

(iv) Metamerism: It arises due to different alkyl chains on either side of the functional group in the molecule. For example, $C_4H_{10}O$ represents methoxypropane ($CH_3OC_3H_7$) and ethoxyethane ($C_2H_5OC_2H_5$).

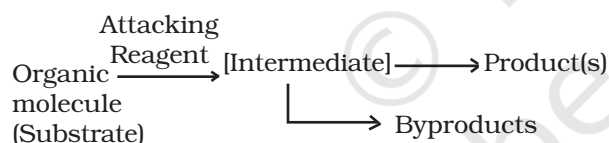
8.6.2 Stereoisomerism

The compounds that have the same constitution and sequence of covalent bonds but differ in relative positions of their atoms or groups in space are called stereoisomers. This special type of isomerism is called as stereoisomerism and can be classified as *geometrical* and *optical isomerism*.

8.7 FUNDAMENTAL CONCEPTS IN ORGANIC REACTION MECHANISM

In an organic reaction, the organic molecule (also referred as a substrate) reacts with an appropriate attacking reagent and leads to the formation of one or more intermediate(s) and finally product(s)

The general reaction is depicted as follows :



Substrate is that reactant which supplies carbon to the new bond and the other reactant is called reagent. If both the reactants supply carbon to the new bond then choice is arbitrary and in that case the molecule on which attention is focused is called *substrate*.

In such a reaction a covalent bond between two carbon atoms or a carbon and some other atom is broken and a new bond is formed. **A sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products (kinetics) is referred to as reaction mechanism.** The knowledge of reaction mechanism helps

in understanding the reactivity of organic compounds and in planning strategy for their synthesis.

In the following sections, we shall learn some of the principles that explain how these reactions take place.

8.7.1 Fission of a Covalent Bond

A covalent bond can get cleaved either by : (i) **heterolytic cleavage**, or by (ii) **homolytic cleavage**.

In **heterolytic cleavage**, the bond breaks in such a fashion that the shared pair of electrons remains with one of the fragments.

After heterolysis, one atom has a sextet electronic structure and a positive charge and the other, a valence octet with at least one lone pair and a negative charge. Thus, heterolytic cleavage of bromomethane will give CH_3^+ and Br^- as shown below.



A species having a carbon atom possessing sextet of electrons and a positive charge is called a *carbocation* (earlier called *carbonium ion*). The $\overset{+}{\text{C}}\text{H}_3$ ion is known as a methyl cation or methyl carbonium ion. Carbocations are classified as primary, secondary or tertiary depending on whether one, two or three carbons are directly attached to the positively charged carbon. Some other examples of carbocations are: $\text{CH}_3\overset{+}{\text{C}}\text{H}_2$ (ethyl cation, a primary carbocation), $(\text{CH}_3)_2\overset{+}{\text{C}}\text{H}$ (isopropyl cation, a secondary carbocation), and $(\text{CH}_3)_3\overset{+}{\text{C}}$ (*tert*-butyl cation, a tertiary carbocation). Carbocations are highly unstable and reactive species. Alkyl groups directly attached to the positively charged carbon stabilise the carbocations due to inductive and hyperconjugation effects, which you will be studying in the sections 8.7.5 and 8.7.9. The observed order of carbocation stability is: $\overset{+}{\text{C}}\text{H}_3 < \text{CH}_3\overset{+}{\text{C}}\text{H}_2 < (\text{CH}_3)_2\overset{+}{\text{C}}\text{H} < (\text{CH}_3)_3\overset{+}{\text{C}}$. These carbocations have trigonal planar shape with positively charged carbon being sp^2 hybridised. Thus, the shape of $\overset{+}{\text{C}}\text{H}_3$ may be considered as being derived from the overlap of three equivalent $\text{C}(sp^2)$ hybridised orbitals with 1s orbital of each of the three hydrogen

atoms. Each bond may be represented as $C(sp^2)-H(1s)$ sigma bond. The remaining carbon orbital is perpendicular to the molecular plane and contains no electrons. [Fig. 8.3(a)].

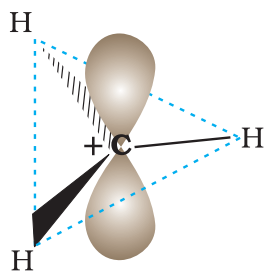
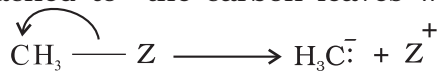


Fig. 8.3(a) Shape of methyl carbocation

The heterolytic cleavage can also give a species in which carbon gets the shared pair of electrons. For example, when group Z attached to the carbon leaves without



electron pair, the methyl anion (H_3C^-) is formed. Such a carbon species carrying a negative charge on carbon atom is called *carbanion*. Carbon in carbanion is generally sp^3 hybridised and its structure is distorted tetrahedron as shown in Fig. 8.3(b).

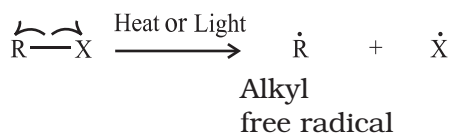


Fig. 8.3(b) Shape of methyl carbanion

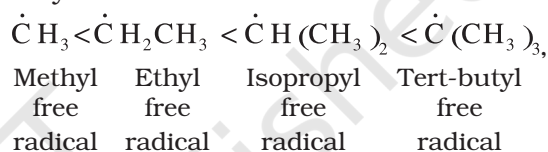
Carbanions are also unstable and reactive species. The organic reactions which proceed through heterolytic bond cleavage are called **ionic** or **heteropolar** or just polar reactions.

In **homolytic cleavage**, one of the electrons of the shared pair in a covalent bond goes with each of the bonded atoms. Thus, in homolytic cleavage, the movement of a single electron takes place instead of an electron pair. The single electron movement is shown by 'half-headed' (fish hook: \curvearrowright)

curved arrow. Such cleavage results in the formation of neutral species (atom or group) which contains an unpaired electron. These species are called *free radicals*. Like carbocations and carbanions, free radicals are also very reactive. A homolytic cleavage can be shown as:



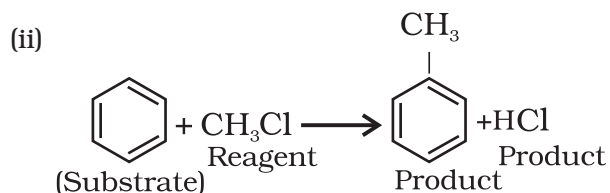
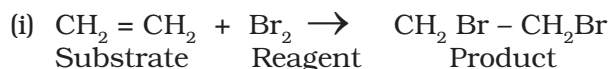
Alkyl radicals are classified as *primary*, *secondary*, or *tertiary*. Alkyl radical stability increases as we proceed from primary to tertiary:



Organic reactions, which proceed by homolytic fission are called *free radical* or *homopolar* or *nonpolar* reactions.

8.7.2 Substrate and Reagent

Ions are generally not formed in the reactions of organic compounds. Molecules as such participate in the reaction. It is convenient to name one reagent as substrate and other as reagent. In general, a molecule whose carbon is involved in new bond formation is called substrate and the other one is called reagent. When carbon-carbon bond is formed, the choice of naming the reactants as substrate and reagent is arbitrary and depends on molecule under observation. Example:



Nucleophiles and Electrophiles

Reagents attack the reactive site of the substrate. The reactive site may be electron