Chapter 4

Saturated Hydrocarbons

Hydrocarbons *are the compounds that are composed of only carbon and hydrogen.* They are divided, like all other organic compounds, into two broad categories, i.e., *aliphatic* and *aromatic*. The name aliphatic was derived from the Greek word *aliphos* meaning 'fat-like' because the first compounds of this category to be studied were the fatty acids. Although with the introduction of millions of new compounds this meaning has now lost its significance, the term aliphatic is still in use, and now the **aliphatic compounds** mean *the open-chain compounds and those cyclic compounds that resemble the open-chain compounds in their behaviour*. Similarly, the name aromatic was derived from the Greek word *aroma* meaning 'fragrant', because most of the early aromatic compounds have characteristic odour. However, at a later stage the aromatic compounds proved to be distinctive in the ways that are far more important than their odours, and benzene was recognized as a parent member of this category of compounds. Thus, the term **aromatic** is now used for *benzene and those compounds that resemble benzene in their chemical behaviour*. The **aliphatic hydrocarbons** include *alkanes, cycloalkanes, alkenes* and *alkynes* and the **aromatic hydrocarbons** include *benzene* and other *benzene-like compounds*.

The aliphatic hydrocarbons are further classified into *saturated* and *unsaturated* hydrocarbons. The **saturated hydrocarbons** are those compounds of carbon and hydrogen in which the carbon atoms are joined to each other only by single bonds, and each carbon atom is bonded to four other atoms. They are called saturated because their valencies are fully satisfied. They include *alkanes* which are open-chain saturated hydrocarbons, and *cycloalkanes* in which the carbon atoms are arranged in one or more rings. The **unsaturated hydrocarbons** are those compounds of carbon and hydrogen which contain carbon-carbon multiple bonds, and to which other atoms can be added to form saturated compounds. They include *alkenes*, having a carbon-carbon double bond, and *alkynes*, having a carbon-carbon triple bond.

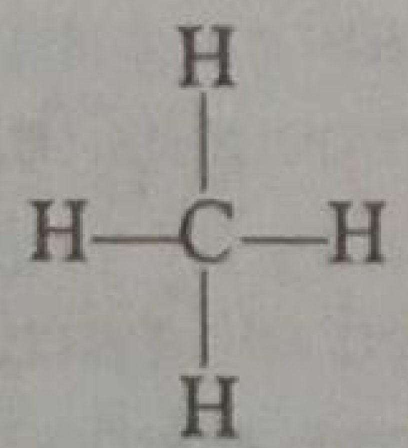
It seems to be more reasonable to classify all the hydrocarbons on the basis of their behaviour and discuss them under three categories: (i) saturated hydrocarbons, (ii) unsaturated hydrocarbons and (iii) aromatic hydrocarbons. The saturated hydrocarbons will be discussed in this chapter taking alkanes first and then the cycloalkanes. The unsaturated and aromatic hydrocarbons will be discussed in *Chapters 5* and *8*, respectively.

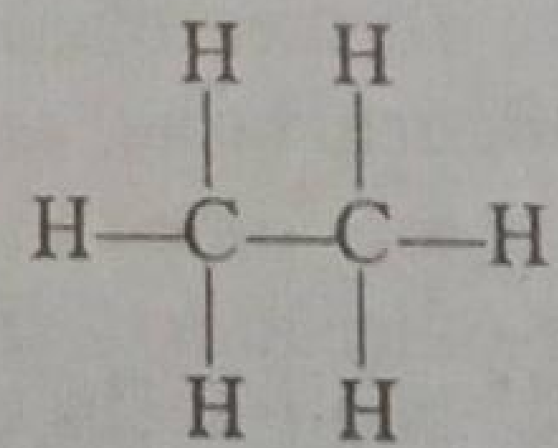
Although this chapter deals with just one class of compounds, i.e., saturated hydrocarbons, several fundamental principles are developed which shall be extensively used in later chapters. For example, the naming of alkanes is quite important because a large number of organic compounds are just the substituted alkanes, and are usually named as such. The physical properties of alkanes set a pattern as to how they change with the molecular weight and the structure within a family of compounds. Similarly, the chemical reactions discussed in connection with alkanes explain certain fundamental principles to be encountered later.

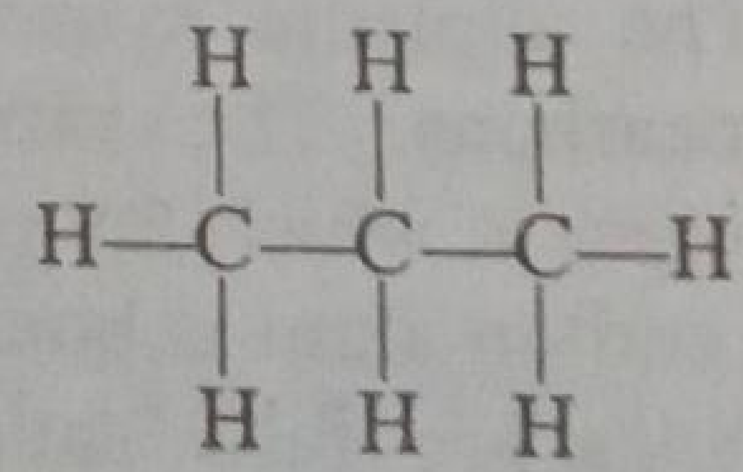
To understand organic chemistry, two things are important. One, which we have concentrated on so far, is the structure of molecules and their representation. The second is the pathway followed by the molecules when they react with each other, i.e., which bonds are formed, which are broken and in which order; how many steps are involved in a reaction and what is the relative rate of each step, etc. This is called the **mechanism** of a reaction. The mechanism of a reaction is described by the movement of electrons either in pairs (in polar reactions) or individually (in free-radical reactions). The movement of electrons in pairs is indicated by the conventional curved arrow (⌒) and the movement of each electron independently is indicated by a fish-hook arrow (⌒).

ALKANES

Alkanes are the open-chain saturated hydrocarbons, methane (CH_4) being the simplest member of this family of compounds. Each carbon atom in alkanes is sp^3 hybridized, and has tetrahedral geometry. The next member of this family is ethane (C_2H_6) the formula of which is derived from that of methane by replacing one of its hydrogen atoms by methyl (CH_3) group. Similarly, the molecular formula of the next higher alkane, i.e., propane (C_3H_8), is obtained by replacing one of the hydrogen atoms of ethane by methyl group.


Methane

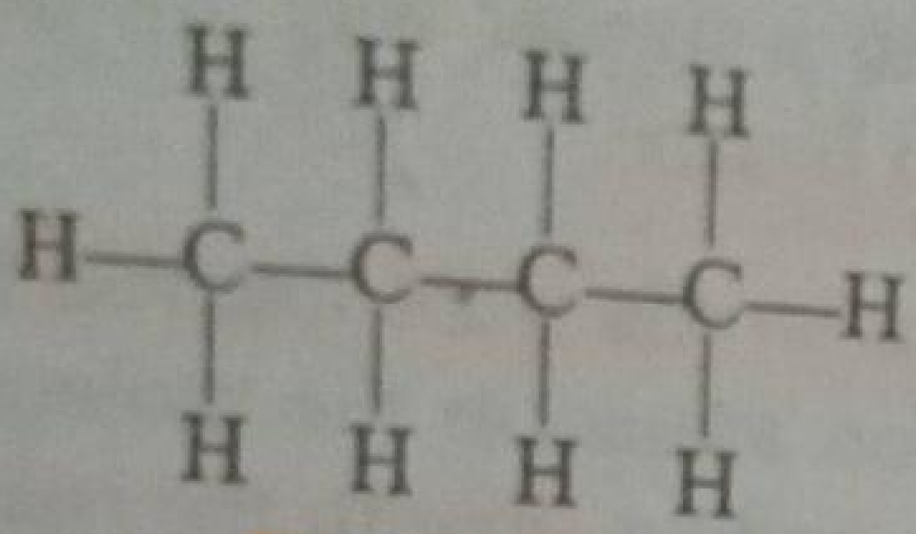

Ethane


Propane

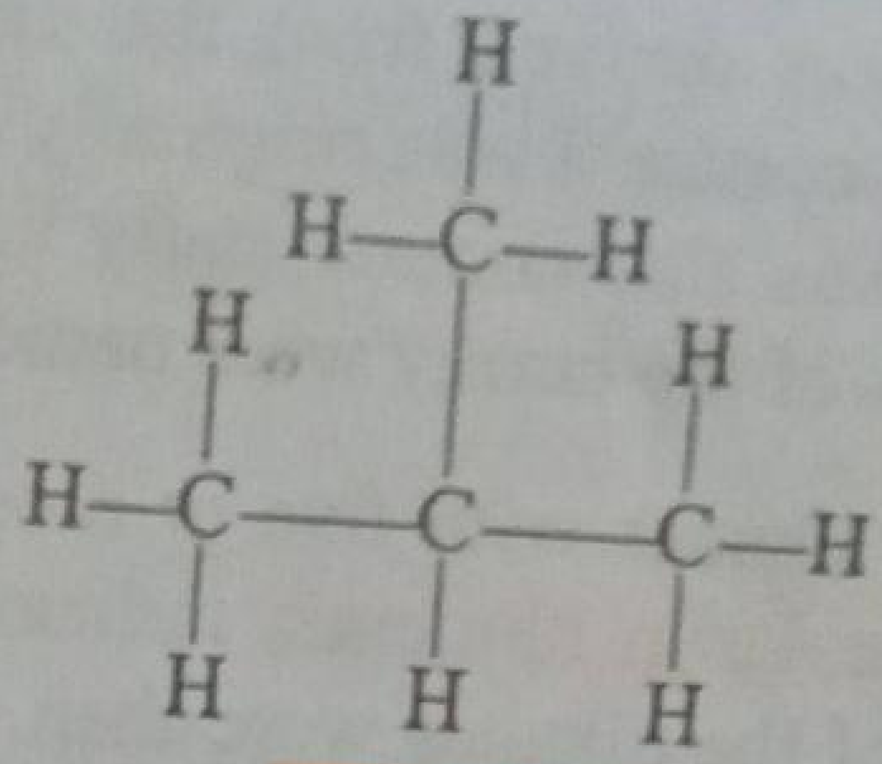
In this way the molecular formulas of the higher alkanes can be derived from the lower ones by successively replacing hydrogens by methyl groups. Thus, the next higher alkane is butane (C_4H_{10}) which is followed by pentane (C_5H_{12}), hexane (C_6H_{14}), and so on.

We notice that the formula of each alkane differs from that of its neighbour by a unit of CH_2, and all alkanes can be represented by a general formula C_nH_{2n+2} (where n is the number of carbon atoms). *A series of compounds that can be represented by a general formula* is called a **homologous series**, and the individual members of the series are called **homologs.**

Keeping in view the quadrivalency of carbon and univalency of hydrogen, we find that there is only one structure possible for each of methane, ethane and propane, as shown above. However, when a hydrogen atom of propane is replaced by methyl group, we obtain two different structures of butane (C_4H_{10}), depending on whether a hydrogen atom of the terminal carbon or that of the middle carbon of propane is replaced by the methyl group. In the former case we get a straight-chain structure of butane, whereas in the latter case we get a branched-chain structure, as shown below:

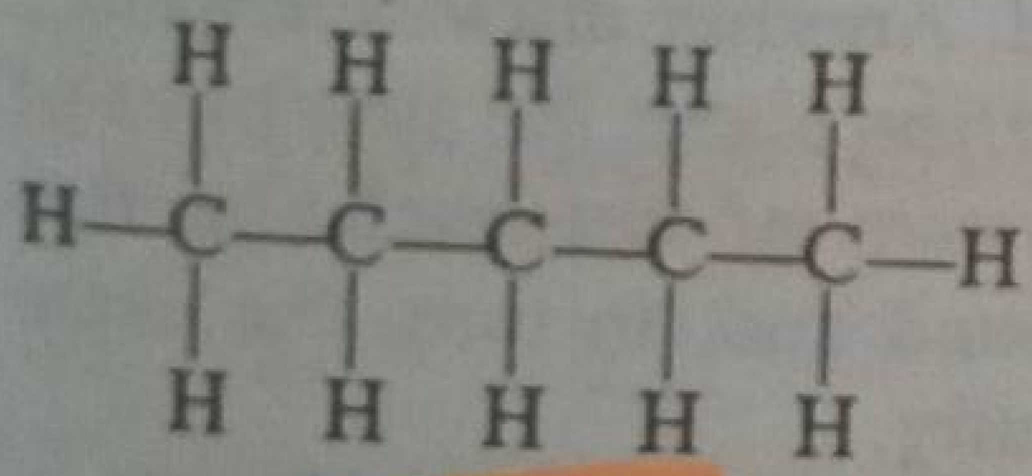


n-Butane

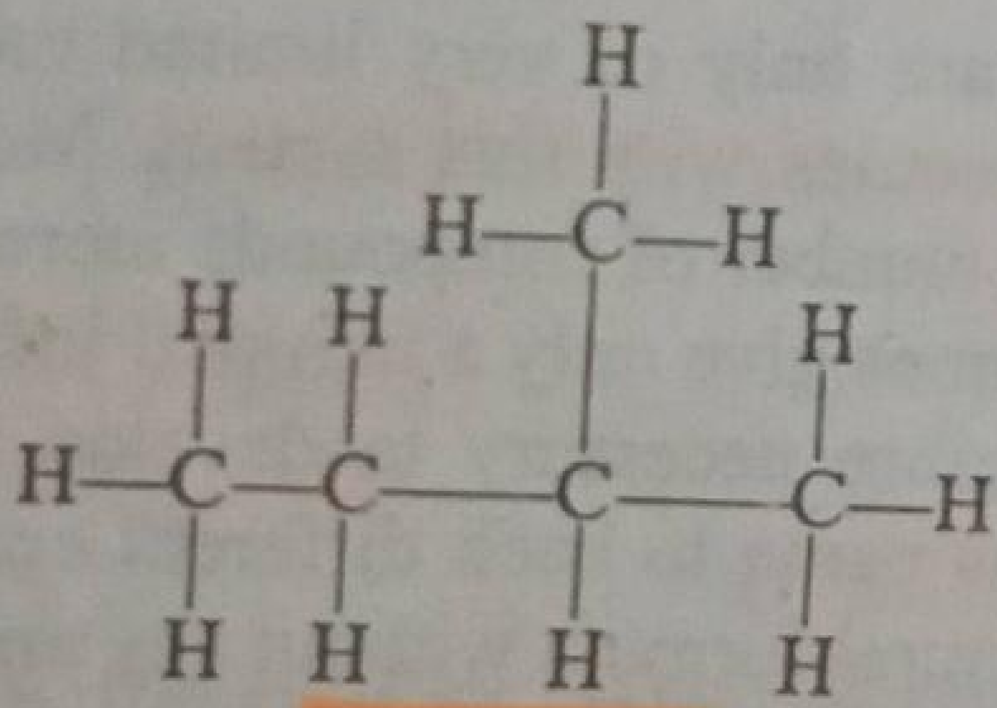


Isobutane

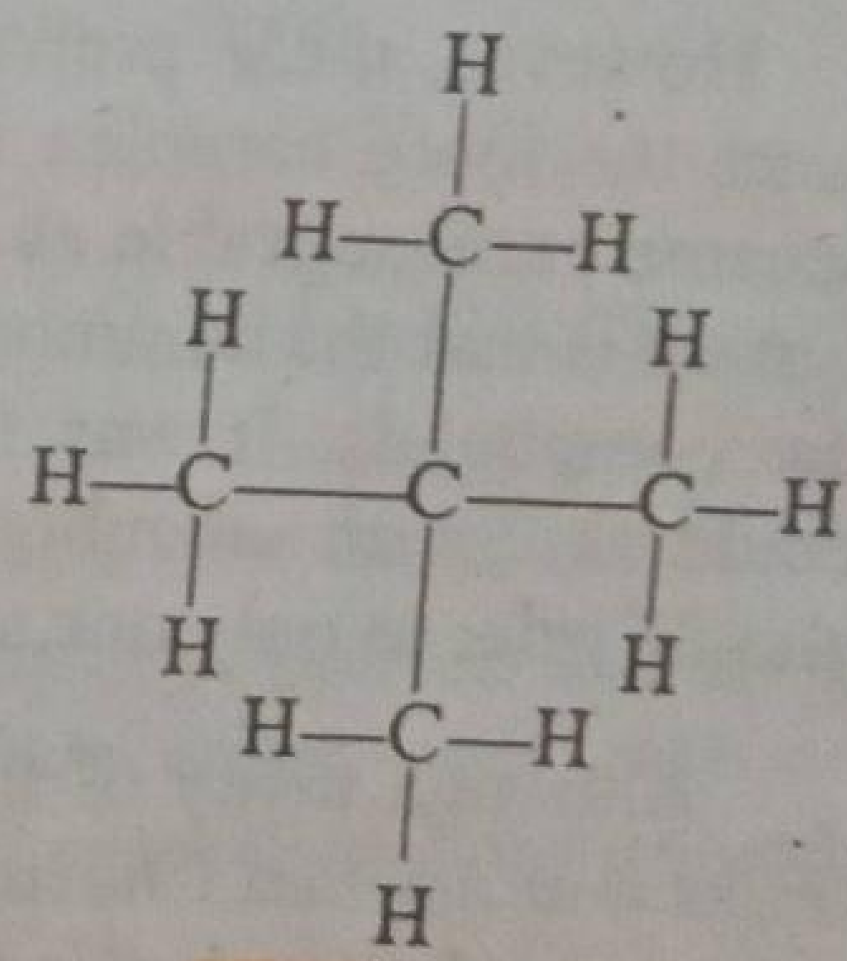
The straight-chain structure was called *normal (n-) butane* and the branched-chain structure was called *isobutane.* In a similar way, we obtain three different structures of pentane (C_5H_{12}) two of which are similar to those of butane, and are named as *n*-pentane and isopentane. The third (new) one is called *neopentane.*



n-Pentane



Isopentane



Neopentane

In general, the prefix *n-* is used for a straight-chain compound, the prefix *iso-* is used for compounds with two methyl groups at the end of an otherwise straight chain, and the prefix *neo-* is employed to denote three methyl groups at the end of a chain.

We have seen that although *n*-butane and isobutane have different structures, they have same molecular formula. Similarly, in spite of different structures, the three pentanes have the same molecular formula. *The compounds that have same molecular formula but differ in structure* are known as **isomers.** The number of possible isomers increases very rapidly with an increasing number of carbon atoms. For example, whereas there is only one methane, one ethane, and one propane, there are 2 butanes, 3 pentanes, 5 hexanes, 9 heptanes, 18 octanes, 35 nonanes and 75 decanes.

Nomenclature of Alkanes

Before we discuss the chemistry of organic compounds it is necessary to know their names. There are two ways of naming the organic compounds that are in common use and that we shall discuss here with reference to alkanes.