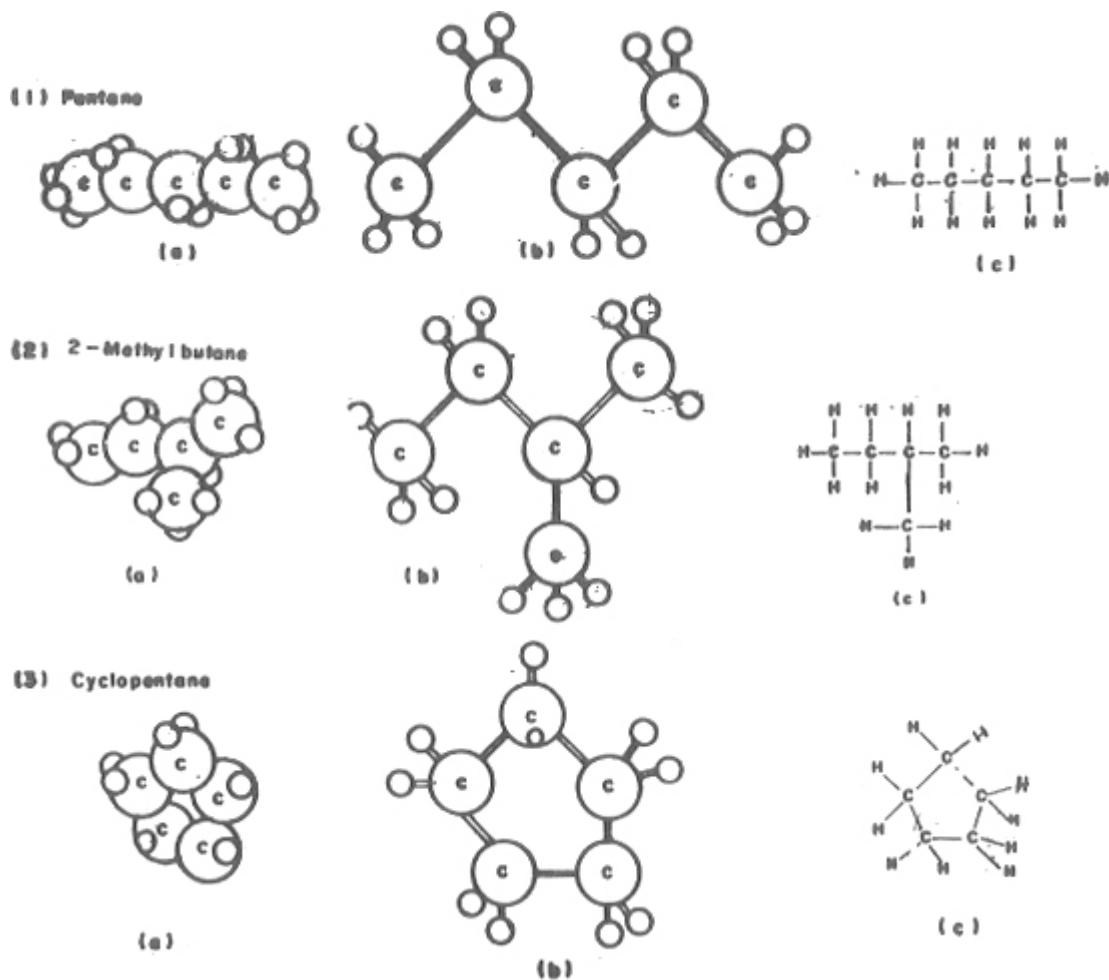
Figure 13.11 Structures of a C$_5$ hydrocarbon (1. straight chain; 2. branched chain; 3. cyclic)

EXERCISE 13D
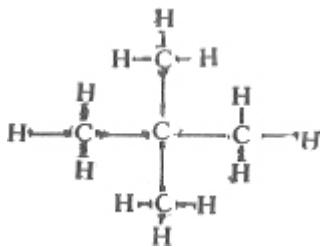
Write down (i) the empirical formula, and (ii) the molecular formula of each of the compounds whose structural formulae are given in the examples above.

Notice that pentane and 2-methyl butane have the same molecular formula, but different structures. They are isomers.

Activity 13.2 Building Models of the isomers of Pentane.

Use balls and spokes. Build the structures of pentane and 2-methylbutane.

There is a third structure with the same molecular formula. Build it also. The compound with that structure is called 2,2-dimethylpropane.

2,2-dimethylpropane

13.7 Nomenclature of Alkanes

The prefix **penta-** in pentane signifies **five**. A pentagon is a five-sided polygon. Recall that the suffix **-ane** is the group name of the alkanes. Thus, the Latin word for the number of consecutively linked carbon atoms, plus the group name, make up the name of the straight-chain alkanes. Examples are given in Table 13.2.

TABLE 13.2 STRAIGHT CHAIN ALKANES

Number of carbon atoms	Molecular formula	Structure of alkane	Name
1	CH_4	H-C-H (with H above and below)	Methane
2	C_2H_6	H-C-C-H	Ethane
3	C_3H_8	H-C-C-C-H	Propane
4	C_4H_{10}	H-C-C-C-C-H	Butane
6	C_6H_{14}	H-C-C-C-C-C-C-H	Hexane
7	C_7H_{16}	H-C-C-C-C-C-C-C-H	Heptane
8	C_8H_{18}	H-C-C-C-C-C-C-C-C-H	Octane
9	C_9H_{20}	H-C-C-C-C-C-C-C-C-C-H	Nonane
10	$C_{10}H_{22}$	H-C-C-C-C-C-C-C-C-C-C-H	Decane

In the name **2-methylbutane**, butane indicates four consecutively linked carbon atoms. 'Methyl' (-CH_3), is a radical derived from methane, CH_4, by loss of a hydrogen atom. 2-methylbutane means that the methyl radical has replaced a hydrogen atom on the second carbon atom in butane. 2,2-dimethylpropane means that two methyl radicals have replaced two hydrogen atoms from the second carbon atom in propane.

The system of naming the branched-chain alkanes therefore, is to select the longest chain of consecutively linked carbon atoms. The number of carbon atoms in that chain is the **root name** of the alkane. To this root name, add the radicals that have replaced hydrogen in forming the branching, and indicate their positions in the chain. To get their positions, number the carbon atoms in the longest chain. **Start numbering from the side that gives the substituents (replacing radicals), the least possible number**.

The replacing groups are called **alkyl radicals**. They have the
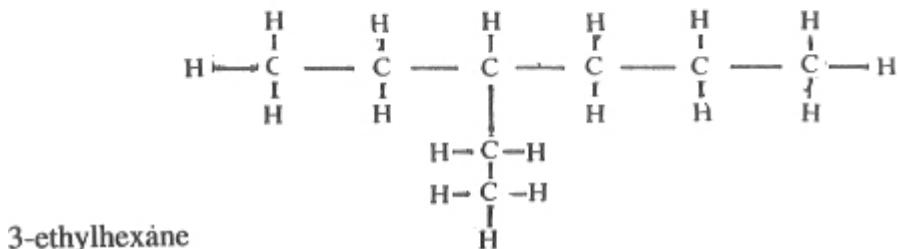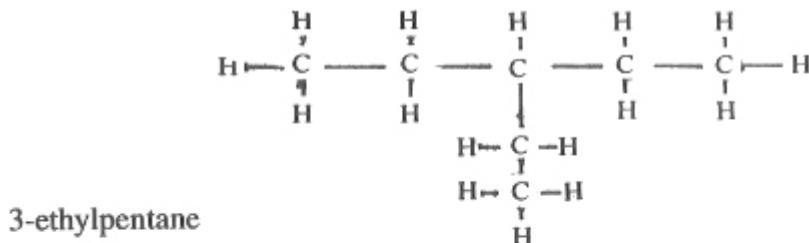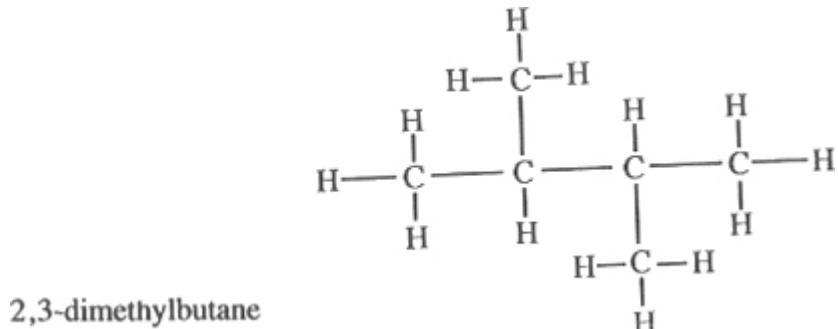
general formula C_nH_{2n+1}. They are derived from alkanes by loss of a hydrogen atom. They are named by replacing the suffix -**ane** of the alkane, by -**yl**.

The common ones are:

From methane: methyl, $-CH_3$. From propane: propyl, $-C_3H_7$.
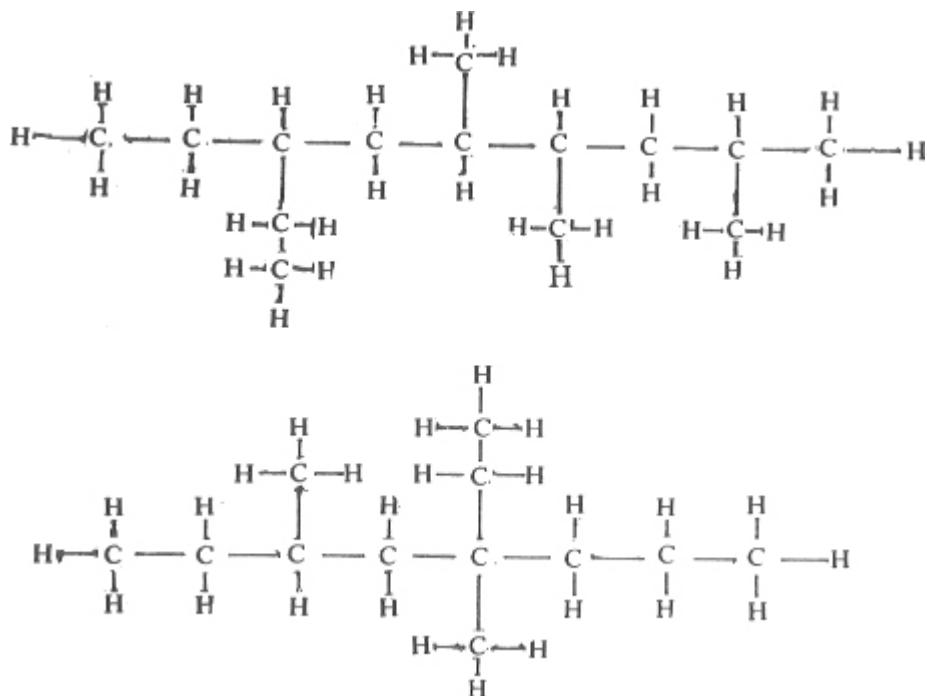
From ethane: ethyl, $-C_2H_5$.　　From butane: butyl, $-C_4H_9$.

Examples of nomenclature:

2,3-dimethylbutane

3-ethylpentane

3-ethylhexáne

EXERCISE 13E

(1)　Name the following alkanes

(2)   Draw the structure of the alkane 2,2,4-trimethylpentane.

(3)   Write the molecular formulae of the alkanes in this exercise. Using these, work out a general formula for the alkanes.

You should have C_nH_{2n+2}, where n is the number of carbon atoms.

Experiment 13. 7 Preparation and study of the properties of methane.

Put 10 spatula-loads of aluminium carbide and about 20 cm³ of water into a boiling tube. Clamp the tube and attach a cork carrying a delivery tube to it (Figure 13.12). Heat the tube, gently at first, then more strongly. Collect the gas given off over water.

$$Al_4C_3(s) + 12H_2O(l) → 4Al(OH)_3(s) + 3CH_4(g)$$
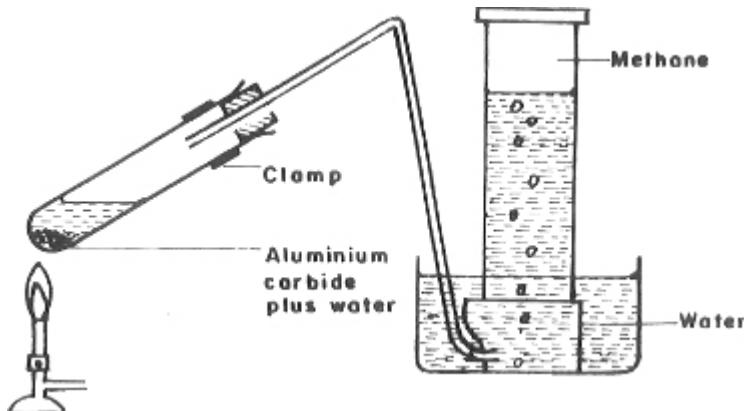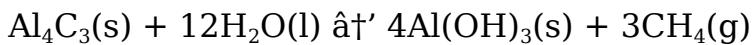
Figure 13.12 Preparation of methane

A mixture of sodium ethanoate and sodalime may be heated in place of aluminium carbide and water, to generate methane.

$$CH_3COONa(s) + NaOH(s) \rightarrow Na_2CO_3(s) + CH_4(g)$$

Sodalime is a mixture of calcium oxide and sodium hydroxide, but the active ingredient in this mixture is sodium hydroxide.

Carry out the following tests on the gas.

1. Note the colour. Smell the gas and note its odour.
2. Hold a flame close to a gas jar of methane, then take off the gas jar cover. Note how readily the gas catches fire. Also note the nature of the flame, and whether a residue remains after burning.
3. Before the gaseous product of the burning escapes, add about $1cm^3$ of lime water into the gas jar and shake.
4. Pass the gas into $1cm^3$ of dilute potassium tetraoxomanganate(VII) solution acidified with 3 drops of dilute tetraoxosulphate(VI) acid, then shake. Does a change in colour occur?

13.8   Properties of Alkanes

The alkanes constitute a homologous series and therefore the members have similar properties. A study of the properties of the first member, methane, illustrates the properties of the alkane family.
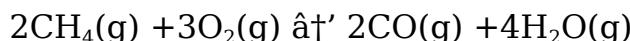
Properties of methane

1. Methane is a colourless, odourless gas. It is non-poisonous.
2. It is insoluble in water. Hence it can be collected over water.
3. It burns in air or in oxygen with a smokeless, non-luminous flame. Carbon(IV) oxide and water vapour are formed. No residue is left.

   The blue flame is a test for saturation. Smoke is not formed because of the low carbon contents. Infact, methane burns explosively if it is in excess. This is the cause of fire disasters in coal mines. The marsh gas associated with coal mines consists mainly of methane.

   $$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) + Heat$$
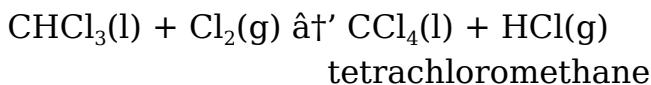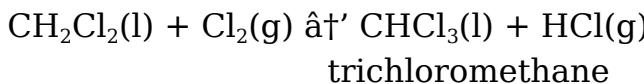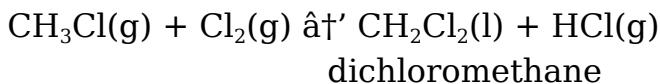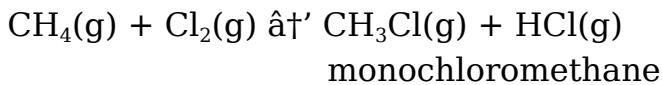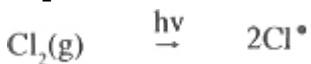
   In insufficient air, carbon(II) oxide is formed.

   $$2CH_4(g) + 3O_2(g) \rightarrow 2CO(g) + 4H_2O(g)$$

4. Action with oxidizing agents: Methane is rather unreactive to oxidizing agents such as potassium tetraoxomanganate(VII). The purple colour of this reagent is therefore not discharged when it is shaken with methane.
5. Action with halogens: In the presence of light, (but not in darkness) methane reacts with halogens, forming halogenomethanes and hydrogen halide. The light energy is necessary for initiating the reaction. It breaks up the halogen molecule into reactive free radicals. The radicals then replace

hydrogen atoms from methane, one after the other. This stepwise replacement reaction is known as **a substitution reaction**.

$$Cl_2(g) \xrightarrow{h\nu} 2Cl^\bullet$$

$CH_4(g) + Cl_2(g) →$ $CH_3Cl(g) + HCl(g)$
<div align="center">monochloromethane</div>

$CH_3Cl(g) + Cl_2(g) →$ $CH_2Cl_2(l) + HCl(g)$
<div align="center">dichloromethane</div>

$CH_2Cl_2(l) + Cl_2(g) →$ $CHCl_3(l) + HCl(g)$
<div align="center">trichloromethane</div>

$CHCl_3(l) + Cl_2(g) →$ $CCl_4(l) + HCl(g)$
<div align="center">tetrachloromethane</div>

13.9 Uses of Alkanes

1. By far the most important use of methane and other gaseous and liquid alkanes, is for fuel. Refinery gases, CH_4 to C_4H_{10}, are compressed and stored in metallic cylinders for use as domestic and industrial fuels. Petrol, kerosene, diesel oil, which are fuel oils from the distillation of petroleum, are all alkanes. A lot of heat is liberated when they burn.

2. The halogenoalkanes are important intermediate compounds in organic synthesis. That is, they are first made from methane and then used to make other compounds. Trichloromethane (chloroform), and its' iodine equivalent, triiodomethane, (iodoform) CHI_3, are important in medicine. Chloroform was used as an anaesthetic, while iodoform is still used as a germicide.
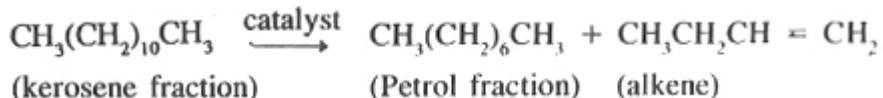
13.10 Cracking and Reformation of Petrol

In the early days of the petroleum industry, petroleum was distilled mainly for kerosene which was the much-needed, fraction. But currently the highest demand is for petrol. Only 20% of the refinery products is petrol, a quantity far less than the demand for the product. To meet the high demand, some of the long-chain hydrocarbons are split into shorter chain (C_5 - C_8) hydrocarbons, which fall into the petrol fraction. This is termed cracking.

> **Cracking is the splitting of long-chain hydrocarbons of kerosene or diesel oil fraction to shorter-chain hydrocarbons to get more petrol.**

Initially, cracking was achieved by subjecting the long-chain hydrocarbons to high temperature, (above 500°C), and high pressure (about 200 atmospheres). It was then termed **thermal cracking**. Today it can be achieved at lower temperatures and near atmospheric pressure, in the presence of catalysts (**catalytic cracking**). Alumina

and silica are used as catalysts.

$$CH_3(CH_2)_{10}CH_3 \xrightarrow{\text{catalyst}} CH_3(CH_2)_6CH_3 + CH_3CH_2CH = CH_2$$

(kerosene fraction)　　　　(Petrol fraction)　(alkene)

Straight-chain alkanes, such as heptane, burn explosively inside internal combustion engines. The engine is said to **"knock"**. Knocking damages the engines. Branched-chain hydrocarbons, such as 2, 2, 3 - trimethylpentane (iso-octane) burn smoothly. That is, they do not knock. They are regarded as good quality petrol. The use of these two alkanes in rating petrol was discussed in Book 1 when we learned that good quality petrol is one that has high octane number.

Cracking does not just break down long-chain hydrocarbons. It also produces branched-chain hydrocarbons. So it improves the quality of petrol. The quality of petrol is also improved by adding various "antiknock" agents. Lead tetraethyl, $Pb(CH_3)_4$, is the most common of the antiknocking agents added to improve petrol quality. Recently, however, its use is being questioned because it pollutes the atmosphere. The lead finds its way into the air as volatile lead halides into which lead deposit in the car exhaust system is coverted.

EXERCISE 13F

What is the action of (i) heat, (ii) potassium tetraoxomanganate(VII), (iii) chlorine on ethane?
Write equations for the reactions if any.

13.11 Gradation in Physical Properties of Alkanes

The alkanes resemble one another in their chemical reactions only. Their physical properties are different, but there is some order in the differences. They show a gradation (stepwise increase) with increasing molecular mass. This is illustrated in Table 13.3.

TABLE 13.3 PHYSICAL PROPERTIES OF ALKANES

Alkane	Formula	State	M.p.(°C)	B.p.(°C)	Density (g cm⁻³)
Methane	CH_4	Gas	-182	-162	—
Ethane	C_2H_6	,,	-183	-89	—
Propane	C_3H_8	,,	-187	-42	—
Butane	C_4H_{10}	,,	-138	0	—
Pentane	C_5H_{12}	Liquid	-130	36	0.626
Hexane	C_6H_{14}	,,	-95	69	0.659
Heptane	C_7H_{16}	,,	-92	98	0.684
Octane	C_8H_{18}	,,	-57	126	0.703
Nonane	C_9H_{20}	,,	-54	151	0.718
Hexadecane	$C_{16}H_{34}$	,,	18.5	286	0.775

Note: Figures are quoted for straight-chain isomers.

C: ALKENES

Alkenes are unsaturated hydrocarbons. They contain at least one carbon carbon double bond. They have the general formula C_nH_{2n} (if there is only one double bond). Their characteristic reaction is addition reaction which results in the formation of saturated compounds.

Activity 13.3 Building a model of ethene

Join two balls which represent carbon atoms with two bent spokes. Each ball still has two holes left. Join these, through straight short spokes to the balls representing hydrogen atoms. The model you have made (Figure 13.13) represents a molecule of ethene.
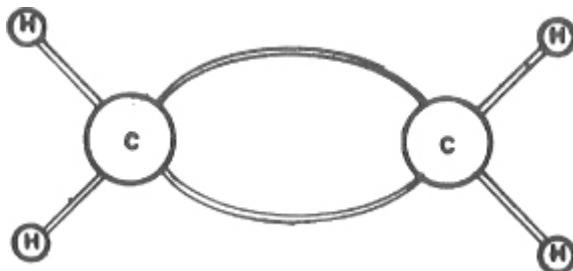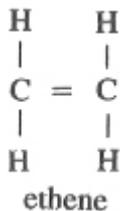
Figure 13.13 Ethene molecule

On paper, it is represented as:

```
H       H
|       |
C   =   C
|       |
H       H
   ethene
```

The two carbon atoms are linked by two bonds, and the compound is said to be **unsaturated** because it can take up two more hydrogen atoms (one on each carbon atom) to become saturated.
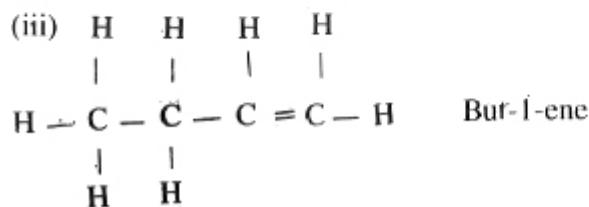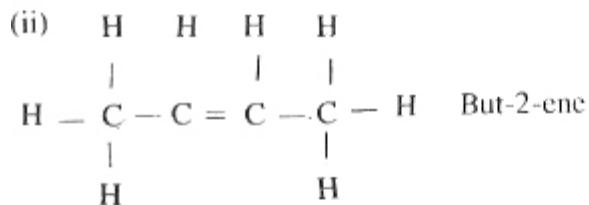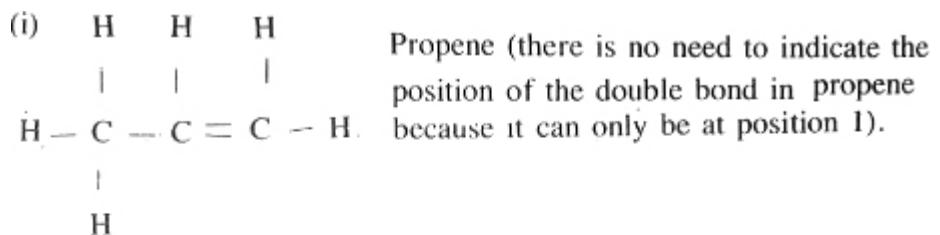
Replacing a hydrogen in ethene with a methyl radical, gives the next member, propene. Further replacements produce other members of the homologous series of alkenes.
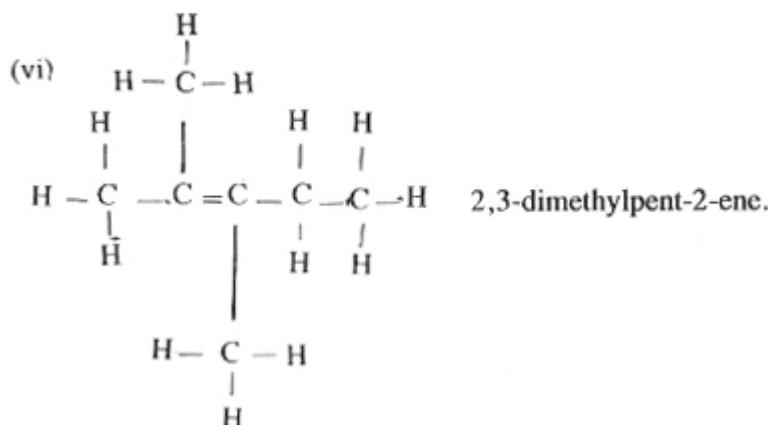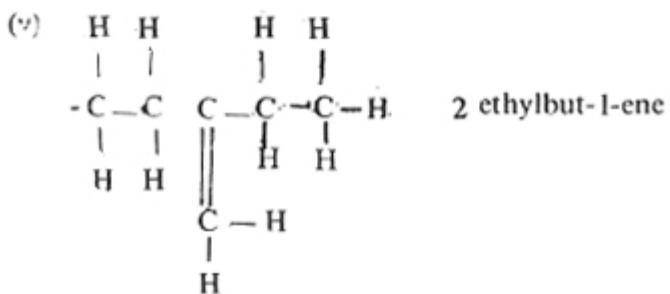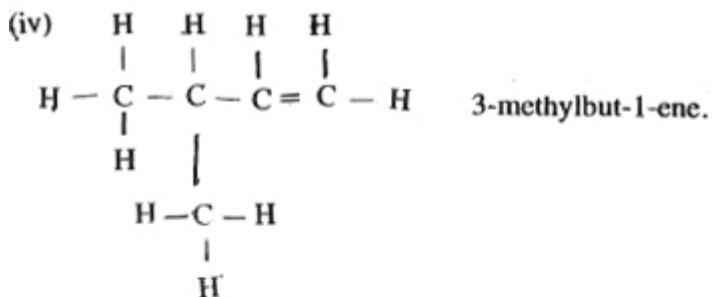
13.12 Nomenclature of Alkenes

The following procedure is used for naming the alkenes.

1.   Select the longest chain of consecutively joined carbon atoms containing a double bond. The alkene derives its name from the Latin word for the number of carbon atoms in that chain.

2.   Number the chain in such a way as to give the carbon atoms of the double bond the least possible numbers.

3.   Indicate the positions of substituents, if any.

4.   Indicate the position of the double bond with the lowest number possible, by starting your numbering from the end of the chain that bears the carbon atoms carrying the double bond.

5.   Complete the naming by adding the suffix **-ene**.

Here are some examples:

(i)

```
     H    H    H
     |    |    |
H —  C —  C =  C  —  H
     |
     H
```

Propene (there is no need to indicate the position of the double bond in propene because it can only be at position 1).

(ii)

```
     H    H    H    H
     |         |    |
H —  C —  C =  C  —  C  —  H
     |              |
     H              H
```

But-2-ene

(iii)

```
     H    H    H    H
     |    |    |    |
H —  C —  C —  C  = C  —  H
     |    |
     H    H
```

But-1-ene

(iv)

$$H-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\underset{\underset{\displaystyle \underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{H-C-H}}}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{C}=\overset{\overset{\displaystyle H}{|}}{C}-H$$ 3-methylbut-1-ene.

(v)

$$-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}\quad C-\overset{\overset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle H}{|}}{C}-H$$ 2 ethylbut-1-ene

(vi)

$$H-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}\quad\underset{\underset{\displaystyle H-C-H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}=C-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H$$ 2,3-dimethylpent-2-ene.
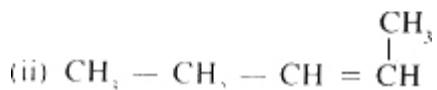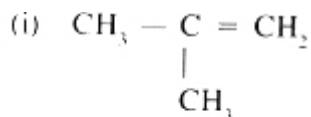
EXERCISE 13G

Name the following alkenes

(i) $CH_3 - \underset{\underset{\displaystyle CH_3}{|}}{C} = CH_2$

(ii) $CH_3 - CH_2 - CH = \overset{\overset{\displaystyle CH_3}{|}}{CH}$

Note the punctuation system in the examples above. Where there are two or more substituents, commas are used to separate the numbers indicating the positions of the substituents; hyphens are used to separate the last number from the alkyl group, while hyphens also separate the number(s) indicating the position(s) of the double bond from the stem name and the suffix -ene. The whole name is written

together without a break.

13.13 Preparation of Alkenes

Gennerally, alkenes are prepared by the dehydration of the corresponding ethanol using concentrated tetraoxosulphate(VI) acid. This is illustrated with the preparation of ethene.

Experiment 13.8 Preparation and study of the properties of ethene.

Put about 50cm³ of ethanol into a round-bottomed flask. Add about 80cm³ of concentrated tetraoxosulphate(VI) acid and some anti-bumping granules to it. Insert a thermometer whose maximum reading is 200Â°C or more. Connect the apparatus as shown in Figure 13.14. Heat the flask till the thermometer reading is 170Â°C. Maintain the temperature between 170Â°C and 180Â°C as the reaction proceeds. The equation for the reaction is:

$$C_2H_5OH(l) \xrightarrow[\text{conc. } H_2SO_4]{170°C} C_2H_4(g) + H_2O(g).$$
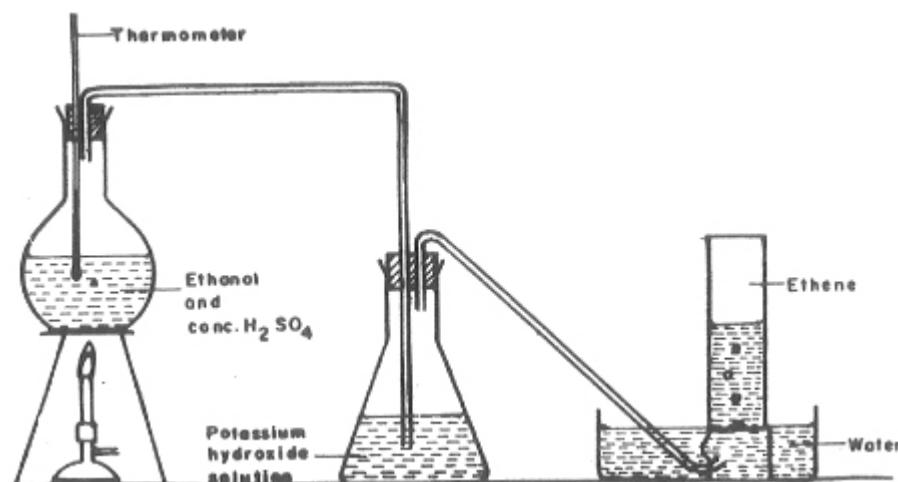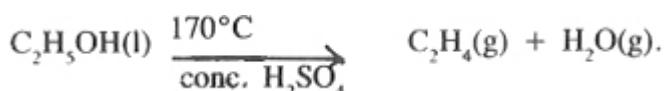
Figure 13.14 Preparation of ethene

The equation can be written in two steps:

1. $C_2H_5OH(l) + H_2SO_4(aq) \rightarrow C_2H_5HSO_4(aq) + H_2O(l)$

2. $C_2H_5HSO_4(aq) \xrightarrow{170°C} H_2SO_4(aq) + C_2H_4(g)$

As the gas is evolved in the round-bottomed flask, it passes through the sodium hydroxide solution in the conical flask. Any acid spray from the round-bottomed flask is removed.

Collect about five gas jars of ethene, and use them for the following tests.

1. Note the colour and odour of the gas.

2. Bring a bunsen flame near the mouth of a gas jar of ethene, then

remove its cover. Note the nature of the burning gas.

3.   And five drops of potassium tetraoxomanganate(VII), then three drops of dilute tetraoxosulphate(VI) acid into another gas jar of ethene. Shake to mix well. Record your observation.

4.   Shake another gas jar of the gas with bromine water and record any colour changes.

5.   Add a drop of sodium hydroxide to silver trioxonitrate(V) solution, then add dilute ammonia solution till the initial precipitate redissolves. Put this ammoniacal silver trioxonitrate(V) solution into the fifth gas jar of ethene and shake. Record your observation.

EXERCISE 13H

(i)   What is the function of concentrated tetraoxosulphate(VI) acid in the preparation of ethene from ethanol?

(ii)   Name the alkanol you would need for the preparation of propane by the same method.

13.14 Properties of Alkenes
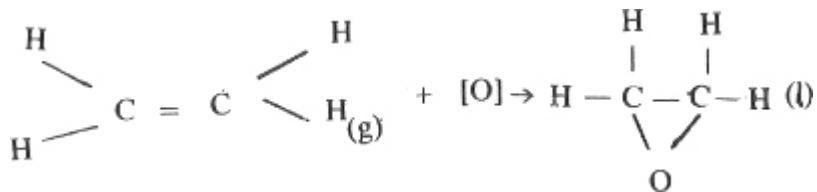
Members of the homologous series of the alkenes undergo similar chemical reactions. The chemical properties of ethene are listed below to illustrate these.

1.   Ethene is a colourless gas.

2.   It is insoluble in water.

3.   It burns in air or oxygen with a luminous flame and some smoke. This is a general test for unsaturation in hydrocarbons.

4.   It decolourises acidified potassium tetraoxomanganate(VII) solution and bromine water, and turns acidified potassium heptaoxodichromate(VI) solution green. These are tests for reducing agents. So ethene and all alkenes act as reducing agents.

The alkanes do not react with these oxidizing agents. This implies that the double bond makes ethene reactive. One of the bonds between the two carbon atoms is weak and is easily broken. When it breaks, each of the two carbon atoms can add on a new atom or group of atoms. This type of reaction is called an **addition reaction**.
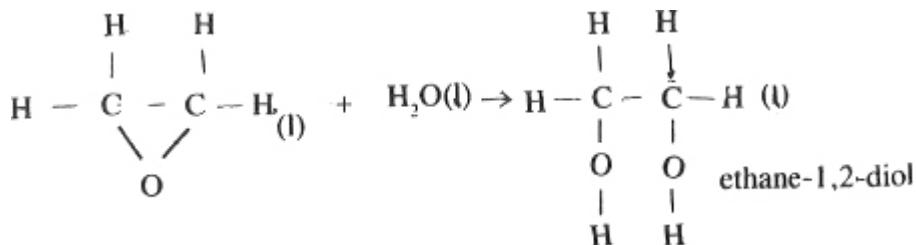
Addition reactions are characteristic of alkenes and all other unsaturated organic compounds.

The atoms or groups that can be added to a double bond include hydrogen, halogens, hydrogen halides, water and tetraoxosulphate(VI) acid. The common addition reactions of the alkenes are listed below.
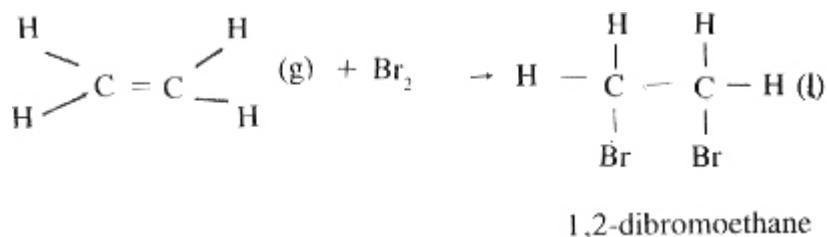
1.   **Addition of oxygen from an oxidizing agent:** This reaction is responsible for the changes in colour recorded in tests 3 and 4 of Experiment 13.8. The oxidizing agent provides oxygen atom for addition across the double bond.

$$\underset{H}{\overset{H}{>}}C = C\underset{H}{\overset{H}{<}}_{(g)} + [O] \rightarrow H - \underset{\underset{O}{\diagdown\diagup}}{\overset{H}{\underset{|}{C}}} - \overset{H}{\underset{|}{C}} - H \ (l)$$
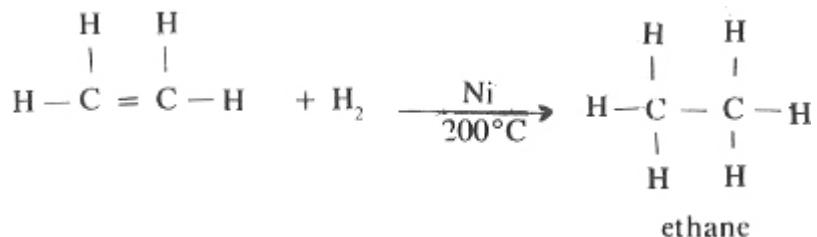
The product, ethene oxide, is quickly hydrolysed by water to ethane-1,2-diol.

$$H - \overset{H}{\underset{|}{C}} - \overset{H}{\underset{\underset{O}{\diagdown\diagup}}{C}} - H_{(l)} + H_2O(l) \rightarrow H - \overset{H}{\underset{\underset{|}{O} \\ \underset{|}{H}}{C}} - \overset{H}{\underset{\underset{|}{O} \\ \underset{|}{H}}{C}} - H \ (l) \quad \text{ethane-1,2-diol}$$

2. **Addition of bromine:** This addition reaction occurs at room temperature between the gaseous molecules, or between the molecules in water. The violet colour of the bromine is discharged as evidence of the addition. This reaction takes place in the absence of sunlight unlike the substitution reaction in alkanes.

$$\underset{H}{\overset{H}{>}}C = C\underset{H}{\overset{H}{<}}_{(g)} + Br_2 \rightarrow H - \overset{H}{\underset{\underset{Br}{|}}{C}} - \overset{H}{\underset{\underset{Br}{|}}{C}} - H \ (l)$$

1,2-dibromoethane
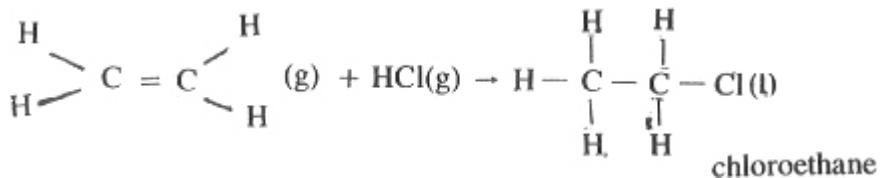
3. **Addition of hydrogen**: Hydrogen adds on well in the presence of a catalyst such as nickel, palladium, or platinum. The reaction is termed a **catalytic hydrogenation**.

$$H - \overset{H}{\underset{|}{C}} = \overset{H}{\underset{|}{C}} - H + H_2 \xrightarrow[200°C]{Ni} H - \overset{H}{\underset{\underset{H}{|}}{C}} - \overset{H}{\underset{\underset{H}{|}}{C}} - H$$

ethane
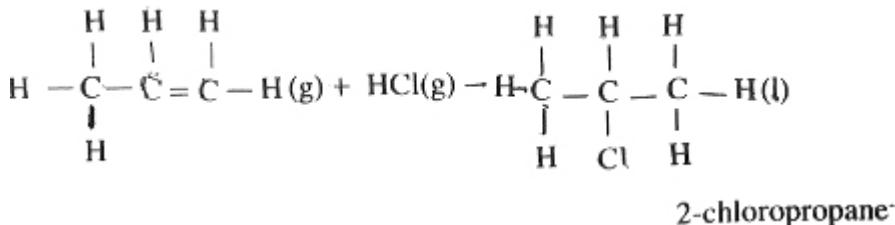
One mole of hydrogen gas is used up when one mole of an alkene which has only one double bond per molecule, is hydrogenated.

4. **Addition of hydrogen halide**: The addition can take place at room temperature. Hydrogen atom adds on to one carbon atom, and the halogen atom to the second carbon atom of the double bond.

$$H_2C = CH_2 \text{ (g)} + HCl\text{(g)} \rightarrow H - \underset{\underset{H,}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - Cl\text{ (l)}$$

chloroethane

With propene and hydrogen chloride, 2-chloropropane is formed.

$$H - \underset{\underset{H}{\downarrow}}{\overset{\overset{H}{|}}{C}} - \overset{\overset{H}{|}}{C} = \overset{\overset{H}{|}}{C} - H \text{ (g)} + HCl\text{(g)} \rightarrow H\text{-}\overset{\overset{H}{|}}{C} - \underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}} - \overset{\overset{H}{|}}{C} - H\text{(l)}$$

2-chloropropane
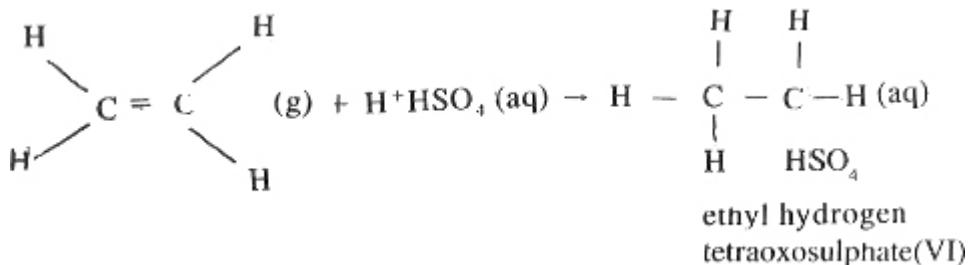
When an unsymmetrical compound containing hydrogen and another atom or group of atoms, e.g, H-Cl, H-OH, H-HSO$_4$, are added to an alkene which has two hydrogens on one of the carbons at the double bond, and only one hydrogen on the other (as in propene, CH$_2$-CH=CH$_2$), the hydrogen atom adds to the carbon to which two hydrogen atoms are already attached. The other atom or group of atoms such as -Cl, -OH, or -HSO$_4$, etc, adds on to the carbon atom with only one hydrogen atom attached to it. This rule i called the **Markownikoffâ€™s rule.**

5. **Addition of tetraoxosulphate(VI) acid:** The product of the addition is ethyl hydrogen tetraoxosulphate(VI). Tetraoxosulphate(VI) acid in water ionises according to the equation.

$$H_2SO_4 \xrightarrow{H_2O} H^+ + HSO_4$$

When it reacts with an alkene, the reaction is:

$$H_2C = CH_2 \text{ (g)} + H^+HSO_4 \text{ (aq)} \rightarrow H - \underset{\underset{HSO_4}{|}}{\overset{\overset{H}{|}}{C}} - \overset{\overset{H}{|}}{C} - H \text{ (aq)}$$

ethyl hydrogen
tetraoxosulphate(VI)
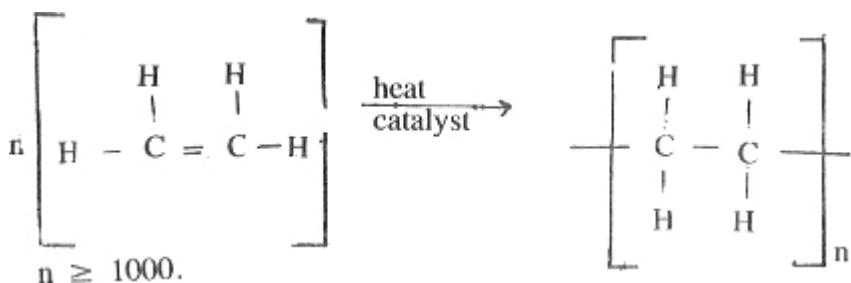
6. **Polymerisation of ethene.**

    Polymerisation is the linking up of many units of small molecules called monomers, to form a single large unit known as a polymer, without a gain or loss in mass.

Many ethene molecules are able to join up in this way (when heated to

a high temperature, under pressure, and in the presence of a peroxide or oxygen) to form a compound with a large relative molecular mass.

$$n \begin{bmatrix} & H & H \\ & | & | \\ H - & C = & C - H \\ & & \end{bmatrix} \xrightarrow[\text{catalyst}]{\text{heat}} \begin{bmatrix} & H & H \\ & | & | \\ - & C - & C - \\ & | & | \\ & H & H \end{bmatrix}_n$$

n ≥ 1000.

The ethene molecules are the monomers, while the large unit (polythene) which is formed, is the polymer. Polymerisation of ethene is now carried out in industries near atmospheric pressure, in the presence of catalysts.

Experiment 13.9: Demonstrating Polymerisation in Phenylethene.

Put 10cm^3 of phenylethene into a 100cm^3 distillation flask. Add 0.lg of an organic peroxide such as lauryl peroxide to it. Fit a reflux condenser to the flask (i.e, a Liebig condenser placed upright as in Figure 13.15. Heat the flask for about one hour at a temperature not exceeding 160Â°C. Allow it to cool after one hour, then pour the contents of the flask into a beaker containing 50cm^3 of methanol. A white solid mass, polyphenylethene, is formed.
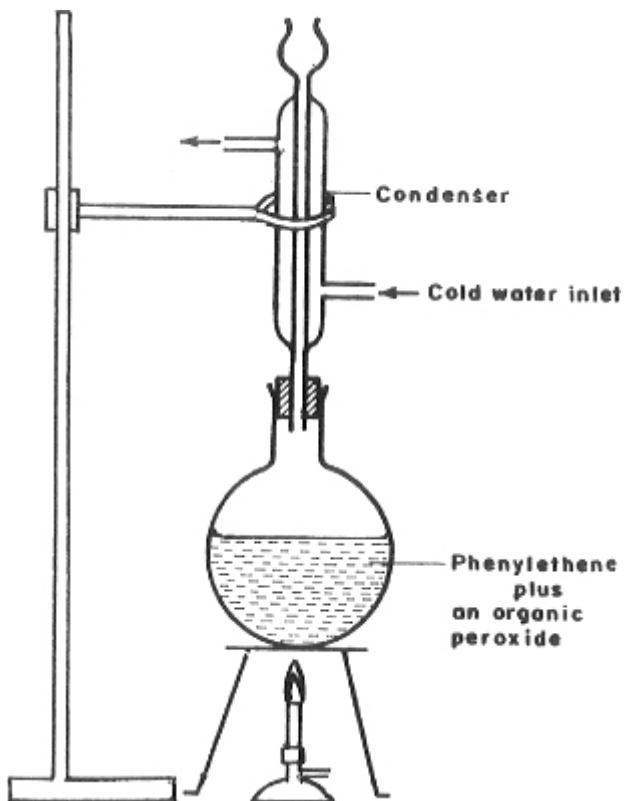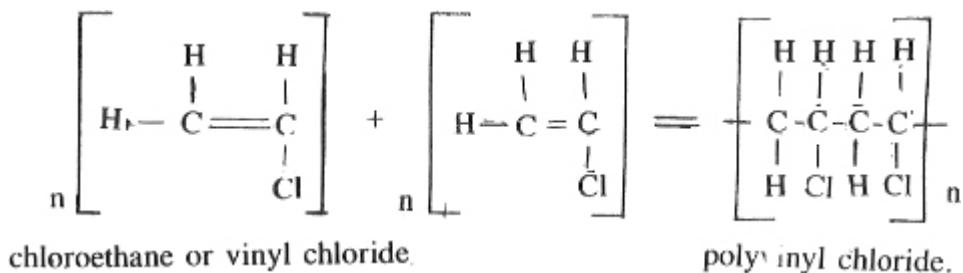

Figure 13.15. Refluxing phenylethene

Chloroethene (vinyl chloride) was the first monomer to be made into a polymer, polyvinyl chloride (PVC), in 1917.

chloroethane or vinyl chloride.   poly inyl chloride.

EXERCISE 13I

(i)   How many isomers does the alkane C_4H_{10} have?

(ii) What is the difference between but-l-ene and but-2-ene?

7.   Geometrical isomerism
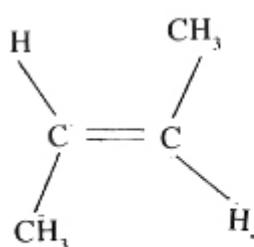
The double bond in alkenes prevents free rotation of the two carbons joined by the double bond. As a result, any atom attached to a particular side of the bond is fixed on that side and can only change to another side if the bond is broken and reformed. This is unlike the case in a carbon to carbon single bond, C-C, where there is free rotation.

When two atoms of the same elements or two identical groups of atoms are on the same side of a double bond, we have a cis isomer, but if they are on opposite sides, we have a **trans isomer**.
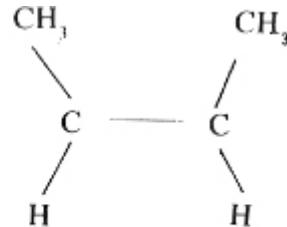
> **Geometrical isomerism is defined as the existence of two organic compounds with the same molecular and structural formulae, but different spatial arrangements of the atoms or groups of atoms at the double bond.**

Activity 13.4 Building Models of the Geometrical Isomers of Trans-but-2-ene.

Build models of the two structures below, and recognise them as different.

trans-but-2-ene   cis-but-2-ene

These two structures represent two isomers of but-2-ene. Their isomerism is due to the different arrangements of the groups in space.
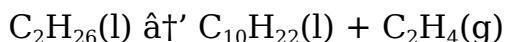
This type of isomerism is called geometrical isomerism, or cis-trans isomerism.

13.15 Uses of Ethene

Ethene is used:

1.   in the making of polythene used for packages, plastic containers, toys, etc.

2.   to quicken the ripening of fruits.

3.   as a starting material for the making of many industrial chemicals.

Note: The ethene used for these purposes is obtained primarily from the cracking of petroleum products.

$C_2H_{26}(l) ât' C_{10}H_{22}(l) + C_2H_4(g)$

D.   ALKYNES

The alkynes are unsaturated hydrocarbons which have a triple bond between two adjacent carbon atoms. The alkynes have the general formula C_nH_{2n-2}. Ethyne, C_2H_2, is the first and the only important and common member of the series.

Activity 13.5: Building a model of ethyne.

Use two black balls to represent carbon atoms and two white balls to represent hydrogen atoms. Join the two carbon balls with three spokes, and each of the hydrogen balls to one carbon ball. The result is a model of the structure of ethyne (Figure 13.16).


H — C ≡ C — H
Paper representation
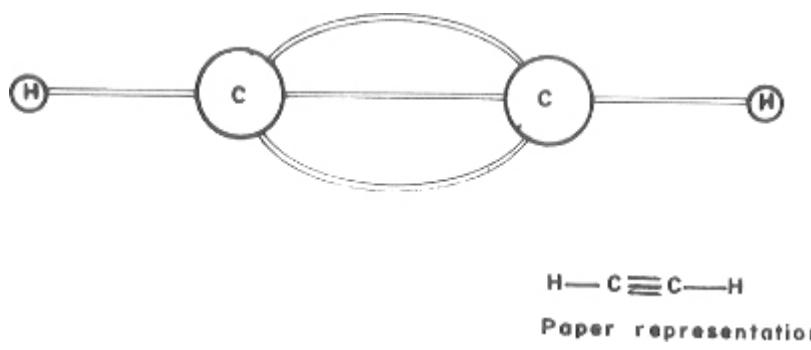
Figure 13.16 Ethyne molecule

13.16 Nomenclature of alkynes

They are named like the alkenes by replacing the suffix **-ene** of alkenes with **-yne**. Some members of the series are as follows.
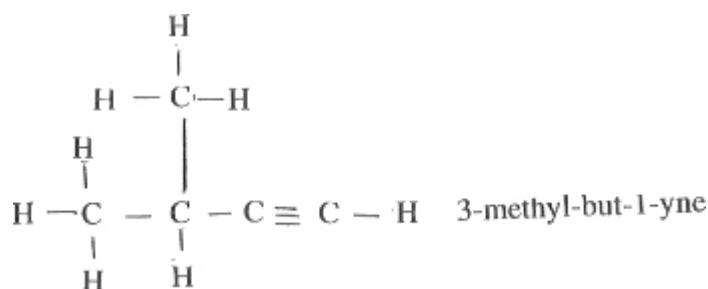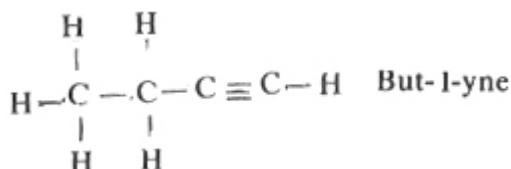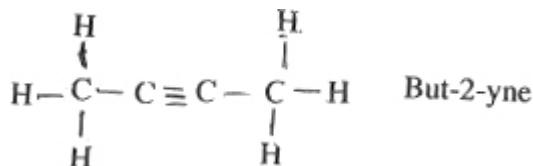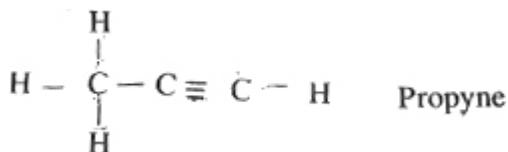
 Ethyne: C_2H_2

Propyne: C_3H_4

Butyne: C_4H_6
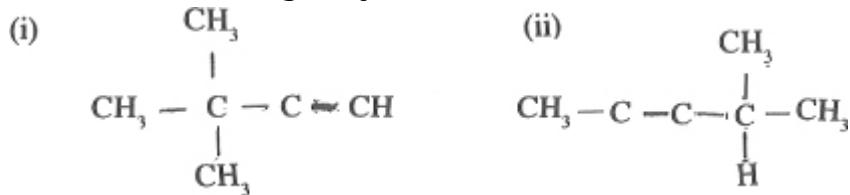
Pentyne: C_5H_8.

The structural formula of some of these alkynes and their isomers are drawn below.

$$H - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - C \equiv C - H \qquad \text{Propyne}$$

$$H - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - C \equiv C - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - H \qquad \text{But-2-yne}$$

$$H - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - C \equiv C - H \qquad \text{But-1-yne}$$

$$H - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\overset{\displaystyle H}{|}}{\underset{\displaystyle H - C - H}{|}}}{\underset{\underset{\displaystyle H}{|}}{C}} - C \equiv C - H \qquad \text{3-methyl-but-1-yne}$$

EXERCISE 13J

1. Write the structural formulae and name all the alkynes with the molecular formula, C_4H_6.

2. Name the following alkynes:

(i)

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

(ii)

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

13.17 Properties of Alkynes

The properties of ethyne are representative of the general properties of the alkynes.

*Experiment 13.10: Preparation and study of the properties of ethyne.*
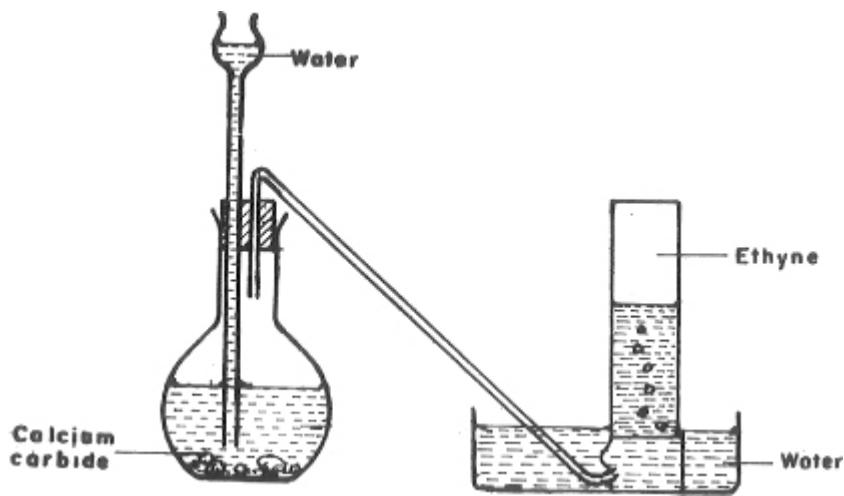
Figure 13.17 Preparation of ethyne

Add some lumps of calcium carbide into a flat-bottomed flask. Insert a cork fitted with a thistle funnel and a delivery tube. Pour water through the thistle funnel into the flask. Allow some bubbles of air to escape, then collect the gas evolved by downward displacement of water. Collect five jars of the gas.

$$CaC_2(s) + 2H_2O(l) → Ca(OH)_2(aq) + C_2H_2(g)$$

Carry out the following tests on the gas collected.

1. Smell the gas and observe its colour.

2. Bring a flame near the mouth of a jar of the gas, then remove the cover. Note how readily it catches fire, and note the nature of the flame.

3. Put about $1cm^3$ of potassium tetraoxomanganate(VII) solution, then a few drops of dilute tetraoxosulphate(VI) acid into a jar of ethyne. Shake and observe any change in colour.

4. Put about $1cm^3$ of bromine water into another jar of the gas and shake. Again, note any change in colour.

5. Bubble the gas into a test-tube containing copper(I) chloride solution in dilute aqueous ammonia, and shake. Note any change that occurs. Immediately after making your observation, pour the contents of the test-tube into about $10cm^3$ of concentrated hydrochloric acid to destroy the explosive product of the reaction!!

6. Add a drop of sodium hydroxide solution to silver trioxonitrate(V) solution to precipitate silver oxide, (N.B., silver hydroxide does not exist). Add dilute ammonia solution, drop by drop, till the precipitate just dissolves. Bubble the gas into the resulting ammoniacal silver oxide solution.
    Note any change occurring.

EXERCISE 13K

From these results, and from the results of the tests on methane and ethene, how can you distinguish between alkanes, alkenes and alkynes?
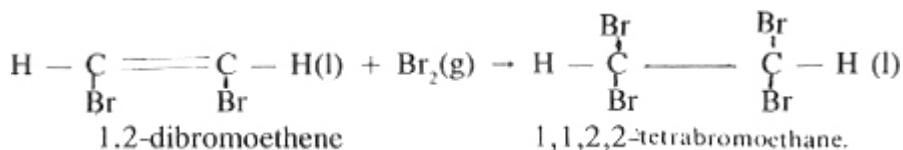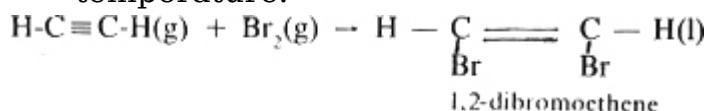
Properties of ethyne

1. Ethyne is a colourless, almost odourless gas.
2. It is insoluble in water.
3. It burns with a luminous sooty flame.

$$2C_2H_2(g) + 5O_2(g) → 4CO_2(g) + 2H_2O(g) + Heat.$$
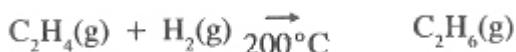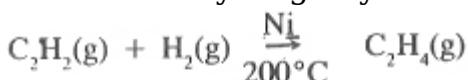
4. Like ethene, the principal reaction of ethyne is addition reaction because it is unsaturated. It therefore decolourises acidified potassium tetraoxomanganate(VII) solution, bromine water or bromine in tetrachloromethane. The addition reactions of ethyne are listed below :-

    (a) **Halogenation:** The halogenation reaction of ethyne is more vigorous than that of ethene because of its greater unsaturation. The addition of bromine takes place at room temperature.
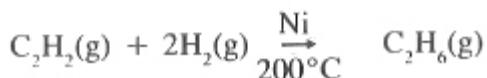

Chlorine reacts similarly, but chlorine is not used to test for reducing agents (or unsaturation) because no colour change will be observed. Moreover, chlorine reacts explosively with ethyne in the presence of sunlight.

    (b) **Hydrogenation reaction:** Ethyne adds on hydrogen at high temperature and in the presence of a catalyst. It first adds on one mole of hydrogen to form ethene. The addition of another mole of hydrogen yields ethane.

$$C_2H_2(g) + H_2(g) \xrightarrow[200°C]{Ni} C_2H_4(g)$$

$$C_2H_4(g) + H_2(g) \xrightarrow{200°C} C_2H_6(g)$$
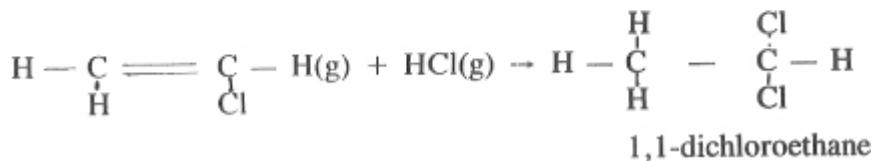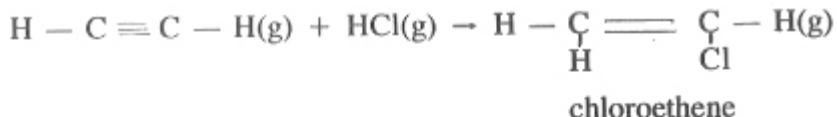
These can be written as one equation.

$$C_2H_2(g) + 2H_2(g) \xrightarrow[200°C]{Ni} C_2H_6(g)$$
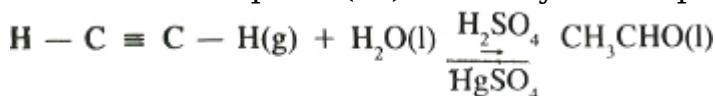
One mole of ethyne therefore adds on two mole of hydrogen to

become fully saturated.
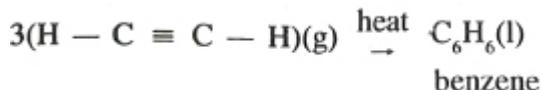
(c) **Addition of hydrogen halides:** Hydrogen halides add on in two steps:

$$H - C \equiv C - H(g) + HCl(g) \rightarrow H - \underset{\underset{H}{|}}{C} = \underset{\underset{Cl}{|}}{C} - H(g)$$

chloroethene

$$H - \underset{\underset{H}{|}}{C} = \underset{\underset{Cl}{|}}{C} - H(g) + HCl(g) \rightarrow H - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}} - H$$

1,1-dichloroethane

(d) **Addition of water:** Water adds on in the presence of tetraoxosulphate(VI) acid, with mercury(II) tetraoxosulphate(VI) as catalyst. The product is ethanal.

$$H - C \equiv C - H(g) + H_2O(l) \xrightarrow[\overline{HgSO_4}]{H_2SO_4} CH_3CHO(l)$$
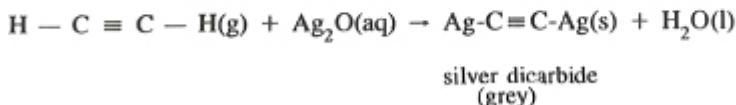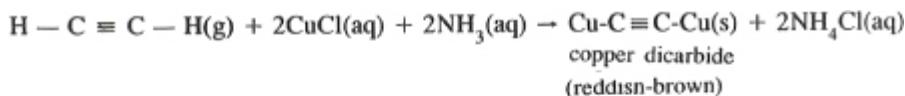
(e) **Polymerization of ethyne:** Polymerisation is limited to three molecules of ethyne linking up to form benzene. This happens when ethyne is passed into a red-hot tube.

$$3(H - C \equiv C - H)(g) \xrightarrow{heat} C_6H_6(l)$$

benzene

5. **Organometallic compounds of alkynes**

The addition reactions of ethyne such as its decolourisation of acidified tetraoxomanganate(VII) or bromine water only serve to distinguish it from the saturated hydrocarbons, alkanes, but not from alkenes. However, ethyne precipitates reddish-brown copper(I) dicarbide (or acetylide) with ammoniacal copper(I) chloride. It also forms a grey precipitate of silver dicarbide with ammoniacal silver oxide solution. Alkenes do not do this.

$$H - C \equiv C - H(g) + 2CuCl(aq) + 2NH_3(aq) \rightarrow Cu-C \equiv C-Cu(s) + 2NH_4Cl(aq)$$

copper dicarbide
(reddish-brown)

$$H - C \equiv C - H(g) + Ag_2O(aq) \rightarrow Ag-C \equiv C-Ag(s) + H_2O(l)$$

silver dicarbide
(grey)

The dicarbides of copper and silver are explosive when dry. They must be destroyed as soon as the observation has been made.

13.18 Uses of Ethyne

1. Ethyne is mixed with oxygen and burnt to produce a very hot flame (oxyacetylene flame) of above 2000Â°C, which is used in welding and cutting of metals.

2. Ethyne is also used for the synthesis of many industrial chemicals.

1. Which of the following hydrocarbons will decolourise bromine water?
    (a) ethane
    (b) ethene
    (c) ethyne
    (d) propane
    (e) propene
    (f) propyne

2. Write the structural formulae of
    (i) 2,3-dimethylbut-l-yne.
    (ii) but-2-yne.

3. Why is ethyne used in welding? What is the name given to its flame which is used in welding?

E: AROMATIC HYDROCARBONS

Benzene and its homologues are aromatic hydrocarbons. Their molecular formulae show high degree of unsaturation, yet they do not take part in many of the reactions typical of unsaturated compounds. This presented a problem for quite some time until Kekule proposed the resonance ring structure for benzene.

Resonance is the ability of a compound to have many structural forms whose energy differences are very small. It explains the relative unreactivity of the aromatic compounds. Because the energy difference between the different resonance forms are small, the structure of the compound changes (resonates) from one form to another at a very fast rate.

13.19 Properties of Benzene

Experiment 13.11 To investigate the reactions of benzene.
   Carry out the following tests on samples of benzene and record your observations.
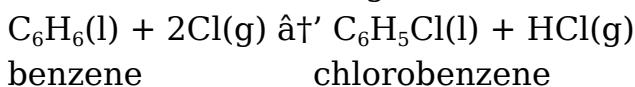
1. Ignite a few drops of benzene in a crucible lid. Note the nature of the flame.

2. To $1cm^3$ of benzene in a test-tube, add two drops of bromine water and shake. Record your observation.

3. To another $1cm^3$ sample of benzene in a test-tube, add two drops of potassium tetraoxomanganate(VII) and two drops of tetraoxosulphate(VI) acid. Shake the test-tube.

4. Put about 5 drops of benzene into a test-tube. Add some iron

fillings to it, then 5 drops of bromine. Watch the test-tube for some time and note what happens.
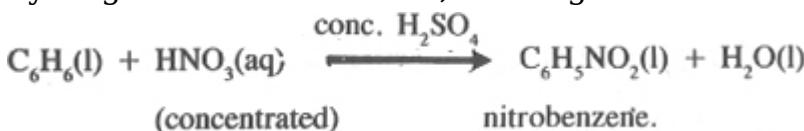
5.   Place about 0.5cm³ of concentrated tetraoxosulphate(VI) acid into a test-tube. Add about 0.5 cm³ of concentrated trioxonitrate(V) acid to it. Cool the test-tube under tap water. Add this mixture of acids to 5 drops of benzene in another test-tube. Shake, while cooling under the tap. Allow to stand for a few minutes.

6.   Place four drops of benzene into a test-tube. Add 10 drops of concentrated tetraoxosulphate(VI) acid to it. Warm to dissolve the benzene. Pour the solution into a small beaker containing 10cm³ of a cold saturated solution of sodium chloride. Record your observation.

The results of the above experiment show that benzene has the following properties.
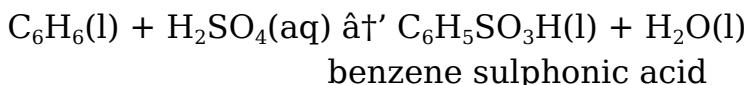
1.   Benzene is a colourless, oily liquid.

2   It burns with a luminous, sooty flame.

3.   It does not decolourise bromine water or acidified potassium tetraoxomanganate(VII) solution.

4.   It reacts with halogens by substitution. The halogen atoms replace hydrogen atoms in benzene. Fumes of hydrogen halide are formed, in addition to the halogenobenzene.

$C_6H_6(l) + 2Cl(g) \rightarrow C_6H_5Cl(l) + HCl(g)$
benzene   chlorobenzene
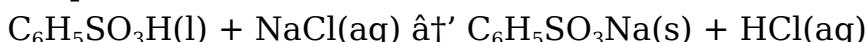
5.   Substitution reaction also occurs with concentrated trioxonitrate(V) acid, in the presence of concentrated tetraoxosulphate(VI) acid. A nitro group, $-NO_2$, replaces a hydrogen atom of benzene, forming nitrobenzene.

$$C_6H_6(l) + HNO_3(aq) \xrightarrow{\text{conc. } H_2SO_4} C_6H_5NO_2(l) + H_2O(l)$$

(concentrated)   nitrobenzene.

6.   A substitution reaction also occurs with fuming tetraoxosulphate(VI) acid. Benzene sulphonic acid is formed.

$C_6H_6(l) + H_2SO_4(aq) \rightarrow C_6H_5SO_3H(l) + H_2O(l)$
                    benzene sulphonic acid

This acid product forms a white precipitate of its sodium salt in the presence of saturated sodium chloride solution.

$C_6H_5SO_3H(l) + NaCl(aq) \rightarrow C_6H_5SO_3Na(s) + HCl(aq)$

13.20 Structure of Benzene

The molecular formula of benzene is C_6H_6. This suggests the presence of three double bonds, or two triple bonds. The luminous sooty flame formed when benzene burns also suggests unsaturation. But benzene

does not decolourise bromine water or acidified potassium tetraoxomanganate(VII), while other unsaturated hydrocarbons do. Also, benzene takes part in substitution, rather than addition reactions. It was therefore difficult to represent the structure of a molecule of it. Kekule suggested a ring structure with three alternating double bonds. If we number the carbon atoms, we see that two such structures are possible (Figure 13.18)
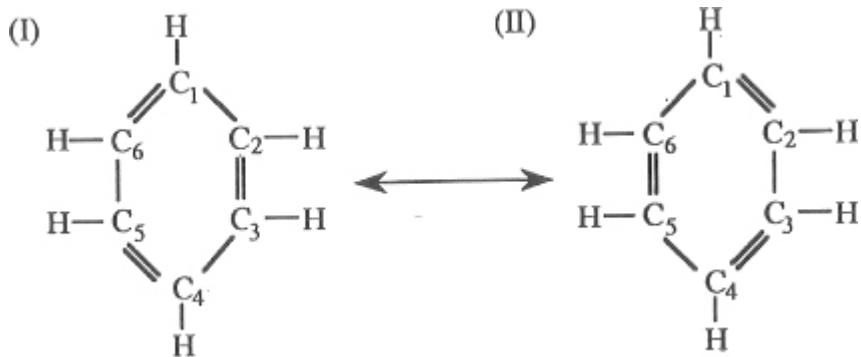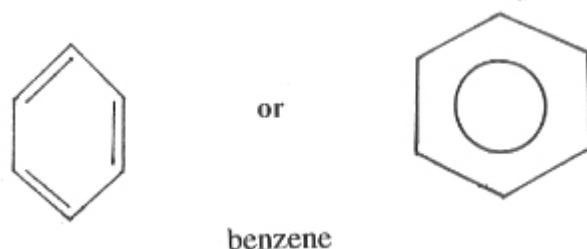

Figure 13.18 Resonance structure of benzene

In structure I, double bonds are located between carbon atoms 2 and 3; 4 and 5; and 1 and 6. In structure II, they are between carbon atoms 1 and 2; 3 and 4; and 5 and 6.

Benzene is said to resonate between these two structures, (and others not shown here).
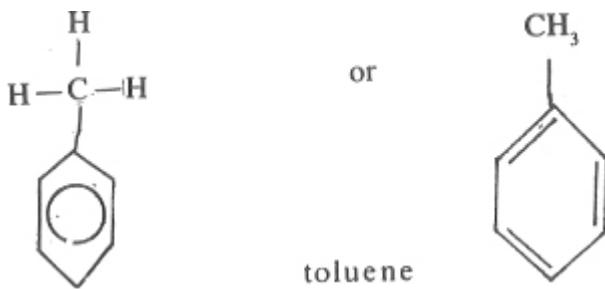
It is more customary to write the structure of benzene as:
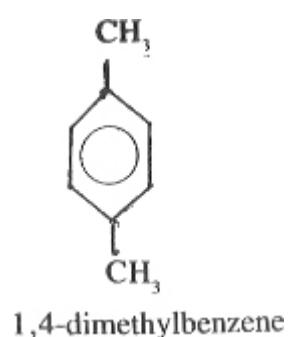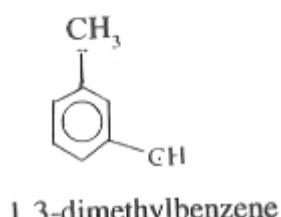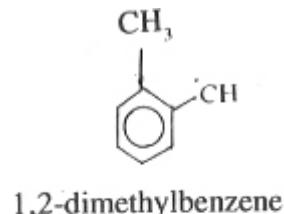
benzene

Hydrogen atoms are understood to be present at each corner of the hexagon. The ring inside the hexagon represents six non-bonding electrons. This structure accounts for the low reactivity of benzene.

13.21 Homologues of Benzene
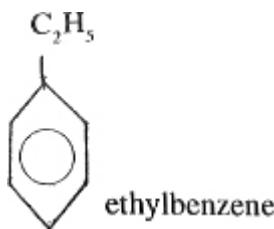
The replacement of one hydrogen atom in benzene by a methyl radical gives methylbenzene (toluene), C_7H_8.

or

toluene

The same compound is formed, no matter which hydrogen atom is replaced. Replacement of two hydrogen atoms by two methyl groups produces three isomers with molecular formula C_8H_{10}

1,2-dimethylbenzene

1,3-dimethylbenzene

1,4-dimethylbenzene

There is a fourth isomer of C_8H_{10}, representing the replacement of a hydrogen atom in benzene by an ethyl radical.

ethylbenzene

The general formula of the benzene homologous series is C_nH_{2n-6} where n is six or a higher number.

The C_6H_5 radical, derived by loss of a hydrogen atom, is called the

phenyl or **aryl** group. It can be linked to many atoms or other radicals. All compounds having it are aromatic compounds because they are oily, and most of them have the aroma of essential oils.

EXERCISE 13M

1.   Give two reactions of benzene in which it resembles alkanes. In what way does it resemble an unsaturated hydrocarbon?

2.   What do you understand by resonance? Write two resonance structures of benzene.

13.22 Uses of Benzene

1.   Benzene is a useful organic solvent.

2.   It is a starting material for the syntheses of many aromatic compounds.

F: PETROCHEMICALS

Petrochemicals are chemicals derived from petroleum and natural gas. Petroleum and natural gas are the most important sources of chemicals for manufacturing products based on organic compounds. The saturated hydrocarbons (alkanes) which make up the bulk of petroleum, are of little use as starting compounds for the synthesis of the petrochemicals. However, by subjecting them to high temperatures and pressures in the presence of catalysts, the alkanes are cracked, dehydrogenated and reformed.

The various petrochemicals and their industrial products are discussed here.
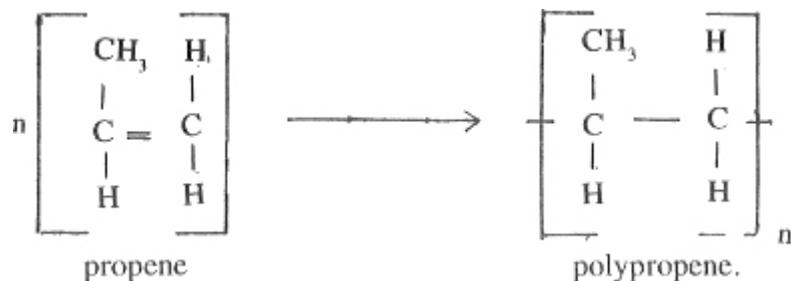
Plate 13.2 Various types of plastic goods

13.23 Plastics

We have seen that the polymerisation of ethene yields polythene, used for making toys, for wrapping materials, etc.. There are many other different types of plastics used for different purposes. They include the following.

Polypropene
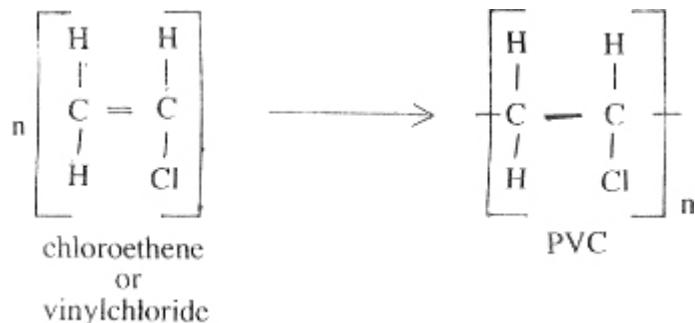
Propene polymerises to polypropene which is even stronger than polythene. It is used for making plastic buckets, plates, etc.

propene → polypropene.

Propene is got from propane present in natural gas, by dehydrogenation.

Polyvinyl chloride (Polychloroethene)

Chloroethene, $CH_2 = CHCl$ polymerises to polychloroethene. The polymer is used in making raincoats, and electrical insulation materials.

chloroethene
or
vinylchloride

PVC

The monomer, chloroethene, is obtained from ethyne.

H-C ≡ C-H(g) + HCl(g) → $CH_2 = CHCl(g)$
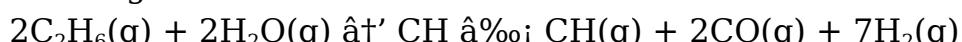
Industrial reactions yielding ethyne include:
1. Cracking of methane-ethane mixture.
    $4CH_4(g) + C_2H_6(g) → 3CH ≡ CH(g) + 8H_2(g)$
2. Heating a mixture of ethane and steam to about 1000°C.
    $2C_2H_6(g) + 2H_2O(g) → CH ≡ CH(g) + 2CO(g) + 7H_2(g)$
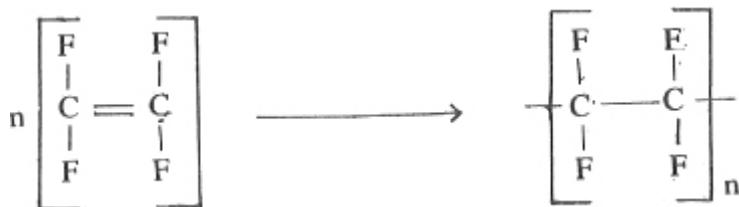
3. Heating a mixture of natural gas and steam to about 1000°C.

Polytetrafluoroethene (Teflon)
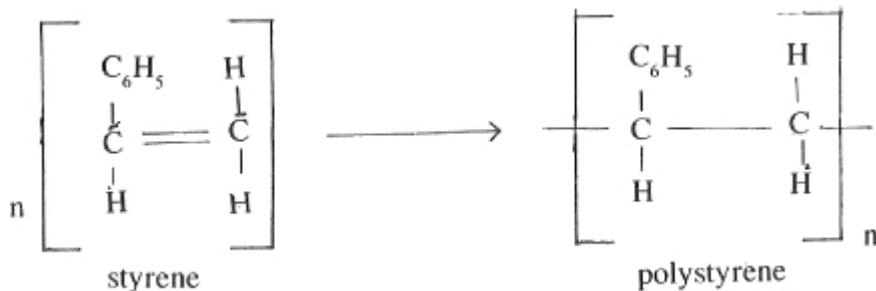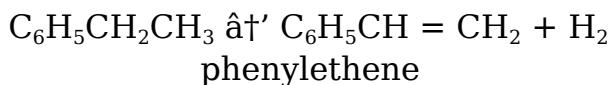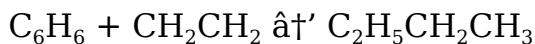
Replacement of the hydrogen atoms in ethene by fluorine gives tetrafluoroethene. This monomer polymerises to polytetrafluoroethene (teflon).

Teflon is resistant to attack by chemicals. It is used for making containers for chemical reagents.

Polyphenylethene (Polystyrene)
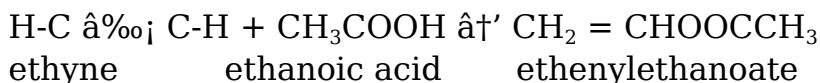
Phenylethene (styrene) is the monomer of polyvinylethene (polystyrene). It is made by the reaction between ethene and benzene.

$C_6H_6 + CH_2CH_2 \rightarrow C_2H_5CH_2CH_3$

$C_6H_5CH_2CH_3 \rightarrow C_6H_5CH = CH_2 + H_2$
          phenylethene

styrene   polystyrene

Polyphenylethene (polystyrene) is used for making ceiling tiles, plastic cup and packaging materials.

Polyethenylethanoate (polyvinylacetate, PVA)
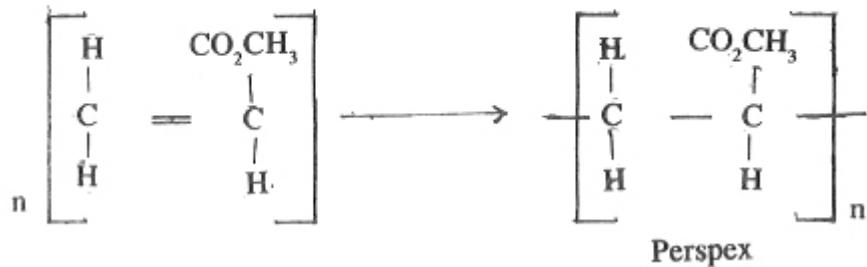
Ethenylethanoate is derived from ethyne by the reaction:

$H-C \equiv C-H + CH_3COOH \rightarrow CH_2 = CHOOCCH_3$
ethyne   ethanoic acid   ethenylethanoate

Its polymer, PVA, is used for making emulsion paints and crease-resistant cotton textiles.

Polymethylpropenoate (polymethacrylate) (Perspex)
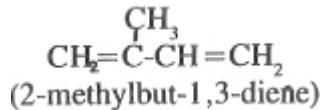
The monomer of this highly transparent polymer is obtained from the reaction:

$$HC\equiv CH + CO + CH_3OH \rightarrow CH_2=CHCO_2CH_3$$
$$\text{methylpropenoate}$$

$$\left[\begin{array}{cc} H & CO_2CH_3 \\ | & | \\ C & = \; C \\ | & | \\ H & H \end{array} \right]_n \longrightarrow \left[\begin{array}{cc} H & CO_2CH_3 \\ | & | \\ C & - \; C \\ | & | \\ H & H \end{array} \right]_n$$
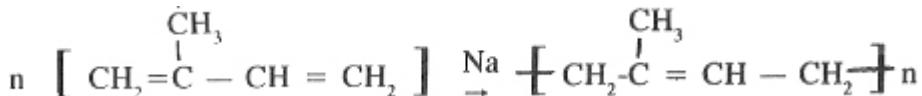
Perspex

Perspex is not only very transparent, it is also resistant to weathering. It is used for making car and aircraft windscreens.

13.24 Synthetic Rubber

Natural rubber, which is the latex from rubber tree, is a polymer of 2-methylbut-1, 3-diene (isoprene).

$$\begin{array}{c} CH_3 \\ | \\ CH_2=C\text{-}CH=CH_2 \end{array}$$
(2-methylbut-1,3-diene)
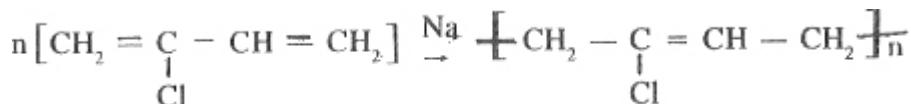
2-methylbut-l,3-diene polymerizes when heated with sodium, to form synthetic rubber.

$$n \left[\begin{array}{c} CH_3 \\ | \\ CH_2=C - CH = CH_2 \end{array} \right] \xrightarrow{Na} \left[\begin{array}{c} CH_3 \\ | \\ CH_2\text{-}C = CH - CH_2 \end{array} \right]_n$$

However, several types of synthetic rubbers of far superior quality are now produced by polymerizing other derivatives of but-1,3-diene.
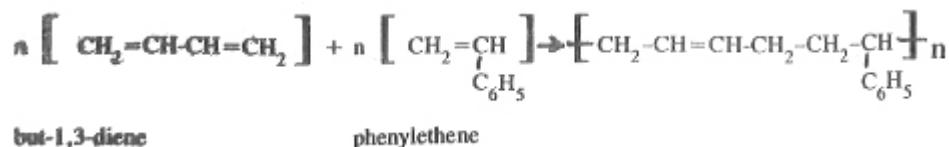
2-chloro-but-l,3-diene (neoprene) polymerises to a good quality rubber, in the presence of sodium.

$$n\left[\begin{array}{c} CH_2 = C - CH = CH_2 \\ | \\ Cl \end{array} \right] \xrightarrow{Na} \left[\begin{array}{c} CH_2 - C = CH - CH_2 \\ | \\ Cl \end{array} \right]_n$$
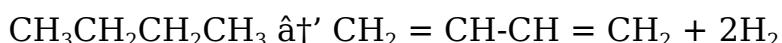
Copolymerisation is the polymerisation between two different monomers.

The Copolymerisation of but-1,3-diene and phehylethene (styrene)

yields very good quality rubber.

but-1,3-diene   phenylethene

All the monomers for the rubber-like polymers are petrochemicals. For example, buta-1,3-diene can be obtained from propane in natural gas or refinery gas, by dehydrogenation.

$CH_3CH_2CH_2CH_3 \rightarrow CH_2 = CH\text{-}CH = CH_2 + 2H_2$
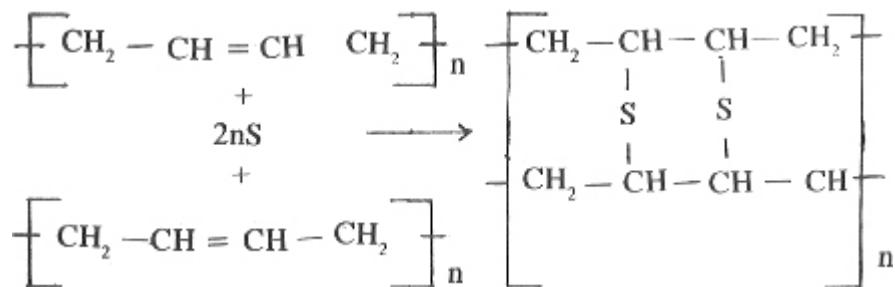
EXERCISE 13N

Observe the structural formulae of the rubber-like polymer closely. How do they differ from the structural formulae of the other polymers? How does this difference arise?
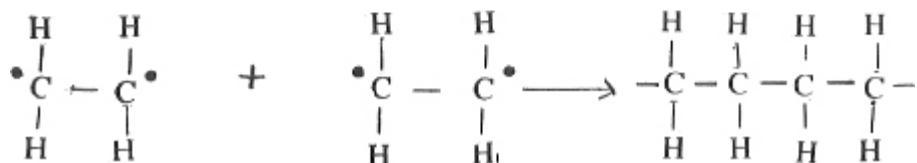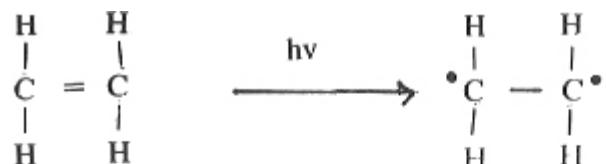
Vulcanization

Vulcanization is the process of heating of rubber with sulphur to form crosslinks of sulphur between long rubber chains at their double bond sites. The result is a rubber with higher tensile strength. It is insoluble in common solvents like petrol and therefore is used for making motor tyres.
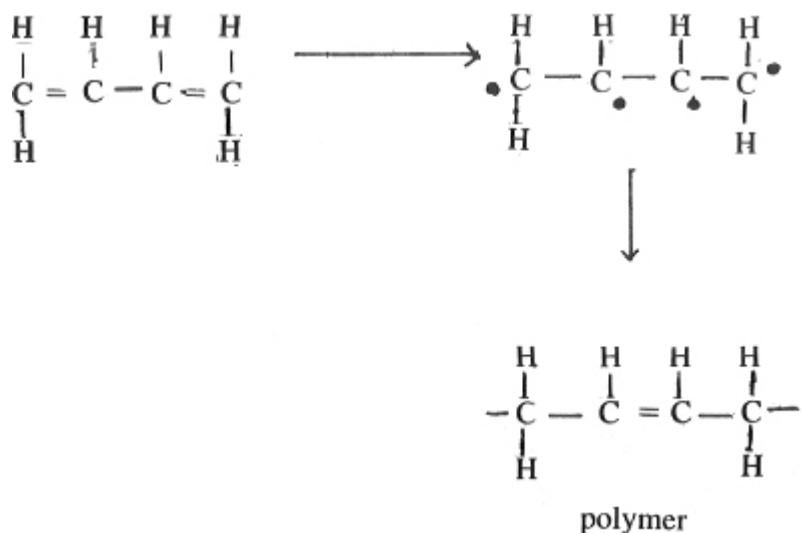
13.25 Mechanism of Polymerization

Polymerization occurs as a result of the breaking of the double bonds in the monomer. Each of the carbon atoms around the broken bond thus carries a free electron and becomes very reactive. They link up with carbon atoms of other monomers which similarly carry free electrons. A polymer results.
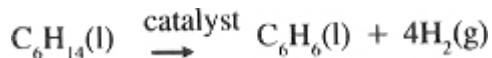
When a molecule has two conjugated double bonds (two double bonds that alternate with a single bond), as in but-l,3-diene, then the reactive intermediate has free electrons on two inner adjacent carbon atoms. These link up to form a new double bond.
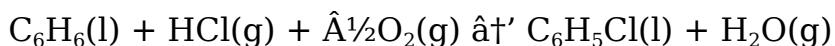

polymer

The polymer which is formed therefore still has a double bond.

13.26 Insecticides
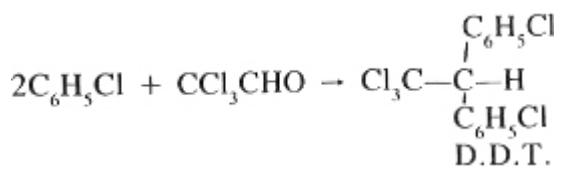
Reforming processes convert alkanes in petroleum products to aromatic hydrocarbons, especially benzene.

$$C_6H_{14}(l) \xrightarrow{\text{catalyst}} C_6H_6(l) + 4H_2(g)$$

Chlorobenzene is produced industrially by passing a mixture of vapour of benzene, air and hydrogen chloride over copper(II) chloride catalyst.

$C_6H_6(l) + HCl(g) + \frac{1}{2}O_2(g) \rightarrow C_6H_5Cl(l) + H_2O(g)$

Chlorobenzene is Used for the manufacture of D.D.T. (dichlorodiphenyl trichloroethane).

$$2C_6H_5Cl + CCl_3CHO \rightarrow Cl_3C-\underset{\underset{\displaystyle D.D.T.}{\overset{|}{C_6H_5Cl}}}{\overset{\overset{\displaystyle C_6H_5Cl}{|}}{C}}-H$$

D.D.T. is a powerful insecticide. Its use is however being discouraged because it is stable (not easily degraded) and harmful, and finds its way through the food chain into human body systems.

Structural modifications of D.D.T. have given rise to many other insecticides which are safer for use. Herbicides and fungicides have also been synthesised from petrochemicals. The structures of most of these compounds are too complex for treatment here.

Plate 13.3 An airplane spraying insecticides.
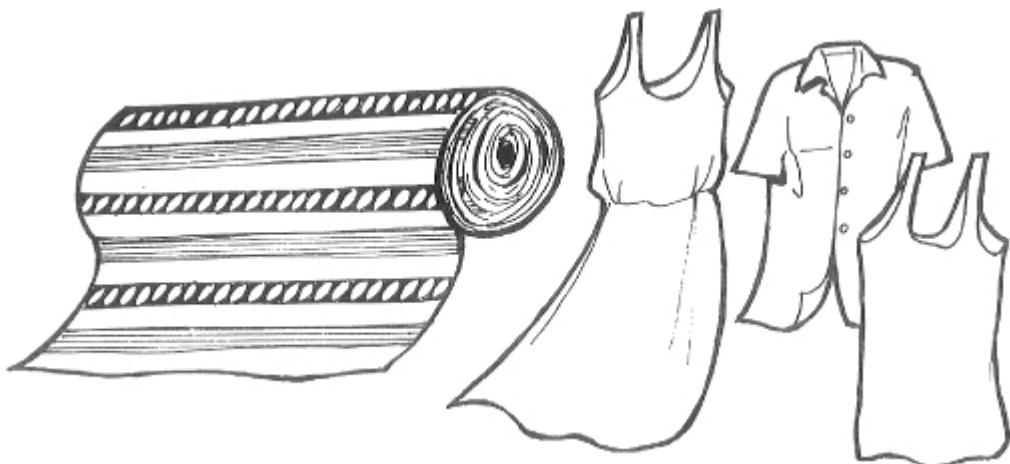
Plate 13.4 Synthetic fibres
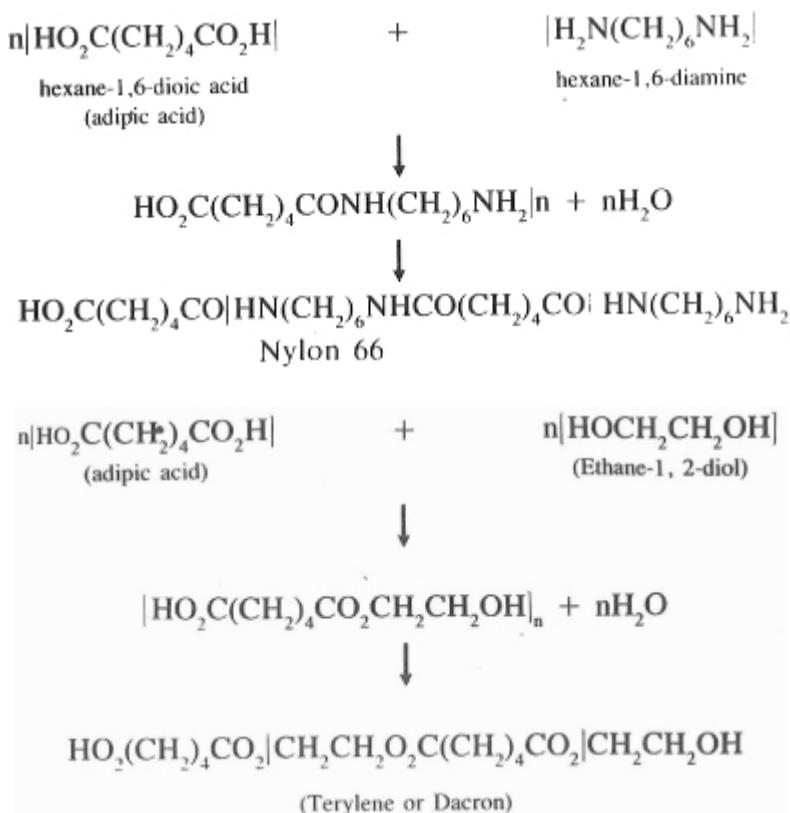
13.27 Synthetic Fibres

Synthetic fibres have revolutionised the clothing industry. Polyester and polyamide fibres are now household names. These are fibres made from petrochemicals by condensation polymerization.

In condensation polymerization two or more low molecular mass organic molecules unite in a repeated manner to form long-chain polymers, by eliminating small molecules, such as water, ammonia or hydrogen chloride.

A long-chain polymer which can be woven into fabrics is formed, if the two uniting monomers are both bifunctional. If they are poly-functional, a net-work solid is formed.

Nylon 66 is made when adipic acid and hexamethylene diamine undergo condensation polymerization.

$$n|HO_2C(CH_2)_4CO_2H| \quad + \quad |H_2N(CH_2)_6NH_2|$$

hexane-1,6-dioic acid   hexane-1,6-diamine
(adipic acid)

$$\downarrow$$

$$HO_2C(CH_2)_4CONH(CH_2)_6NH_2|n + nH_2O$$

$$\downarrow$$

$$HO_2C(CH_2)_4CO|HN(CH_2)_6NHCO(CH_2)_4CO|HN(CH_2)_6NH_2$$

Nylon 66

$$n|HO_2C(CH_2)_4CO_2H| \quad + \quad n|HOCH_2CH_2OH|$$

(adipic acid)   (Ethane-1, 2-diol)

$$\downarrow$$

$$|HO_2C(CH_2)_4CO_2CH_2CH_2OH|_n + nH_2O$$

$$\downarrow$$

$$HO_2(CH_2)_4CO_2|CH_2CH_2O_2C(CH_2)_4CO_2|CH_2CH_2OH$$

(Terylene or Dacron)

EXERCISE 13P

1   (a)   What types of monomers give rise to (i) plastics, (ii) rubber-like polymers, (iii) synthetic fibres?

    (b)   Differentiate between addition and condensation polymerization.

2   (a)   Heavy chemicals are those produced in large quantities. Name two petrochemicals which could rightly be regarded as heavy chemicals.

    (b)   A chemical industry produces raw materials for other industries. Name the raw materials the petrochemical industry produces for the plastics industry.

Table 13.4 gives a summary of the common industrial chemicals derived from petroleum products, and their uses.

TABLE 13.4 PETROCHEMICALS AND THEIR USES

Hydrocarbon source	Petrochemical	Industrial product/use
Methane	(1) Hydrogen (2) Chloromethane (3) Di-, tri-, and tetrachloromethanes	Ammonia and fertilizers Refrigerant Solvents
Ethane	(1) Lead tetraethyl (2) Ethene	Petrol additive. Other petrochemicals.
Ethene	(1) Ethane - 1,2-diol (2) Ethanol, ethanoic acid (3) Phenylethene (4) 1,2-dibromoethane	Antifreeze in car radiators, polyesters. Various uses including laboratory chemicals. Plastics, synthetic rubber. Petrol additive.
Ethyne	(1) Chloroethene (2) Vinyl acetate (3) Propenonitrile (4) Methylpropeonate (5) Ethanal	PVC polymer. PVA polymer. Polyamide fibre, synthetic rubber.
Benzene	(1) Styrene (2) Cyclohexane (3) Chlorobenzene (4) Phenylamine	Perspex glass. Ethanol, ethanoic acid. Plastics, synthetic rubber. Cyclohexanone, adipic acid, polyesters, nylon. Insecticides. Dyes, drugs, foam.
Toluene	(1) Sodium benzoate (2) Trinitrotoluene	Food preservative. Explosives.

Chapter Summary

1. A pure organic compound has a sharp melting or boiling point by which it can be identified.

2. Members of a homologous series

(i)   react alike,

(ii)   show a gradation of physical properties, and

(iii) have a general formula.

3.   Hydrocarbons are obtained from petroleum, coal and natural gas.

4.   Alkanes:

(i)   have the general formula C_nH_{2n+2},

(ii)   are saturated hydrocarbons (i.e. they contain only single bonds),

(iii) undergo substitution reactions.

5.   Alkenes:

(i)   have the general formula C_nH_{2n},

(ii)   possess at least one carbon to carbon double bond,

(iii) undergo addition reactions.

6.   Alkynes:

(i)   have the general formula C_nH_{2n-2},

(ii)   have at least one carbon to carbon triple bond.

(iii) undergo addition reactions.

7.   Polymerisation of ethene and other alkenes yield useful products such as polythene, PVC, PVA polypropene, artificial rubber, etc.

8.   Cross-linking of long chains of rubber polymers with sulphur, yields harder and tougher rubber known as vulcanised rubber.

9.   Double and triple bonding restricts rotation about a carbon-carbon bond and gives rise to geometrical (cis-trans) isomerism.

10. Benzene, an aromatic hydrocarbon exhibits resonance. Its characteristic reaction is substitution. The benzene homologous series has the general formula C_nH_{2n-6}, where n â‰¥ 6.

Members of the series with two or more substituents show position isomerism (1,2-; 1,3-; and 1,4- substituted benzenes).

11. Methane, ethene, ethyne, benzene and toluene are common petrochemicals. They are starting materials for the manufacture of other chemical raw materials and industrial products.

Assessment

1.   (a)   With the aid of a labelled diagram, describe the laboratory preparation of ethyne.

(b)   Describe what is observed and explain what happens when ethyne is passed into

(i)   an acidified solution of potassium tetraoxomanganate(VII),

(ii)   bromine water,

(iii) ammoniacal silver trioxonitrate(V) solution.

(c)   What would be the observations if ethene is used in place of

ethyne in the above reactions?

2. (a) Write chemical equations for the preparation of ethane, ethene and ethyne.

(b) How would you distinguish between the three gases in the laboratory?

(c) Give two uses of ethene and two uses of ethyne. What are the sources of the ethene and ethyne for these uses?

3. Explain the terms
(i) cracking,
(ii) octane number of petrol.

Name four fractions of petroleum refining.

What are the uses of the fractions named?

4. Give one reaction in which benzene resembles the alkanes and one reaction in which it resembles the alkenes. What is resonance? Write two resonating structures for benzene.

Write all the structures of the homologues of benzene with the molecular formula C_8H_{10}.

5. (a) Write equations to show how you would prepare
(i) chloroethene from ethyne;
(ii) ethanol from ethene;
(iii) ethanal from ethene;
(iv) tetrachloromethane from methane.

(b) A hydrocarbon contains 75 % carbon and 25 % hydrogen by mass. What is the empirical formula of the hydrocarbon?