Chapter **6**

Organic Reactions and their Mechanisms

While inorganic reactions take place between ions, organic reactions are essentially molecular in nature. They may involve a single molecule or may take place between two or more molecules. The organic reactions are generally represented by means of equations in which the formulae of the reacting molecules and those of the products are separated by an arrow in between. The arrow points away from the reactants and toward the products. The conditions of the experiment (catalyst, temperature, pressure, etc.) are mentioned above or below the arrow.

$$\text{REACTANTS} \xrightarrow{\text{conditions}} \text{PRODUCTS}$$

THE CLASSICAL STRUCTURAL THEORY

Till recently the reactions of organic compounds were explained on the basis of their structural formulae. The classical 'structural theory' visualised that the chemical behaviour of an organic compound was determined by the functional groups present in its molecule. Thus the course of an organic reaction could be easily interpreted by indicating the interaction between the functional groups of the reacting molecules. The incompetence of the classical structural theory became evident when it was established that compounds having the same functional group behaved differently under similar experimental conditions. Thus,

(*i*) The carbon-carbon double bond in ethylene formed addition compounds readily while the double bonds in benzene did so under forced conditions.

(*ii*) The Br atom in ethyl bromide (C_2H_5Br) could be easily replaced by OH group upon reaction with aqueous alkalies but the Br in phenyl bromide (C_6H_5Br) could not be exchanged for OH under similar conditions.

(*iii*) The carbonyl group $>C=O$ in aldehydes ($R—HC=O$) readily formed addition compounds (the cyanohydrins) with HCN, while the carbonyl group present in carboxyl group $—\overset{\overset{O}{\|}}{C}—OH$ did not.

The above and scores of such other examples proved beyond doubt that the structural theory of organic reactions was made inadequate to offer satisfactory interpretation of the course of reactions, and that factors other than functional groups played a significant role in determining the chemical behaviour of organic compounds.

In this chapter we will acquaint ourselves with some fundamental modern aspects of organic reactions and their mechanism. The amplification of these concepts will be done while discussing specific reactions encountered throughout the remainder of the book.

REACTION MECHANISMS – FUNDAMENTAL ASPECTS

From a mechanistic approach, an organic reaction is believed to take place by the attack of a reagent (Cl_2, HBr, etc.) on a compound containing carbon ; designated as a *substrate*—literally meaning a substance lying below. Thus an organic reaction may be represented as

$$\text{ATTACKING REAGENT} + \text{SUBSTRATE} \longrightarrow \text{PRODUCTS}$$

A **substrate** may be defined as *the reactant that contains carbon atoms some of whose bonds with other atoms are broken and some new ones formed as a result of reaction with the attacking reagent.*

The carbon bonds in the substrate molecule are broken (or cleaved) to give fragments which are very reactive and constitute *transitory intermediates.* At once they may react with other similar species or with molecules present in their environments, thus establishing new bonds to give the products.

The steps of an organic reaction depicting the breaking and making of new bonds of carbon atoms in the substrate leading to the formation of the final product through transitory intermediates, are often referred to as its **Mechanism.**

$$\text{SUBSTRATE} \longrightarrow \underset{\textit{(Transitory)}}{\text{INTERMEDIATE}} \longrightarrow \text{PRODUCTS}$$

It would be seen that most of the attacking reagents bear either a positive or a negative charge. Naturally these would not attack the substrate successfully unless the latter somehow possessed oppositely charged centres in the molecule. In other words, the substrate molecule although as a whole electrically neutral must develop polarity on some of its carbon atoms and substituents linked together.

This is made possible by the displacement of the bonding electrons (partially or completely) resulting in the development of polarity in the molecule. Such changes or effects involving the displacement of electrons in the substrate molecule are often referred to as **Electron displacement effects**. These displacement effects are of great significance in understanding reaction mechanisms.

ELECTRON DISPLACEMENT EFFECTS

There are four types of electron displacement mechanisms frequently observed in organic molecules :

(*a*) *Inductive effect* ;
(*b*) *Electromeric effect* ;
(*c*) *Mesomeric effect* ; *and*
(*d*) *Hyperconjugative effect.*

Inductive effect. When a carbon atom is joined to a hydrogen atom by a covalent (σ) bond (C—H) such as in alkanes, it is understood that the shared electron-pair is symmetrically

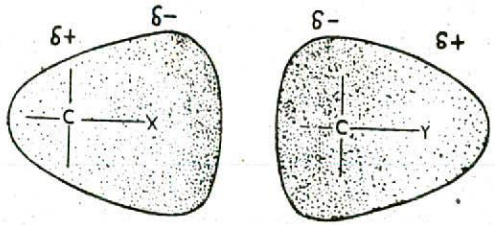


Fig. 6·1. Electron cloud in the orbitals C—X and C—Y whose symmetry is disturbed in the opposite directions.

placed between them. If instead of hydrogen atom, we have a substituent X having higher electronegativity or electron-attracting power than the C-atom, in the bond C—X, the shared electron pair will be displaced away from the carbon atom and toward the more electronegative substituent X. On the other hand if a substituent Y having lower electronegativity is attached to it, the shared pair of the bond C—Y will be displaced toward the carbon atom and away from the electron releasing group Y. In other words the symmetry of the molecular orbital of

C—X will be disturbed in favour of X, the more electronegative substituent, while in case of C—Y the molecular orbital will be disturbed in favour of the carbon atom which is more electronegative.

As a result of the minor displacements of the bonding electron-pair, the joined atoms develop small fractional charges on them as illustrated below.

$$C : H \quad \text{or} \quad C\text{——}H \quad \text{(standard)}$$

$$C : X \quad \text{or} \quad \overset{\delta+}{C}\text{——}\overset{\delta-}{X} \quad (-I)$$

$$C : Y \quad \text{or} \quad \overset{\delta-}{C}\text{——}\overset{\delta+}{Y} \quad (+I)$$

The polarization thus induced in the substrate molecule is of a permanent nature.

The permanent effect whereby polarity is induced on the carbon atom and the substituent attached to it due to minor disptacement of bonding electron pair caused by their different electronegativities, is known as **Inductive effect** *or simply as* **I-effect**. When the substituent linked to carbon is electron-attracting (X), it develops a negative charge and it is said to exert a negative inductive effect or **—I effect**. If the substituent Y bonded to carbon atom is electron-releasing, it acquires a positive charge and the inductive effect produced is called **+ I effect**.

Writing structural formula of the polar molecules, the inductive effect is represented by an arrow-head in the middle of the covalent bond pointing in the direction of the electron displacement. Thus,

$$C \rightarrow X \qquad C \leftarrow Y$$
$$(-I) \qquad (+I)$$

Now let us consider an organic molecule having a highly electron-attracting substituent X attached to the terminal carbon atom.

$$\overset{\gamma}{C}\text{—}\overset{\beta}{C}\text{—}\overset{\alpha}{C}\text{—}X$$

The substituent X pulls towards it the electron-pair between α-carbon and X. This produces a slight positive charge (δ^+) on the α-carbon. When a small positive charge is acquired by the α-carbon, it will tend to attract to itself the electron-pair linking it with β-carbon. This causes β-carbon also to acquire a fractional positive charge which, of course, would be smaller than that of the α-carbon due to the decreasing influence of X. Similarly, the β-carbon influences the electron-pair bonding it with γ-carbon, but to a lesser degree and a still smaller positive charge is developed on the γ-carbon. Denoting the decreasing magnitude of positive charge on α, β and γ carbon atoms by δ^+, $\delta\delta^+$ and $\delta\delta\delta^+$, the inductive effect relayed along the carbon chain may be represented as follows.

$$\overset{\delta\delta\delta+}{C} \rightarrow \overset{\delta\delta+}{C} \rightarrow \overset{\delta+}{C} \rightarrow \overset{\delta-}{X}$$

With an electron-pumping substituent Y, the inductive effect will be reversed and the situation would be

$$\overset{\delta\delta\delta-}{C} \leftarrow \overset{\delta\delta-}{C} \leftarrow \overset{\delta-}{C} \leftarrow \overset{\delta+}{Y}$$

Some common groups which cause negative or positive I-effect are given below in order of their decreasing effect.

(*a*) *—I effect groups (electron-attracting)* :

$$NO_2 > F > COOH > Cl > Br > I > OH > C_6H_5$$

(*b*) *+I effect groups (electron pumping)* :

$$\underset{\text{tertiary butyl}}{(CH_3)_3C\text{—}} > \underset{\text{isopropyl}}{(CH_3)_2CH\text{—}} > \underset{\text{ethyl}}{CH_3CH_2\text{—}} > \underset{\text{methyl}}{CH_3\text{—}}$$

In general the Inductive effect of the alkyl groups is in the order 3° > 2° > 1° groups. In other words the electron-releasing power of a primary carbon (1°) is less than that of a

secondary carbon (2°), while that of a tertiary carbon (3°) is the maximum. The inductive effect caused by the presence of an electron-attracting or electron-pumping substituents relayed on a chain falls rapidly as the distance from the functional group increases. Actually, it dies down completely after the third or fourth carbon atom of the chain.

Electromeric Effect. This effect is very helpful in explaining polarization produced in a substrate molecule containing multiple bonds. When a double or a triple bond is exposed to attack by an electrophilic reagent, a pair of bonding electrons is transferred completely from one atom to the other. The atom that takes charge of the eletron-pair becomes negatively charged and the other positively charged. Thus, taking a very general case we have

$$A=B \xrightleftharpoons{\text{Electrophilic reagent}} \overset{+}{A}-\overset{-}{B}$$

This is a purely temporarily effect and remains into play only in the presence of the electrophilic reagent. As soon as the attacking reagent is removed, the polarized molecule reverts to its original electronic state.

$$A=B \xrightleftharpoons[\text{Reagent removed}]{\text{Reagent added}} \overset{+}{A}-\overset{-}{B}$$

The effect which causes a temporary polarization in the substrate molecule at the seat of a multiple bond by shift of an electron-pair from one atom (or part) to the other under the influence of an electrophilic reagent, is called **Electromeric effect** (*electro* = electron ; *meros* = part).

The electromeric effect differs from the inductive effect in the following respects.

Electromeric Effect	*Inductive Effect*
1. Shown by substrate molecules containing double (C=C) or triple (C≡C) bonds.	1. Shown by molecules containing single bonds.
2. Takes place when the molecule is exposed to an attack by electrophilic reagent.	2. Takes place under the influence of a substituent (electron-attracting or electron-pumping) linked to the terminal carbon atom.
3. Polarity caused by complete transfer of an electron-pair to one of the two atoms joined by multiple bond.	3. Polarity caused by the displacement of bonding electron-pair from one atom towards the other.
4. The charge acquired by the atom that gains the electron-pair is **+1** while the other gets **−1**.	4. The charge developed by the carbon linked to the substituent is small fractional δ^+ or δ^- according as the substituent is electron attracting or electron pumping.
5. Temporary effect ; disappears with the removal of the attacking reagent.	5. Permanent effect ; depending on the structure of the substrate molecule.

Let us discuss the example where an electrophile attacks a carbon-to-carbon double bond in the substrate molecule. According to modern concepts, a double bond is made of one σ bond (—) and one π bond ($\frown$). The electron cloud of the π bond is rather extensive and surrounds that of the σ bond in space. Under the influence of the electric field of an electro-

phile, symmetry of the π electron cloud is disturbed entirely in favour of one carbon atom as shown in the illustration given below.

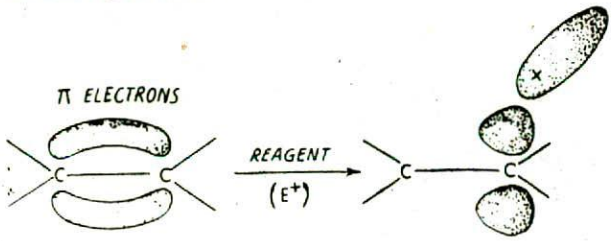


Fig. 6·2. The presence of an electrophile disturbs the symmetry of the π electron cloud completely in favour of one of the double bonded carbon atoms.

This gives a negative charge to the carbon atom to which the π electron-pair shifts, while the other atom gets a positive charge. For the convenience of writing, the above change may be represented as

$$-\overset{|}{C}\overset{\frown}{-}\overset{|}{C}- \quad \overset{\text{Attacking reagent}}{\rightleftharpoons} \quad -\overset{|}{\overset{+}{C}}-\overset{|}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}}-$$

The π bond is ruptured by the attack of the electrophile and one carbon to which the bonding electrons shift becomes negative while the other that loses its own shared electron gets a positive charge. Therefore, a more correct definition of the electromeric effect would be :

"A temporary effect which causes extreme (or whole unit) polarity on atoms joined by a multiple bond owing to a complete transfer of the π electron pair to one or the other atom under the influence of an electrophile."

While writing reaction mechanism, electromeric effect or change is represented by a curved arrow pointing away from the centre of the π bond towards the carbon that gains the electron pair. To be more correct π bond should be represented by (⌢) to distinguish it from σ bond (—). But for convenience, a π bond is also generally written as a straight line like the σ bond. Thus,

$$>C=\overset{\curvearrowright}{C}< \quad \overset{\text{Electrophile}}{\rightleftharpoons} \quad >\overset{+}{C}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}<$$

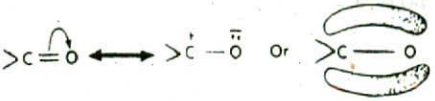
Let us now consider the example of ethylene molecule. Here under the influence of an electrophile the direction of displacement of electron pair can take place on to any of the two carbon atoms.

$$H_2C=CH_2 \quad \overset{\text{Attacking Reagent}}{\rightleftharpoons} \quad H_2\overset{+}{C}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}H_3 \quad \text{or} \quad H_2\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}-\overset{+}{C}H_2$$

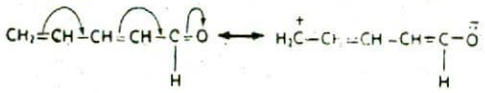
Mesomeric Effect. It affords yet another case of electron displacement in the molecules causing permanent polarization. This electron displacement is relayed through π electrons of multiple bonds in the carbon chain of the molecule. Unlike the inductive effect which operates in molecules having σ bonds, the mesomeric effect operates in only those systems which have an extended chain with conjugate π bonds (alternate σ and π bonds). For this reason this effect is also referred to as **Conjugative Effect**. The π electrons get delocalized as a consequence of mesomeric effect, giving a number of resonance structures of the molecule. This leads to a greater magnitude of the mesomeric effect than the corresponding inductive effect for a given difference of electronegativities of the bonded atoms.

When an electron pumping or electronic withdrawing group is conjugated with a π bond or a set of alternately arranged σ and π bonds, the electron displacement is transmitted through π electrons in the chain. Consider a carbonyl group (>C=O) to be linked with a con-

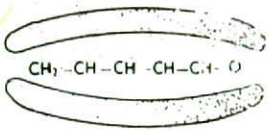
jugated system as $CH_2{=}CH{-}CH{=}CH{-}CH{=}O$. The π electrons of the carbon-oxygen bond get displaced toward oxygen—the more electronegative atom, giving the resonance structures as



In the whole molecule, this polarization can be transmitted further via the π electrons as

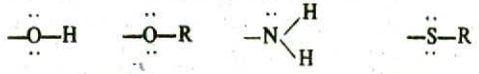


Or



The difference between the transmission through a conjugated system of π bonds and the inductive effect along a σ bond chain lies in the fact that the effect suffers very little decrease in intensity. The terminal carbon is almost as positive as the first carbon.

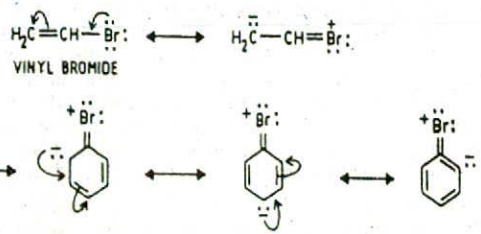
Mesomeric effect like the inductive effect may be + or and is usually denoted by $+M$ or $-M$. A group or atom is said to have **+M effect** when the direction of electron displacement is away from it. Such groups as have lone pair of electrons, furnish the pair for conjugation with an attached unsaturated system. This extends the degree of delocalization bringing about greater stability to the molecule. The groups



have one or more lone pairs of electrons and have $+M$ effect. The presence of an amino group $-\ddot{N}H_2$ at the end of a conjugate π bond system brings about electron displacement as



The +M effect of halogen atom (—Br:) accounts for low reactivity of the halogen atom (getting attached by a double bond) in vinyl halides and aryl halides.



On the other hand, a group or atom is said to have **−M effect** when the direction of electron displacements is toward it. The groups such as >C=O, $-NO_2$, −C≡N, $-SO_3H$ etc., have *−M* effect owing to the presence of a highly electronegative atom like oxygen or nitrogen functioning as an '*electron sink*'. The *−M* effect of the nitro group is illustrated below.



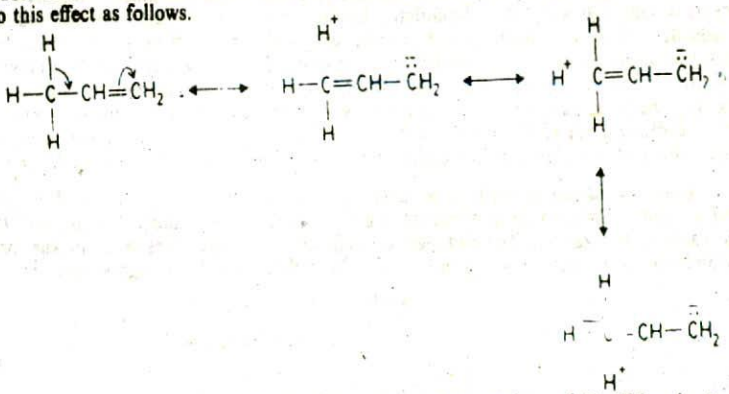
Hyperconjugative Effect. While discussing inductive effect, it was pointed out that the inductive effect of the alkyl groups is in the order :

tertiary > secondary > primary.

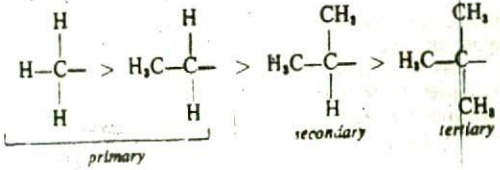
This order, however, is reversed when an unsaturated system (>C=C<) is attached with the alkyl group. Under the circumstances, the alkyl group becomes capable of giving rise to electron-release in a way entirely different from the inductive effect. This mechanism of electron release is known as **Hyperconjugation**. For its operation, hyperconjugation requires a carbon-hydrogen bond at the α-position to the double bond.



Hyperconjugative effect results in an electron displacement towards the double bond carbon marked by an asterisk. Baker and Nathan suggested that hyperconjugative effect takes place through the interaction of σ electrons of the carbon-hydrogen bond with π electrons of the double bond. The three C—H bonds of the methyl group in the propylene molecule contribute to this effect as follows.



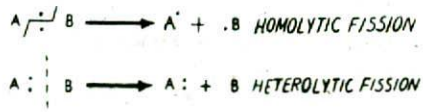
It is fairly reasonable to believe that greater the number of C—H bonds at α carbon to the unsaturated system, greater would be the electron release towards the terminal carbon (bearing asterisk mark) creating high electron density. Consequently, the hyperconjugative release of electrons would be maximum with a methyl group (three C—H bonds at α-position) and least for an isopropyl group (one C—H bond). However, for a tertiary butyl group, this effect is zero due to the absence of a C—H bond at the α-position. The order of hyperconjugative electron release for the alkyl groups will be



To understand the reaction mechanisms it is also necessary to know as to how do the processes of bond-breaking (fission) and bond-making in the substrate take place.

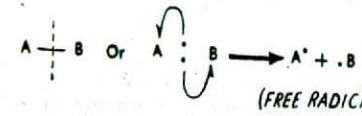
low Bond Fission Occurs ?

A covalent bond (σ bond) joining two atoms exists because of the shared pair of electrons. When the two atoms are separated from each other, bond fission (or cleavage) is said to have aken place. The fission process can occur in two ways. The separating atoms may take away ne electron each of the bonding pair, or one of atoms may get away with both the electrons.



In the first case when one electron of the bonding pair goes with each of the departing toms the fission is symmetrical or homogeneous and is called **Homolytic Fission or Homolysis**. In the second case since both the electrons are taken over by one atom the other atom goes without an electron, the fission is unsymmetrical or heterogeneous and is called **Heterolytic Fission** or **Heterolysis**.

Homolytic Bond Fission. As described above, *a covalent bond undergoes homolytic fission when each of the two departing atoms makes away with one of the bonding pair of electrons.*



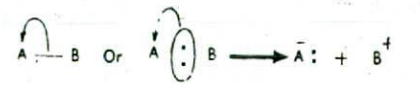
Such a single electron shift is represented by a 'fish-arrow' as illustrated above. The two fragments produced as a result of homolytic fission carry an odd electron each and are called **Free radicals**. These are transitory and at once react with other radicals or molecules by gaining one more electron to restore the stable bonding pair. It may be noted that the presence of an odd electron on such species *i.e.*, A· or ·B does not make them charged because this electron belonged to the electrically neutral atom itself before the covalent bond came into existence. So, the free radicals are not at all ionic in character and their high reactivity as reaction intermediates is entirely due to the tendency of the odd electron to 'pair up' with another available electron.

Homolytic fission proceeds to produce free radicals by the application of energy — may be heat or light. This process is prevalent in gaseous reactions and adequately explains the substitution reactions of alkanes. The cleavage of chlorine molecule takes place in the presence of ultraviolet light or by heat resulting in free chlorine radicals which are highly reactive.

$$Cl : Cl \xrightarrow{\text{light/heat}} Cl\cdot + \cdot Cl$$

(Chlorine free radicals)

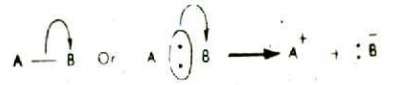
Heterolytic Bond Fission. When a covalent bond breaks in a fashion that both the bonding electrons are appropriated by one of the two departing fragments (atoms or groups), it is said to have undergone heterolytic fission. This type of fission in a molecule **A—B may be represented** as



...(1)

The curved arrow-head points toward the atom (or group) that makes away with both the shared electrons and, therefore, becomes negative leaving behind its partner with a positive charge. In the above example, it may be noticed that the atom B loses its original share of electron in the bonding pair and thus gives the positive ion (B^+), while the atom A which gains one more electron in addition to its own gives the negative ion ($\bar{A}:$). Thus speaking in general, the heterolytic bond fission yields one positive and one negative ion.

As a result of the heterolytic fission of the molecule A B, which of the two atoms (A or B) takes away the bonding electron pair, is a pertinent question since the change could as well have followed the course



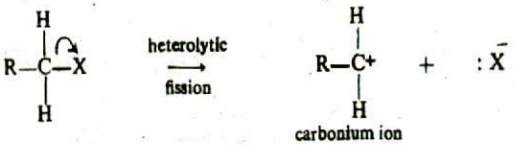
...(2)

giving (A^+) and ($:B^-$) ions. In fact, the course of heterolytic fission is determined by the electronegativities or 'power to attract electrons' of the covalently joined atoms or groups. If A has greater electronegativity than B, the former atom will take away the bonding electron pair and the fission will adopt the course (1). On the other hand if B has higher electronegativity than A, the course of fission will be as shown in (2).

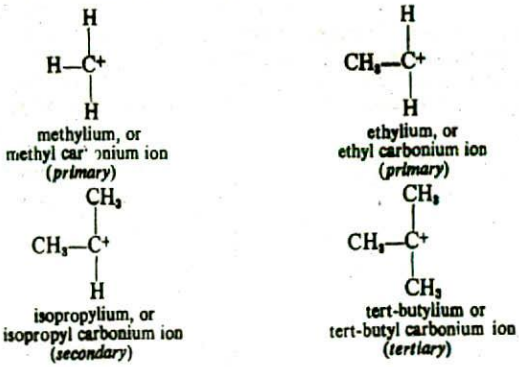
Heterolytic fission is most common in organic reactions taking place in solutions since the energy required to break the bond can be partly drawn from the energy of solvation of the ions produced. Thus the progress of a heterolytic reaction such as $A—B \rightarrow A^+ + B$ depends significantly on the nature of the solvent. These reactions take place more readily in polar solvents like water and are catalysed by the presence of ionic catalysts (*e.g.*, acidic or basic)

CARBONIUM IONS

Let us consider the heterolytic fission of the bond C—X present in an organic molecule. If the atom X has greater electronegativity than the carbon atom, the former takes away the bonding electron pair and becomes negatively charged while an ion bearing a positive charge is produced. For illustration,



An ion containing a positively charged carbon centre is called a **Carbonium ion** as analogy with positive ammonium **ion.** In general, the carbonium ions are named by adding the suffix *-ium* to the name of the parent alkyl group *i.e.*, Alkylium. For example,



The carbonium ions which are produced as reaction intermediates, are very reactive. This is due to the fact that the central positively charged carbon in them has only six electrons (two to a covalent bond) in the outer shell and has a marked tendency to complete the octet. Hence a carbonium ion combines readily with any substance that can donate a pair of electrons to form the fourth covalent bond.

Carbonium ion being deficient in electrons is ordinarily very unstable. However, if an electron repelling group such as alkyl group) is present adjacent to the carbon bearing positive

charge the former makes the carbonium ion stable by pumping electrons through the connecting bond in an attempt to annul the positive charge.

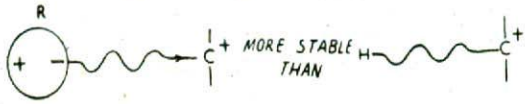
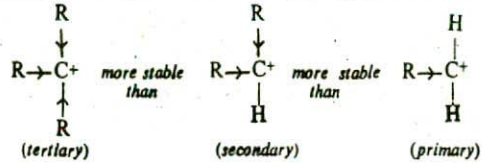


Fig. 6·3. The group R pumps electrons through the connecting bond (shown wavy) to the positive charge-bearing carbon of the carbonium ion.

That is why a tertiary carbonium ion is more stable than a secondary carbonium ion ; and a secondary carbonium ion is more stable than a primary carbonium ion. That is,



The stability of the carbonium ions is reduced by electron-attracting groups ($-NO_2$; $>C=O$) linked to the central positive carbon atom.

Here the groups like 'nitro' or 'carbonyl' withdraw electrons through the connecting bond, thus rendering the carbonium ion less stable.

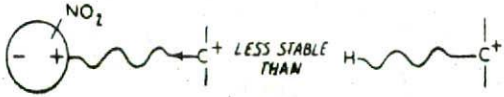
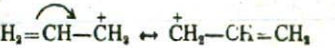


Fig. 6·4. The NO_2 group withdraws electrons through the connecting bond (shown wavy), thus enhancing the positive charge of the central carbon and reducing the stability of the carbonium ion.

The stability of carbonium ions could also be explained in terms of resonance. A particular carbonium ion may delocalize its positive charge through the analogous canonical structures in its hybrid. Thus the positive charge on the central carbon of the carbonium ion gets dispersed over other carbon atoms and this makes the ion stable. As a rule, the more canonical structures which may be written, the more stable the carbonium ion proves to be. Benzyl carbonium ion and allyl carbonium ion are considerably more stable than propyl carbonium ion because of the marked stabilization of their resonance hybrids through the canonical structures shown below.

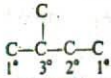


Canonical structures of the Allyl carbonium ion Hybrid :



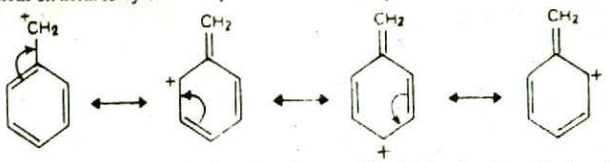
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*Primary carbon atom is that which is linked directly to none or one other carbon atom ; Secondary carbon is linked to two and tertiary carbon to three other carbon atoms. These are designated 1°, 2° and 3° respectively.



The carbonium ions containing 1°, 2° and 3° carbon atoms are, therefore, called *primary*, *secondary* and *tertiary* carbonium ions respectively.

Canonical structures of the Benzyl carbonium ion Hybrid :



Since the carbon of the carbonium ion is an sp^2 hybridized state, the ion is planar with a vacant p orbital prependicular to the plane of the three covalent bonds to carbon.

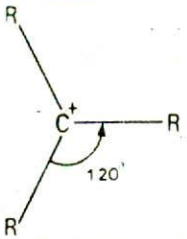
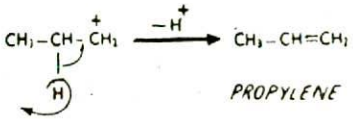


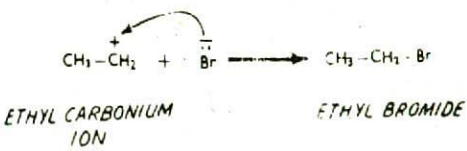
Fig. 6·5. The geometry of alkyl carbonium ion.

Reactions of Carbonium ions. A carbonium ion once produced during a reaction may react further in any one of the following ways.

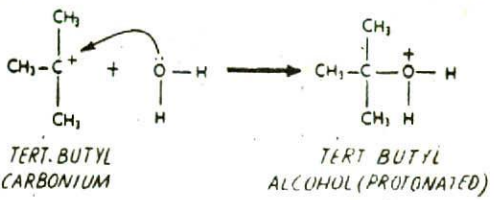
(*a*) *Proton loss.* A carbonium ion may expel a proton forming an alkene. The proton is lost from the α-carbon. A propyl carbonium loses a proton to produce propylene as



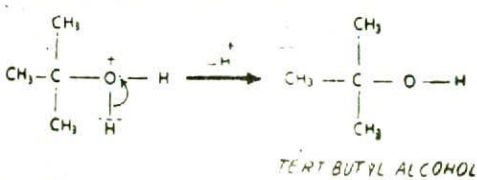
(*b*) *Combination with nucleophiles.* A carbonium ion accepts a pairof electrons from a nucleophile to form a bond. For example, a highly reactive ethyl carbonium ion reacts with a bromide ion to form ethyl bromide



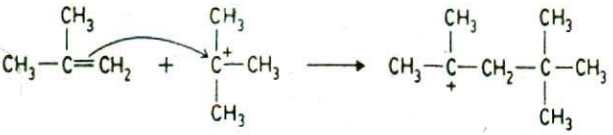
A neutral nucleophile, H_2O, reacts with tertiary butyl carbonium ion to produce protonated tertiary butyl alcohol as



The protonated alcohol further loses the proton to produce butyl alcohol as



(*c*) *Addition to an alkene* A carbonium ion may add to an alkene to produce a bigger carbonium ion as



(*d*) *Molecular Rearrangement* A carbonium ion would undergo a molecular rearrangement when it could produce a more stable carbonium ion, the stability of carbonium ions being in the order :

tertiary > *secondary* > *primary*

a primary carbonium ion would have a tendency to rearrange to a secondary or a tertiary carbonium ion. Similarly a secondary carbonium would have a tendency to rearrange to a tertiary carbonium ion. These rearrangements occur provided the changes are permitted by the structure of the original carbonium ion.

(*i*) *From primary into secondary carbonium ion,*



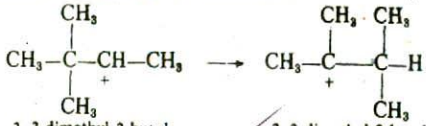
pri-butyl carbonium ion — *sec*-butyl carbonium ion

(*ii*) *From primary into tertiary carbonium ion,*



2-methy-1-butyl carbonium ion (*pri*-) — 2-methyl-2-butyl carbonium ion (*sec*-)

(*iii*) *From secondary into tertiary carbonium ion,*

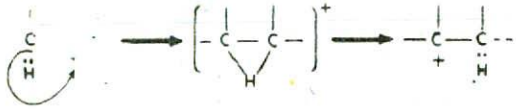


3, 3-dimethyl-2-butyl carbonium ion(sec-) — 2, 3-dimethyl-2-butyl carbonium ion (tert-)

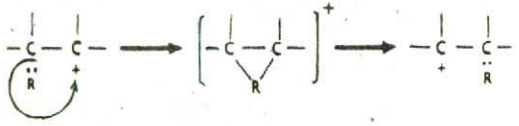
The driving force for these rearrangements is obviously the gain in stability. These rearrangements have been visualised to take place by migration of either a hydrogen atom [case (*i*) and (*ii*)] or an alkyl group (*iii*) with its pair of bonding electrons from the carbon atom adjacent to the carbon bearing positive charge.

Migration of hydrogen with its pair of bonding electrons is called **Hydride shift**. Migration of an alkyl group with its pair of bonding electrons is called **Alkyl shift**. These rearrangements in which the migrating group moves from one atom to the very next atom are often referred to as **1, 2-shifts**. Their mechanism is represented as

HYDRIDE SHIFT

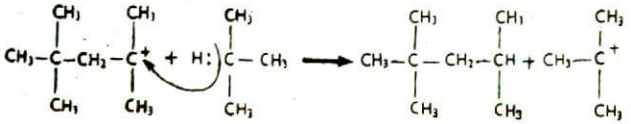


ALKYL SHIFT



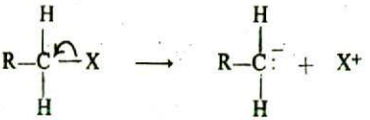
These rearrangements have been used as evidence for intermediate formation of carbonium ions in a variety of reactions.

(*e*) *Abstraction of a Hydride Ion.* A carbonium ion may remove a hydride ion $\ddot{H}$, to form an alkane as



CARBANIONS

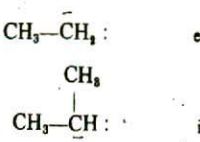
Let us revert for a while to the heterolytic fission of the bond C—X present in an organic molecule. If the carbon atom has greater electronegativity than the atom X, the former takes away the bonding electron pair and acquires a negative charge while a positive ion X^+ is produced. Thus,



carbanion

An organic ion with a pair of available electrons and a negative charge on the central carbon atom is called a **Carbanion** (**carb**, *from carbon* + **anion**, *negative ion*).

Individual carbanions are named after the parent alkyl group and adding the word carbanion. Thus,



ethyl carbanion

isopropyl carbanion

Though carbanions are electron-rich fragments of heterolytic fission, but they are very reactive intermediates. They are readily attacked by electron-poor reagents (electrophiles).

Ordinarily carbanions are unstable because of their negative charge. They are *stablized* by the presence of an adjacent electron-attracting group as $-C\equiv N$ or $>C=O$.



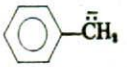
Fig. 6·6. The $-C\equiv N$ group withdraws electrons through the connecting bond (shown wavy) and thus the negative charge on the carbon decreases while the carbanion becomes more stable.

On the other hand, the presence of an adjacent electron-releasing group such as alkyl group increases the negative charge on the central carbon atom and thus makes the carbanion less stable.



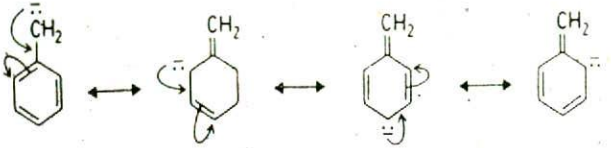
Fig. 6·7. The group R pumps electrons through the wavy bond to the central carbon atom thereby increasing its negative charge and rendering the carbanion less stable

Carbanions can also be stabilised due to resonance when they have double bond or an aromatic ring adjacent to the charged carbon centre. Thus,



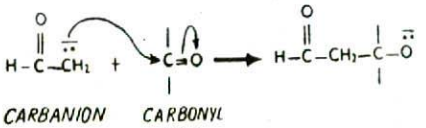
benzyl carbanion ethyl carbanion

The stabilisation by resonance is due to the delocalization of the negative charge which is then distributed over other carbon atoms in the hybrid structure. The canonical forms of Benzyl-carbanion in its resonance hybrid structure responsible for its stabilization are :



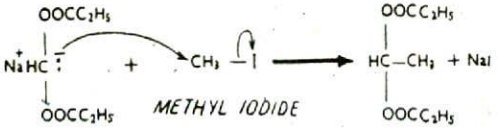
Reactions of Carbanions. Since carbanions are electron rich species, they behave as potent nucleophiles. These are known to take part in a number of addition and substitution reactions. Some representative examples are as follows.

(*a*) *Addition Reactions.* Carbanions add to the carbonyl group of aldehydes (aldol condensation) and ketones.



A number of condensation reactions like aldol consideration, Perkin and Claisen condensations are nice examples of addition reactions of carbanions.

(*ii*) *Substitution Reactions.* Carbanion obtained from sodium salt of malonic ester gets substituted in place of halogen atom in a molecule of alkyl halide as



The synthetic applications of malonic ester, cyanoacetic ester and acetoacetic ester are primarily due to the ease with which these form carbanions which subsequently combine with a variety of compounds to form products.

Unlike carbonium ions, the carbanions do not undergo rearrangement reactions.

ATTACKING REAGENTS AND THEIR ROLE

We have described before that an organic reaction proceeds by the attack of a reagent on substrate. Under the influence of the attacking reagent and suitable experimental conditions, the substrate molecule undergoes heterolysis to form reactive intermediates such as carbonium ion and carbanions. These then combine with the attacking reagent to give the final product. Therefore, to understand the reaction mechanisms it is imperative to know the nature of the various attacking reagents They can be classified as :

(*i*) *Electrophilic Reagents* : and (*ii*) *Nucleophilic reagents.*

Electrophilic Reagents. As signified by the name electrophilic (*electro*=electron ; *philic*=loving), these reagents are electron loving species. Their lust for electrons is accounted for by the fact that they are short of a pair of electrons than the stable number (duplet or octet).

The electrophilic reagents are of two types :

(*a*) POSITIVE ELECTROPHILES (E^+) that are deficient in two electrons and carry a positive charge *e.g.*, Carbonium ions and Bromonium ion,

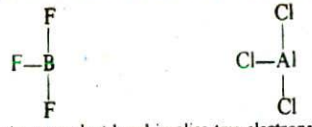


carbonium ion (C atom has 6 electrons in the outer shell)

bromonium ion (has 6 electrons in the outer shell)

Both of these have a sextet of electrons in their outer shell and hence are deficient by two electrons. Other common examples of positive electrophiles are : nitronium ion, $\overset{+}{N}O_2$; nitrosonium ion, $\overset{+}{N}O$; diazonium ion, $C_6H_5\overset{+}{N}_2$; bisulphonium ion, $\overset{+}{S}O_2H$, and a proton H^+ or hydronium ion, H_3O^+.

(*b*) NEUTRAL ELECTROPHILES (E) such as boron trifluoride (BF_3) and aluminium chloride ($AlCl_3$) in which the central atom has six electrons but no charge.



(one covalent bond implies two electrons)

Other typical examples of neutral nucleophiles are carbenes and nitrenes



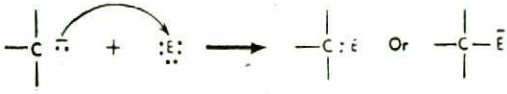
dichlorocarbene (6 electrons)

nitrene (6 electrons)

How electrophiles attack the substrate ? Both types of electrophiles can attack the substrate ion or molecule which is electron-rich and can donate an electron-pair to the attacking reagent to form a new bond.

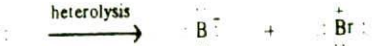


CARBANION (SUBSTRATE) POSITIVE ELECTROPHILE PRODUCT



CARBANION (SUBSTRATE) NEUTRAL ELECTROPHILE PRODUCT

How positive electrophiles are produced ? Positively charged electrophiles are produced as a result of heterolytic fission of neutral molecules. For example, bromonium ions are obtained by heterolysis of bromine molecule (Br—Br).



bromine molecule bromide ion bromonium ion

So are produced carbonium ions by heterolytic fission of carbon bonds as described before.

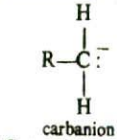
It may be noted that it is some times difficult to distinguish between an attacking reagent and a substrate. Compounds such as acid chlorides (RCOCl) could be either reagent or substrate. Carbonium ions and carbanions both could play the role of a reagent as also of a substrate.

Table. *Some Electrophiles*

POSITIVE (+)		NEUTRAL	
Proton	H^+	Sulphur trioxide	SO_3
Hydronium	H_3O^+	Boron trifluoride	BF_3
Nitronium	NO_2^+	Aluminium trichloride	$AlCl_3$
Nitrosonium	NO^+	Ferric chloride	$FeCl_3$
Sulphonium	$\overset{+}{S}O_2—OH$	Acid chlorides	$R—C(=O)Cl$
Bromonium	Br^+	Carbonyl group	$>C=O$
Diazonium ion	$C_6H_5N_2^+$		
Carbonium ion	$—\overset{|}{C}^+$		

Nucleophilic Reagents. As implied by the name nucleophilic (*nucleo* = nucleus; *philic* = loving), these reagents are nucleus-loving and are often referred to as **nucleophiles**. Since the nucleus is electrically positive, the nucleophiles would be electrically negative or electron-rich substances. Thus there are two types of nucleophiles.

(*a*) NEGATIVE NUCLEOPHILES ($\ddot{N}u$) which have an excess electron-pair and carry a negative charge *e.g.*, carbanions and chloride ion.

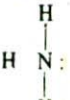


carbanion
(C atom has a spare pair of electrons and a negative charge

chloride ion
(has available pairs of electrons and a negative charge)

Other examples of negative nucleophiles are : hydroxide ion, $:\ddot{O}H$; cyanide ion, $C\equiv\ddot{N}:$; bisulphide ion, $\ddot{S}H$; alkoxy ion, $:\ddot{O}R$; hydride ion, $\ddot{H}$; and halide ions, $:\ddot{X}:$.

(*b*) NEUTRAL NUCLEOPHILES (Nu :). Such as ammonia and water, possess spare pairs of electrons but no charge.



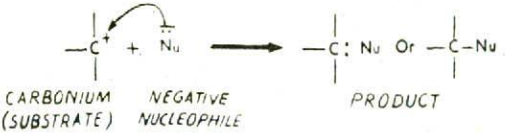
ammonia

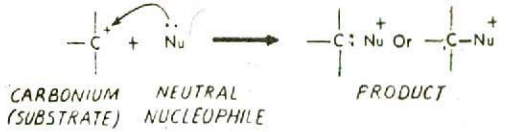


water

Other examples of neutral nucleophiles are : alcohols, R—Ö—H ; thioalcohols, R—S̈—H : ethers R—Ö—R or any other compound containing a hetero atom (*e.g.*, O, S, N etc.) which should have an unshared pair of electrons.

How nucleophiles attack the substrate ? Both charged and neutral nucleophiles have a spare pair of electrons. When they attack a substrate deficient in two electrons, the latter accepts the spare electron-pair from the reagent to establish a new bond. Let us illustrate the results of attack by both types of nucleophiles on the carbonium ion as the substrate.





It may be noted that with the charged nucleophile the product is neutral while with the neutral nucleophile, the Nu part of the product develops a positive charge.

REACTION MECHANISMS — THEIR TYPES

From the mechanistic viewpoint described earlier in this chapter, organic reactions could be divided into two classes :

(*i*) *Homolytic reactions involving homolytic bond fission* ;

(*ii*) *Heterolytic reactions involving heterolytic bond fission.*

The reaction mechanism in the two cases is of entirely different type.

Free-radical Mechanism. In homolytic reactions, the first step is the production of a free radical (R·) from a normal molecule by the application of energy (heat or light). The free radical then attacks the substrate to bring about homolytic fission.

$$R\cdot + \underset{\text{substrate}}{X—Y} \longrightarrow R—X + \cdot Y$$

This type of reaction mechanism when the attacking species is a free radical, is called **Free-radical Mechanism**.

The Free-radical mechanism may be illustrated by the chlorination of methane in sunlight. In the first step, illumination causes a molecule of chlorine to break homolytically into two chlorine free radicals. These then attack a molecule of methane forming hydrogen chloride and methyl radical ($H_3C\cdot$). In turn, the methyl free radical attacks a molecule of chlorine giving methyl chloride (CH_3Cl) and fresh chlorine atom.

$$Cl : Cl \xrightarrow{light} 2\,Cl\cdot$$

$$\left.\begin{aligned} Cl\cdot + CH_4 &\longrightarrow HCl + H_3C\cdot \\ H_3C\cdot + Cl_2 &\longrightarrow CH_3Cl + Cl \end{aligned}\right\} \text{Chain reaction}$$

Once the free radical $H_3C\cdot$ is produced, the reaction proceeds by the last two steps in a sort of endless chain. Such a self-propagating reaction is often referred to as a **Chain reaction**.

Since the free radical carries no charge, it can attack any part of the substrate molecule regardless of the electronic distribution of the latter.

Polar or Ionic Mechanism. This type of mechanism applies to organic reactions in which heterolytic fission takes place. Here the substrate molecule develops negative and positive charge centres, or partial ionic character, by the displacement of electrons due to inductive effect, electromeric effect etc. These negative and positive poles of the molecule are so to say activated for attack by an electrophilic or nucleophilic reagent. The mechanism of reactions involving the attack of electrophilic or nucleophilic reagents on the polar or ionic molecules of the substrate is referred to as **Polar** or **Ionic Mechanism.**

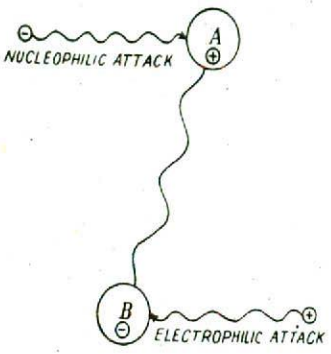
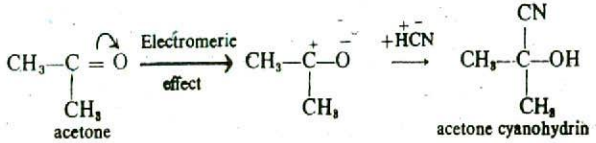


Fig. 6·8. How nucleophilic and electrophilic reagents attack the polar AB molecule.

The cardinal principle of electrostatics that 'the unlike charges attract while like charges repel each other' forms the basis of polar or ionic mechanism. The negatively charged nucleophilic reagents are anionic in character and attack the substrate molecule at the positive centre causing a **Nucleophilic reaction.** On the other hand, the positively charged electrophilic eagent would attack the molecule at the negative centre causing **Electrophilic reaction.**

The Polar or Ionic mechanism may be beautifully illustrated as in Fig. 6·8. The imaginary molecule AB of the substrate has a positive end A and a negative end B. This would be expected to be attacked by anionic nucleophilic reagent at A and cationic electrophilic reagent at B.

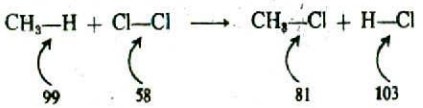
An example of the above reaction mechanism is afforded by the addition of HCN ($H^+ + CN^-$) to acetone.



More examples of the ionic mechanism will be discussed in the subsequent treatment.

ENERGY REQUIREMENTS OF A REACTION

In an organic reaction, some bonds break while some new ones are formed. Energy is required for the breaking of bonds and also it is liberated in the formation of bonds. Let us consider, for example, the reaction between methane and chlorine to give chloromethane (CH_3Cl) and hydrogen chloride. Here one C—H bond and one Cl—Cl bond is broken, requiring a total energy of 157 kcal/mole. At the same time one C—Cl bond and H—Cl bond is formed, liberating total energy of 184 kcal/mole. The net result is that the reaction occurs with a liberation of energy equal to 27 kcal/mole and is, therefore, said to be **exothermic.** Thus,



Conversely, the reverse reaction would require the consumption of 27 kcal/mole energy and will be **Endothermic.** Thus an exothermic reaction could be considered like a ball rolling down a hill side and would be expected to occur of its own accord. On the other hand an endothermic reaction which is like a ball rolling uphill, would not occur normally, unless energy is supplied to the system. The total 'chemical energy' stored in the molecules before and after the reaction could be described as the 'potential energy' of the system.

Activation Energy. We have discussed above that a reaction proceeds by breaking of bonds in the reacting molecules. Therefore, whether a reaction is exothermic or endothermic, to start with energy must come from some source to break the bonds.

We know from our knowledge of Physical Chemistry that molecules of the reactants are in a state of rapid motion and possess kinetic energy. The reaction occurs when the reacting molecules approach in proper alignment with respect to one another and collide. On such collisions, the kinetic energy possessed by the molecules is transformed into 'chemical energy' or 'potential energy' of the system. Thus to start a reaction, the required energy is supplied by the collisions of the reacting molecules, whose rate could be enhanced if necessary, say by heating.

Not all collisions between the reacting molecules are fruitful. Rather, it is only the collisions of such molecules as possess a certain minimum energy which bring about the reactions while others do not. The molecules that come to possess higher potential energy through collisions are said to have been *'activated'* to enter into reaction.

The minimum amount of 'chemical' or 'potential' energy that must be provided by collisions of the reacting molecules for the reaction to occur is termed the **Activation energy.**

It is true that for an exothermic reaction, the collisions of the reactant molecules readily supply the required initial energy and the reaction takes place spontaneously. On the other hand, for an endothermic reaction the molecules need to be activated by supplying energy, say in the form of heat to make the reaction go.

For illustration, imagine some balls attempting to climb over a hill from one valley to another Only those will cross over which possess a certain minimum of energy to reach the hill-top from where they would get over the barrier or the 'energy cliff'.

From analogy, only such reacting molecules that possess a certain minimum energy could change into products but before doing so, these would have to cross over the 'activation energy barrier'.

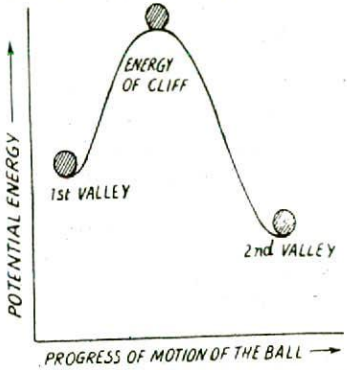


Fig. 6·9. A ball crossing the hilltop must possess a minimum potential energy to get over the 'energy barrier'.

Let us consider the energy changes during the course of the reaction.

$$X + Y{-}Z \longrightarrow X{-}Y + Z$$

In the beginning both X and Y—Z possess certain potential energy represented by the point (*a*) on the curve (*see* Fig. 6·10). The reacting molecules also possess kinetic energy which

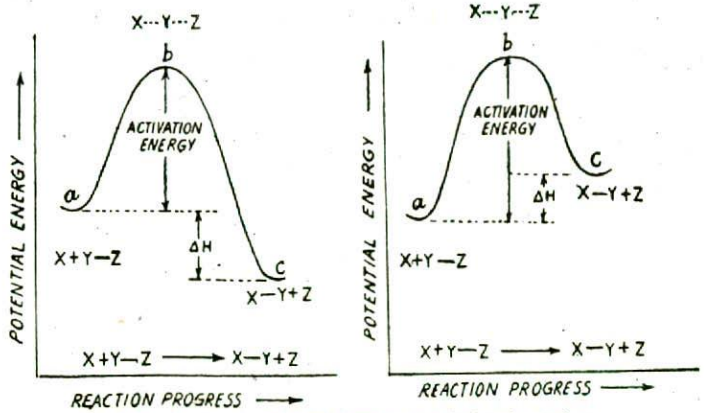


Fig. 6·10. Energy changes in exothermic and endothermic reactions.

on collision is transformed into potential energy. This results in the increase of potential energy and the system moves up along the curve till the cliff (*b*) is reached. The 'energy cliff state' is a sort of temporary phase and leads to the products (*c*), when the potential energy of the system is again changed into kinetic energy and then into heat or any other form of energy.

Fig. 6·10 illustrates that for an exothermic reaction, the system originally possesses more potential energy than the products and the excess energy ($\triangle H$) is liberated as heat). For an endothermic reaction, the system to start with has less potential energy than at the end ($-\triangle H$) and, therefore, it absorbs heat from the surroundings.

The reaction $X+Y-Z \longrightarrow X-Y+Z$ could be visualised to take place by the following steps. The molecule X approaches Y—Z from a direction remote from Z (proper alignment). While X draws nearer to Y, Z starts being repelled from Y until a stage is reached when X and Z are rather loosely attached to Y and are approximately equidistant from it. Thus an 'activated complex' X ··· Y ··· Z is formed in which X to Y and Y to Z distances are slightly more than the normal bond lengths. This is the least stable arrangement and is called the **Transition state** or **Activated complex**. The sequence of events may be represented by the following equation.

$$\underset{\text{Reactants}}{X + Y-Z} \longrightarrow \underset{\substack{\text{Transition state} \\ \text{(activated complex)}}}{X\cdots Y\cdots Z} \longrightarrow \underset{\text{Products}}{X-Y + Z}$$

The activated complex is not a true molecule, the bonds being partial. In this state, the system possesses maximum energy and is most unstable. Hence the transition state of a system could be described as an extremely transitory specific arrangement of atoms and groups through which a reaction system must pass on its way to the products. In other words, the activated complex has infinitesimally short life-time and at once decomposes to give the products.

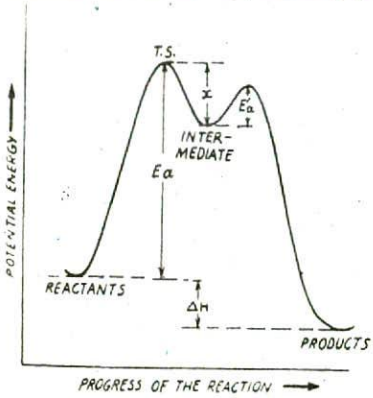


Fig. 6·11. Energy diagram of a reaction proceeding through an intermediate.

Transition state (T.S.) : an Intermediate. A transition state or an 'activated complex' refers to an imaginary molecule and hence cannot be isolated. Whi'' on the other hand, an intermediate is quite a stable chemical entity and can be isolated under the given experimental conditions. A reaction that proceeds through an intermediate has to surmount two energy barriers ; one for the conversion of the reactants to the intermediate and the other for the conversion of the intermediate into the products as depicted in the energy diagram, Fig. 6·11.

For a true intermediate, the energy of activation, E_a, for the conversion of reactants into products is necessarily higher than the energy of activation E'_a for conversion of the intermediate into the products. Had the energy of activation E'_a been higher than the energy of activation E_a, then the very idea of an intermediate would have been forfeited ? The greater the dip '*x*', the more stable will be the intermediate. Consequently, the shallower the dip '*x*' the less stable will be the intermediate in the extreme case, it may become so shallow that it would be difficult to distinguish the intermediate from the transition state.

Effect of Catalyst on the Energy of activation. It is a well known fact that the presence of catalysts makes the reactions faster. Since a faster reaction has a lower energy of activation, the function of a catalyst is to reduce the energy of activation. Consequently more of the molecules can now **have** the minimum energy required to climb the energy barrier and hence more and more molecules would be converted into the products. The energy diagram of a catalysed and an uncatalysed reaction is given below.

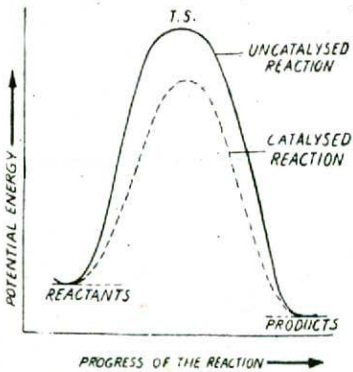


Fig. 6·12. The energy diagram of a catalysed reaction.

APPLICATION OF GENERAL MECHANISTIC CONCEPTS

The concepts discussed above have successfully been employed to interpret the course of a majority of organic reactions known so far, and also to transgress the possibility of reaction between any two species.

The various organic reactions may be classified as belonging to one of the relatively small number of types listed below.

(*a*) *Substitution reactions* ; (*b*) *Addition reactions* ;

(*c*) *Elimination reactions* ; (*d*) *Rearrangement reactions*.

Let us now discuss the mechanisms of these reactions in terms of mechanistic concepts developed above.

SUBSTITUTION REACTIONS

Reactions proceeding by the replacement or substitution of one or more atoms or groups of a compound by other atoms or groups are referred to as *substitution reactions*. They are known to proceed by a free radical or ionic mechanism.

Free Radical substitution. These reactions are initiated by free radicals. The replacement of hydrogen atoms in alkane molecules is probably the best example of this type.

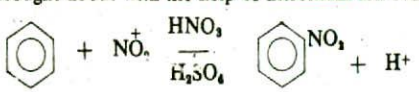
$$Cl_2 \xrightarrow{h\nu} 2Cl\cdot$$
(free radicals)

$$\underset{\text{methane}}{CH_4} + 2Cl\cdot \longrightarrow \underset{\text{methyl chloride}}{CH_3Cl} + HCl$$

A detailed account of the conditions of the reaction and its mechanism will be dealt under alkanes.

Ionic substitution. Substitution reactions may be brought about by electrophiles or nucleophiles acting as attacking reagents. Most of such reactions are initiated by nucleophiles, while substitution reactions involving electrophiles are very rare indeed.

Electrophilic substitution (S_E). When a substitution reaction involves an attack by an electrophile, the reaction is referred to as S_E (here S stands for substitution and $_E$ for electrophile). The substitution reactions of benzene are the best examples of electrophilic substitution *e.g.*, the nitration of benzene is brought about with the help of nitronium ion NO_2^+ (an electrophile).



A detailed mechanism will be discussed in the chapter on Benzene.

NUCLEOPHILIC SUBSTITUTION REACTION (S_N)

When a substitution reaction is brought about by a nucleophile, the reaction is termed as S_N (S stands for substitution and $_N$ for nucleophilic). One of the best known examples of such a reaction is the hydrolysis of alkyl halides by aqueous alkalis to furnish alcohols. Thus,

$$R{-}X + \bar{O}H \longrightarrow R{-}OH + \bar{X}$$

These reactions may be divided into two classes :

(1) S_N2 (*substitution, nucleophilic, bimolecular*),

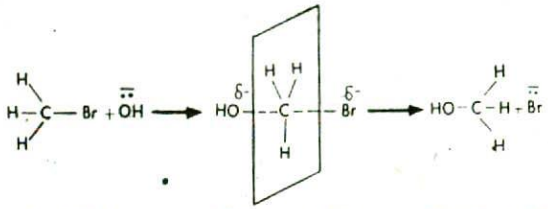
nd (2) S_N1 (*substitution, nucleophilic, unimolecular*).

Bimolecular Nucleophilic Substitution Reactions (S_N2). When the rate of a nucleophilic substitution reaction is dependent both upon the concentration of the substrate and the nucleophile, the reaction is of second order and is represented as S_N2.

$$Rate \propto [substrate]\,[nucleophile]$$

Evidently, the rate-determining step involves the participation of both the substrate and

the nucleophile molecules. Thus the transition state of such a reaction may be represented as follows.



METHYL BROMIDE TRANSITION STATE METHYL ALCOHOL

When hydroxide ion collides with a methyl bromide molecule at the face most remote from bromine, and when such a collision has sufficient energy, a C—OH bond is formed and a C—Br is cleaved with the expulsion of a bromide ion. Thus, the transition state may be pictured as a structure in which both OH and Br are partially bonded (shown by dotted line) to the carbon atom of the methyl group. Furthermore, the C—Br bond is not completely broken and C—OH bond is not completely formed. Hydroxide ion has diminished negative charge since it has begun to share its electrons with the carbon atom while bromine atom carries a negative charge because it has started removing its shared pair of electrons from the carbon atom. At the same time, ion dipole bonds with the solvent molecules and the hydroxide ion are being broken and the ion dipole bonds between the bromide ion and the solvent molecules are being formed. The energy needed for the cleavage of C—Br bond is partly provided by the energy liberated by the C—OH bond formation.

In the transition state, the three C—H bonds are in a plane while the C—OH and C—Br bonds are perpendicular to the plane of the C—H bonds.

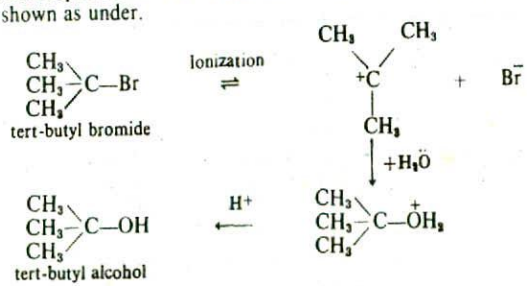
Stereochemistry of S_N2 Reactions. In S_N2 reactions, attack of the nucleophile (*e.g.*, $\bar{O}H$) takes place from the back *i.e.*, from the side remote from the leaving group (*e.g.*, Br) and hence such reactions are always attended by inversion of configuration just in the same way as an umbrella turns inside out in a strong gale. Consequently, if an optically active alkyl halide is hydrolysed, the product would also be optically active. Thus (+)-chlorosuccinic acid on hydrolysis with pot. hydroxide gives (−)-malic acid,



(+)-chlorosuccinic acid (−)-malic acid

Most of the primary aliphatic alkyl halides undergo hydrolysis by this mechanism.

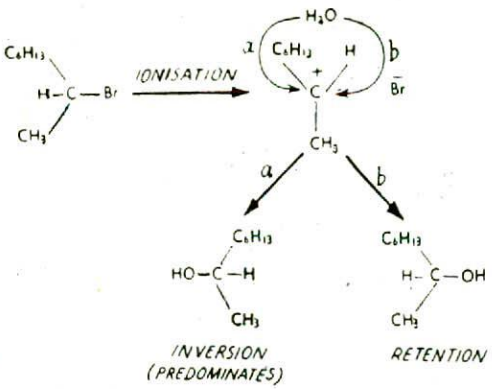
Unimolecular Nucleophilic Substitution Reactions (S_N1). When the rate of a nucleophilic substitution reaction is dependent only upon the concentration of the alkyl halide and is independent of the concentration of the nucleophile *i.e.*, $\bar{O}H$ etc., the reaction is obviously of first order and is designated as S_N1. This rate law has been interpreted as follows. The reaction consists of two steps. The first step involves the slow ionization of the alkyl halide to produce the carbonium ion and is obviously the rate determining step. The second step involves the fast attack of the nucleophile onto the carbonium ion. Thus the hydrolysis of tertiary butyl bromide may be shown as under.



tert-butyl bromide tert-butyl alcohol

The first step involving the cleavage of C—Br bond is energy consuming. The energy needed for this rupture is provided by the energy released by the solvation of the two ions (carbonium ion and the bromide ion).

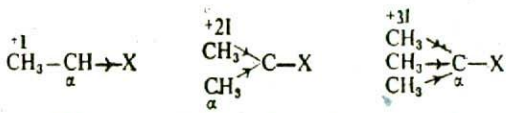
Stereochemistry of S_N1 Reactions. In S_N1 reactions, carbonium ions are the intermediates and these are planar chemical species. The attack of the nucleophile on this carbonium ion can take place with equal ease from either face of this flat ion. Thus, if the alkyl halide is optically active, the product would not be optically active but it would be a racemic mixture. But in actual practice, the results may vary from complete inversion to complete racemisation. Let us illustrate this by taking 2-bromooctane as an example.



2-Bromooctane ionises to produce the planar 2-octyl carbonium ion. Now if the attack were purely random, then we would expect equal amounts of the two isomers *i.e.*, we would get a racemic modification. But the product is not completely racemised because the inverted product exceeds its enantiomer. The most plausible answer to this question lies in the fact that the attack of the nucleophile occurs before the departing ion has completely left the neighbourhood of the carbonium ion. Thus the departing ion shields the carbonium ion from the frontal attack (*i.e.*, path *b*). As a result backside attack (*i.e.*, path *a*) is somewhat preferred.

Factors that regulate S_N1 and S_N2 mechanisms. The course of a particular substitution reaction is influenced by the following factors.

(1) **Structure of the alkyl halides.** Generally, primary alkyl halides react by S_N2 mechanism, tert-alkyl halides by S_N1 mechanism and secondary alkyl halides by both S_N2 and S_N1 mechanisms. Thus in going from left to right in the following series of alkyl halides, the mechanism changes



S_N2 $S_N2 + S_N1$ S_N1

from S_N2 to S_N1. This is due to the fact that the electron density on α-carbon atom goes on increasing by inductive effect of the alkyl groups as we move from left to right. This increased electron density on the α-carbon atoms repels the direct attack of the nucleophile and thus retards S_N2 reaction. Moreover, the transition state of S_N2 reactions becomes more crowded as the size of the alkyl group increases. This also slows down the S_N2 reaction. On the other hand, the increased electron density on the α-carbon atoms increases the tendency of ionization of the alkyl halide and thus favours S_N1 mechanism. Furthermore, the ionization relieves the steric hindrance and thus accelerates S_N1 mechanism.

(2) **Nature of the Nucleophile.** Powerful nucleophiles like alkoxide ions and hydroxide ions favour S_N2 mechanism while weak nucleophiles like water and alcohols favour S_N1 mechanism. Furthermore, high concentration of the nucleophile favours S_N2 mechanism and low concentration favours the S_N1 mechanism.

(3) **Nature of the Solvent.** The higher the polarity of the solvent the greater is the tendency of the alkyl halide to undergo substitution by S_N1 mechanism.

(4) **Nature of the Halogen atom.** The nature of the halogen atom does not have much influence on reaction mechanism though it does alter the rate of the reaction which follows ne order

$$R-I > R-Br > R-Cl \quad \text{(both for } S_N1 \text{ and } S_N2 \text{ reactions)}$$

ELIMINATION REACTIONS

Elimination reactions are reverse of addition reactions. Here, two or four atoms or groups attached to the adjacent carbon atoms in the substrate molecule are eliminated to form a multiple bond. A typical example is the dehydrohalogenation of the alkyl halides with alcoholic alkalis.

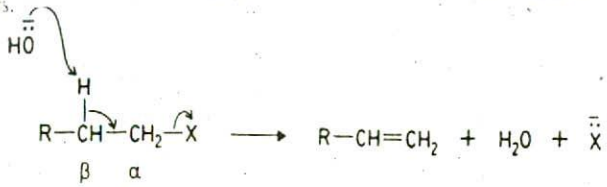
$$R-CH_2-CH_2-X \xrightarrow{\bar{O}H} R-CH=CH_2 + H_2O + \bar{X}$$

These reactions like nucleophilic substitution reactions may also be divided into two classes :

(1) E2 (*Elimination bimolecular*) ;

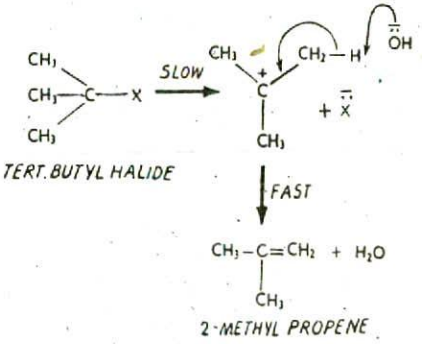
(2) E2 (*Elimination unimolecular*).

Bimolecular Elimination Reactions (E2). When the rate of an elimination reaction is dependent both upon the concentration of a substrate and the nucleophile, the reaction is of second order and is represented as E2. E2 like S_N2 is also a one step process in which the abstraction of the proton from the β-carbon and the expulsion of the leaving group *i.e.*, halide ion etc from the α-carbon atom occur simultaneously. The mechanism for such a reaction may be represented as follows.



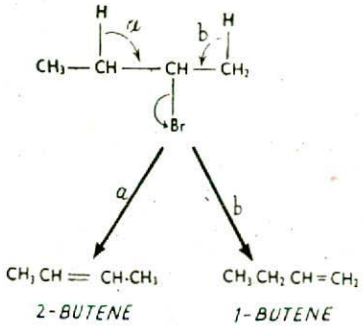
In these reactions, the two groups to be eliminated *i.e.*, H atom and X are trans to each other and hence E2 reactions are generally trans elimination reactions.

Unimolecular Elimination Reactions (E1). When the rate of an elimination reaction is dependent only upon the concentration of the substrate and is independent of the concentration of the nucleophile, the reaction is of first order and is designated as E1. E1 like S_N1 reactions are also two-step processes. The first step involves the slow ionisation of the alkyl halide to give the carbonium ion and the second step involves the fast abstraction of a proton by the base from the adjacent β-carbon atom leading to the formation of an alkane. Thus,



If the dehydrohalogenation of an alkyl halide can yield more than one alkene, then according to *Saytzeff rule*, the main product is the most highly substituted alkene. The

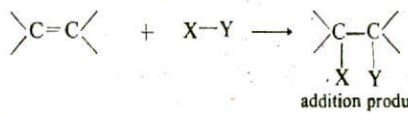
the action of ethanolic KOH on sec-butyl bromide can, in principle, yield two isomeric alkenes, *viz*, 1-butene and 2-butene as shown below



In accordance with the *Saytzeff Rule*, the main product is the disubstituted alkene, 2-butene, rather than the monosubstituted, 1-butene.

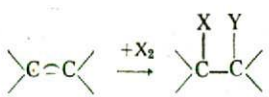
ADDITION REACTIONS

This type of reaction is characteristic of (*a*) alkenes, (*b*) alkynes, and (*c*) aromatic hydrocarbons. In fact, all organic compounds containing double or triple bonds display addition reactions. Thus,

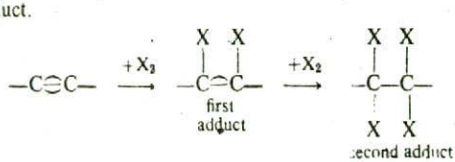


addition product

We have already studied that a double bond is made of one σ bond and one π bond, while a triple bond consists of one σ bond and two π bonds. It requires less energy to break a π bond than the σ bond, since the *p* orbitals experience a sidewise overlap to a lesser extent and form a weak π bond, while a σ bond that is formed by a head-on overlap of orbitals is quite significant and lends strength to the bond. An ethylenic π bond is approximately 15 kcal/mole weaker than a σ bond. Therefore, in addition reactions of a double linkage, which consists of one σ bond and one π bond, the weaker π bond breaks open leaving the stronger σ bond intact.



As already stated, a triple bond or acetylene linkage is made of one σ bond and two π bonds. Here the addition of a reagent will take place in two steps, when first one π bond will break open and then the second. The σ bond being the strongest remains intact in the final addition product.



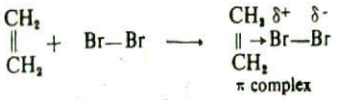
second adduct

Agents which readily add to double or triple bonds are halogens, hydrogen, halogen acids, sulphuric acids, hypohalous acids, etc. The addition of hydrogen to unsaturated hydrocarbons is commonly referred to as **Hydrogenation**.

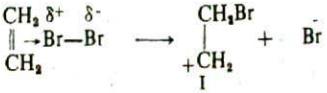
Electrophilic Addition Reactions. It has been observed that when an alkene is treated with bromine (or chlorine) dissolved in a solvent (CCl_4 or petrol) a rapid reaction takes place

and the bromine solution is decolourised. Further, this reaction is seen to be catalysed by polar reagents, indicating a polar mechanism of the addition reaction.

MECHANISM. When an alkene molecule comes in close proximity of a bromine molecule, the π electrons of alkene induce polarization in the bromine molecule, thereby creating a dipole. The positive end of this bromine dipole gets loosely attached to π cloud of the alkene molecule resulting in the formation of a π complex of the type shown below.



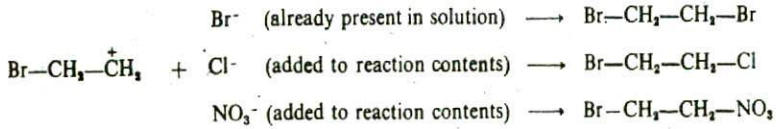
This π complex then breaks down to a carbonium ion (I) and the bromide ion.



The carbonium ion (I) thus produced, has a transitory existence and thus combines readily with the nucleophilic bromide ion leading to the formation of the product.



The above cited mechanism is supported by the fact that mixed products are obtained when alkenes are treated with bromine in presence of other nucleophiles such as chloride or nitrate ions. Thus the addition takes place stepwise and not by the direct addition of a halogen molecule across the double bond.



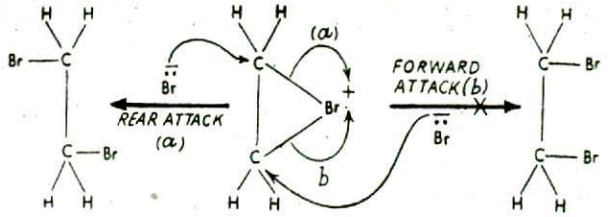
Since in the above reaction, the addition of bromine to the alkene is initiated by an electrophile (*i.e.*, positive end of the bromine dipole) it is named as **Electrophilic addition reaction**.

The above mechanism suffers from the defect that it cannot account for the fact that the addition reactions of alkenes normally give *trans* products. Evidently, the reaction cannot proceed through the intermediacy of carbonium ions like I, because the free rotation is possible about the carbon-carbon single bond in I and hence the stereospecificity is lost. To account for the sterespecificity of bromine to alkenes, we visualise that a cyclic intermediate (II) called the bromonium ion is formed. Thus,



I II

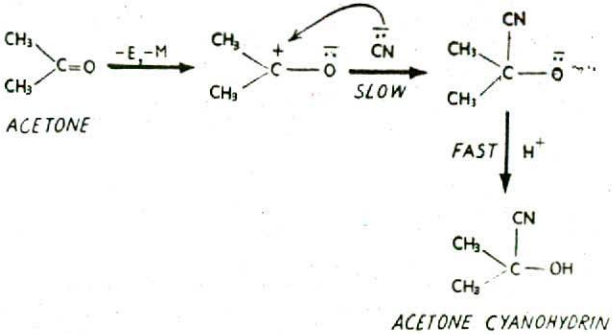
The nucleophilic attack of the bromide ion can now occur only from the back side because the bulky bromine atom in the bromonium ion (II) hinders the attack from the front. This explains the formation of a *trans* product.



Nucleophilic Addition Reactions. These reactions are frequently encountered in carbonyl compounds. The carbonyl group $>C=O$ is made up of two bonds, one of which is a σ bond and the other a π bond. Because oxygen is more electronegative than carbon, the electrons forming the carbon-oxygen double bond do not distribute themselves evenly between the two nuclei. There is a greater electron density on oxygen as compared to carbon. The true structure of the carbonyl group is somewhere between the following structures.

$$\text{>C=O} \longleftrightarrow \text{>}\overset{+}{\text{C}}\text{–}\overset{-}{\text{O}} \quad \text{or} \quad \text{>}\overset{\delta+}{\text{C}}\text{=}\overset{\delta-}{\text{O}}$$

This suggests that the carbonyl compounds should be prone to nucleophilic attack at the carbonyl carbon atom, and to electrophilic attack at the carbonyl oxygen atom. This is indeed the case, though electrophilic attack on oxygen is only of significance where the electrophile is a proton. An example of this type of addition is provided by the reaction of HCN to acetone.



REARRANGEMENT REACTIONS

In this type of reactions, some atoms/groups shift from one position to another within the substrate molecule itself, giving a product with a new structure. *The reactions which proceed by a rearrangement or reshuffling of the atoms/groups in the molecule to produce a structural isomer of the original substance* are called **Rearrangement reactions.**

These rearrangement reactions may proceed either by an intramolecular or intermolecular change. Those rearrangements in which the migrating group is never fully detached from the system during the process of migration, are called *Intramolecular Rearrangements*, whereas those in which the migrating group gets completely detached and is later on re-attached are called *Intermolecular Rearrangements.*

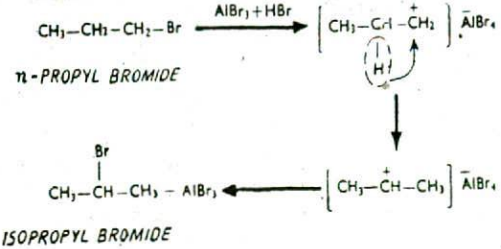
Intramolecular Rearrangements. Some examples of intramolecular change are given below.

I. Isomerization. Butane changes to isobutane on heating in presence of aluminium chloride.

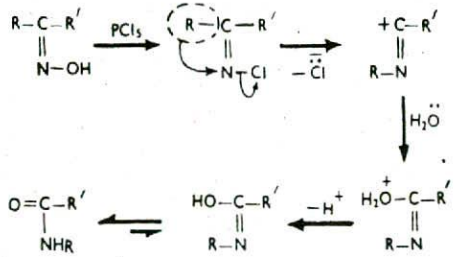
$$\underset{\text{butane}}{CH_3{-}CH_2{-}CH_2{-}CH_3} \xrightarrow[\text{heat}]{AlCl_3} \underset{\text{isobutane}}{CH_3{-}\overset{CH_3}{\overset{|}{C}}H{-}CH_3}$$

Such reactions which produce chain isomers of the original substrates are called *isomerization reactions.*

Similarly n-propyl bromide on heating with $AlBr_3+HBr$ gives isopropyl bromide. This change may be visualized to be taking place *via* the following steps.

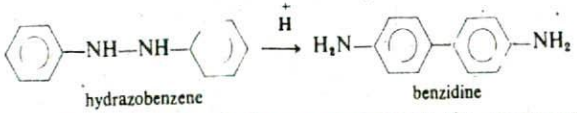


II. Beckmann Rearrangement. When a ketoxime is treated with an acidic catalyst such as H_2SO_4, polyphosphoric acid, thionyl chloride, phosphorous pentachloride, benzene sulphonyl chloride etc., it gets converted into a substituted amide. The main mechanistic features of the rearrangements are given below.



It should be emphasized that it is always the *trans* hydrocarbon radical R with respect to the hydroxyl group that migrates. Furthermore, R radical or group never gets completely detached from the remainder of the molecule during the course of transformation.

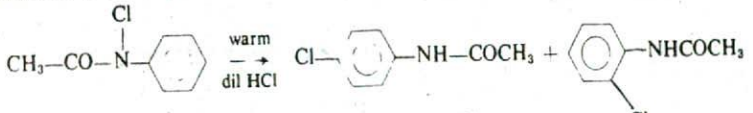
III. Benzidine Rearrangements. Another interesting example of intramolecular rearrangement is provided by Benzidine Rearrangement. The, on warming hydrazobenzene with mineral acids, benzidine (4,4-diamino-diphenyl) is formed.



hydrazobenzene benzidine

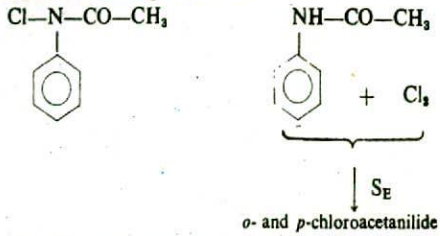
Intermolecular Rearrangements. In these rearrangements the atom or group undergoing migration becomes completely free from the rest of the molecule and later on gets reattached at some site of the rest of the molecule producing thereby a structural isomer of the original substance. Some examples of such inter-molecular changes are mentioned below.

I. Orton Rearrangement. In this rearrangement, N-chloroacetanilide gets converted into a mixture of *o*- and *p*-chloroacetanilide on treatment with dil HCl. Thus,

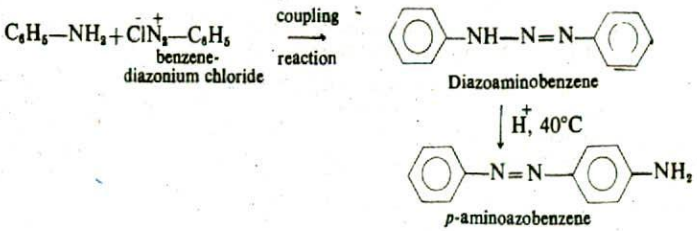


N-chloroacetanilide *p*-chloroacetanilide *o*-chloroacetanilide

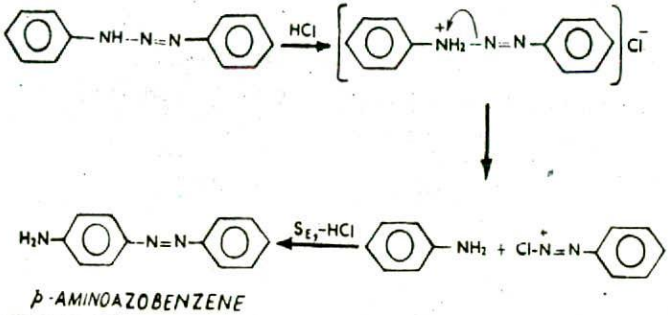
A probable mechanism for this change is as under



II. **Diazoaminobenzene Rearrangement**. Diazoaminobenzene in weekly acidic m. rearranges to *p*-aminoazobenzene.



Mechanism



p-AMINOAZOBENZENE

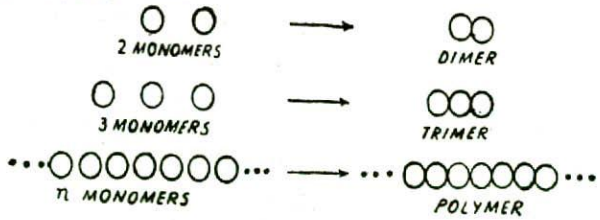
POLYMERIZATION

This is one of the most significant reactions of alkenes and conjugated dienes (containing alternate single and double bonds) and several other compounds containing multiple bonds. Under suitable conditions, two or more molecules of such compounds react together by combination to yield complex molecules.

The union of two or more molecules of a substance to form a large single molecule is called **Polymerization** *and the product thus obtained is called a* **Polymer**.

$$nX \xrightarrow{\text{ploymerization}} X_n$$

The simple molecules are called **monomers**, and the products are named as **dimers**, **trimers** and **polymers** according as the number of molecules joining in the formation of the complex molecule is 2, 3, or *n* (many). Thus,



Polymerization reactions are again of two types :

(*a*) *Addition Polymerization* ; and

(*b*) *Condensation Polymerization.*

Addition Polymerization involves the joining together of many simple molecules (*monomers*) to give a new compound (*addition polymer*) having the same empirical formula but higher molecular weight. For example, when ethylene is heated under pressure in the presence of oxygen, an open chain alkane-like compound, having a very high molecular weight (20,000) is obtained.

$$\underset{\text{ethylene}}{n\ CH_2{=}CH_2} \xrightarrow[[O_2]]{200^\circ C,\ 1000\ \text{atmos}} \underset{\text{polyethylene}}{(-CH_2-CH_2-)_n}$$

Polyethylene, commonly called '*polythene*', is a useful plastic material for the preparation of toys, flexible bottles and laboratory ware as also for packing films.

Polymerization reactions require the presence of an '*initiator*' —a foreign substance which simply starts the reaction and thus acts as a catalyst. Peroxides are very common initiators ; these contain —O—O— group in the molecule. Peroxides are believed to furnish a free radical which adds to a molecule of alkene and then generates another free radical which in turn add to still another molecule of ethylene giving a free radical; and so on. This 'chain reaction' set up results in the formation of complex polymers. Peroxide simply starts the chain reaction. Its oxygen supplies the free radical in the polymerization of ethylene as a result of the homolytic fission of its molecule.

(*i*)* $\quad$ Peroxide $\longrightarrow$ F· (free radical)

(*ii*) $\quad F\cdot + CH_2{=}CH_2 \longrightarrow FCH_2-CH_2$

(*iii*) $\quad FCH_2-CH_2 + CH_2{=}CH_2 \longrightarrow FCH_2-CH_2-CH_2-CH_2$; and so on.

Polymerization of conjugated dienes is of special interest since the polymer obtained resembles natural rubber. Thus,

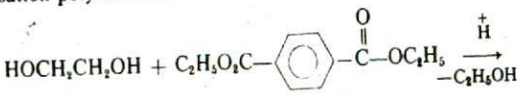
(*i*) $\quad$ Peroxide $\longrightarrow$ F· (free radical)

(*ii*) $\quad F\cdot + \underset{\text{1, 3-butadiene}}{CH_2{=}CH-CH{=}CH_2} \longrightarrow FCH_2-CH{=}\dot{C}H-\dot{C}H_2$

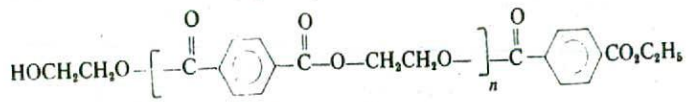
(*iii*) $\quad FCH_2-CH{=}CH-\dot{C}H_2 + CH_2{=}CH-CH{=}CH_2$

$\longrightarrow FCH_2-CH{=}CH-CH_2-CH_2-CH{=}CH-\dot{C}H_2$; and so on.

In **Condensation Polymerization**, two or more simple molecules join together with the elimination of a simple molecule (*e.g.*, water, ammonia, hydrogen chloride) to form a new substance of high molecular weight. Thus the polyester of ethylene glycol and terephthalic acid is obtained by condensation polymerization.



ethyl tetraphthalate



dacron

Dacron is an important fibre.

Note. Polymerisation generally (but not always) implies that the original simple substance should be recoverable from the complex componnd. The splitting of such compounds to their originals is termed **Depolymerisation.**

*F· should not be confused by the beginner as the fluorine atom ; it is simply a fragment of the peroxide molecule having an odd electron.

CONDENSATION

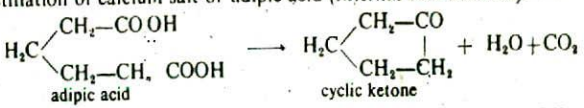
The term condensation is very loosely used in organic chemistry and it is difficult to give an exact definition of this type of reaction. It refers to all possible changes which result in the lengthening of the carbon chain and may be defined as follows.

All reactions which proceed by a direct union between the carbon atoms of the same molecules or different molecules of the same or different substances to form a new compound are termed **Condensation reactions** *and the products so obtained are termed* **Condensation products.** The condensation between molecules is very frequently attended by the elimination of H_2O, HCl, HBr, Br_2, etc., but that is not always necessary. The term condensation has also been extended to the union between carbon and nitrogen atoms. Some typical examples of condensation are given below.

(1) In the presence of sodium metal, two molecules of alkyl halides condense to form a longer molecule of a higher hydrocarbon.

$$\underset{\text{ethyl bromide (2 molecules)}}{CH_3CH_2Br} + Br\,CH_2CH_3 + 2Na \longrightarrow \underset{\text{n-butane}}{CH_3CH_2CH_2CH_3} + 2NaBr$$

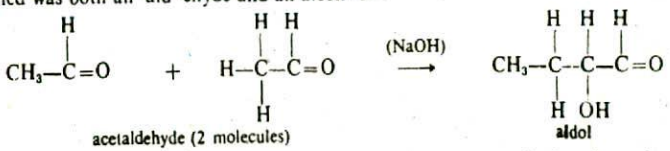
(2) Distillation of calcium salt of adipic acid (*Internal condensation*).



(3) Condensation of aldehydes and ketones with hydroxylamine, NH_2OH.

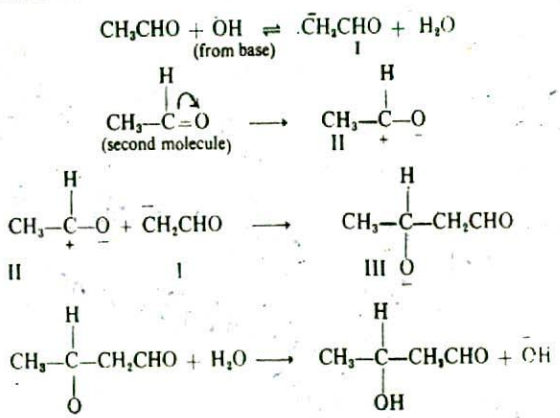
$$\underset{\text{acetaldehyde}}{CH_3CH{=}O} + H_2NOH \longrightarrow \underset{\text{oxime}}{CH_3CH{=}NOH} + H_2O$$

(4) **Aldol Condensation.** In the presence of a dilute base (catalyst) two molecules of an aldehyde or a ketone may combine to form a β-hydroxyaldehyde or a β-hydroxyketone. The reaction is termed 'aldol condensation' since originally it was applied to aldehydes and the product obtained was both an 'ald'-ehyde and an alcoh-'ol'.



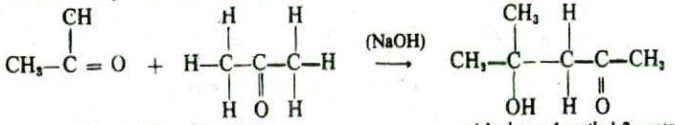
Here, the α-carbon atom of one molecule of acetaldehyde becomes attached to the carbonyl group of the second molecule.

The possible mechanism of aldol condensation involves the following steps.



The first step is the formation of a carbanion as a result of removal of a proton by a hydroxyl ion of the base. In the second step the electromeric effect operates and creates a carbonium ion. The carbanion produced in step I attacks the carbonium ion and another nucleophile with negative charge on oxygen atom is generated. The third nucleophile then extracts hydrogen ion from water and OH^- ion is regenerated.

A similar mechanism explains the formation of 4-hydroxy-4-methyl -2-pentanone from two molecules of acetone in the presence of dilute sodium hydroxide solution, which as already stated, is also an example of aldol condensation.



(2 molecules of acetone) 4-hydroxy-4-methyl-2-pentanone

Difference between Condensation and Polymerization. It is true that polymerisation and condensation present many common examples, but **polymerisation is not necessarily condensation.** The points of difference between the two types of reactions are :

1. Condensation always proceeds by new union between carbon atoms while in polymerization it is not necessary. For instance, in the polymerisation of aldehydes any change in structures only involves oxygen bonds.

2. Unlike polymerization condenzation reactions are not reversible.

3. In polymerization the reaction takes place between identical molecules but in condenzation the reaction may take place even between different molecules.

REDUCTION AND OXIDATION REACTIONS

Reduction and oxidation reactions are very common in organic chemistry. They are shown especially by compounds containing double and triple bonds such as alcohols, aldehydes and ketones. The definition of reduction and oxidation as applied in organic chemistry is very simple.

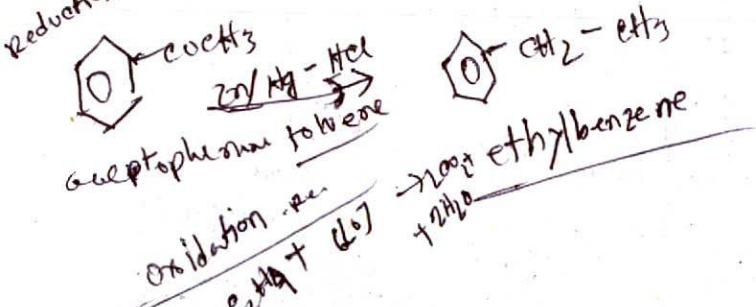
A reaction which proceeds by the addition of hydrogen is termed **Reduction** *and the one that involves the addition of oxygen is called* **Oxidation.** The products formed in the two cases are referred to as **Reduction products** and **Oxidation products** respectively.

The result of reduction and oxidation depends upon the nature of the original compound and that of the reagent employed to effect the change. While reduction seldom causes a rupture of the carbon chain, oxidation does it very often.

EXAMPLES OF REDUCTION

Some of the reduction processes which are frequently used in Organic Chemistry are given below.

(1) **Catalytic Hydrogenation.** This is brought about by hydrogen in presence of catalysts like Raney Nickel, Pt and Pd etc. More drastic reductions are carried out at elevated temperatures and under high pressures. This process is commonly used for unsaturated systems such as alkenes, alkynes and aromatic compounds. Ketones and aldehydes may also be reduced by this method.



MECHANISM. In contrast to the addition of bromine to alkenes, hydrogen addition by side this method is a *cis* addition process *i.e.*, both the hydrogens add to the alkene from the same of the molecule. Following is the sequence of reactions taking place during the process of hydrogenation,

(*i*) Hydrogen molecules approach the catalyst surface where they are probably adsorbed as reactive free-atoms on the surface of the catalyst.

(*ii*) The alkene then approaches the catalyst surface and forms an intermediate addition complex with the catalyst through π electrons of the double bond.

(*iii*) Transfer of hydrogen atoms from the catalyst on to the same side of the alkene double bond now takes place and the reduced product is readily desorbed to leave the catalyst surface free for further reaction.

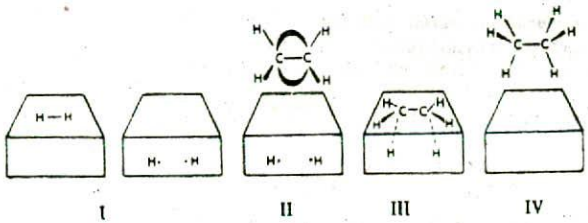
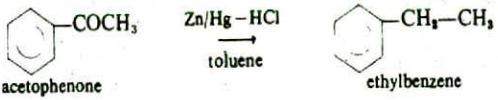


Fig. 6·13. Mechanism of catalytic hydrogenation : (I) Hydrogen adsorbed by catalyst ; (II) alkene molecule approaches the catalyst surface ; (III) Intermediate bonding of the alkene and the cis-transfer of hydrogen ; (IV), The product leaves the surface.

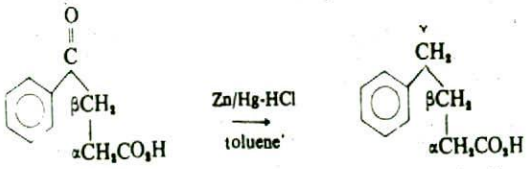
(2) **Clemmensen and Wolff-Kishner Reduction.** Aldehydes and ketones can be reduced to their corresponding hydrocarbons either by Clemmensen or by Wolff-Kishner method.

Clemmensen reduction employs amalgamated zinc and conc. hydrochloric acid as the reducing agent. Thus,



acetophenone ethylbenzene

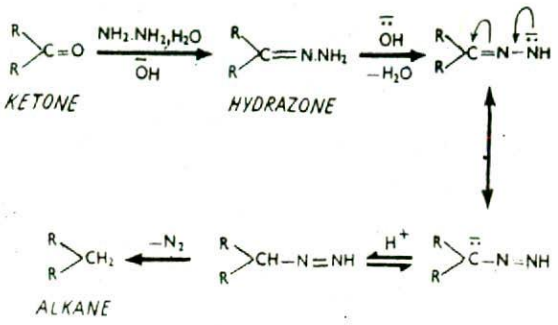
This method is particularly useful for such ketones as contain phenolic and carboxylic groups. For example, the reduction of β-benzoylpropionic acid in toluene gives γ-phenylbutyric acid in 85% yield.



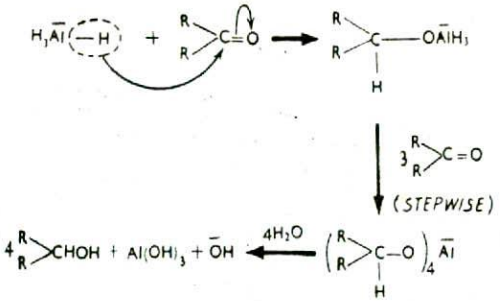
β-benzoylpropionic acid γ-phenylbutyric acid

This reagent also reduces alkene bonds in αβ-unsaturated ketones, acids and esters.

Wolff-Kishner reduction of ketones to hydrocarbons can be effected by heating the ketone with hydrazine hydrate under strongly alkaline conditions (C_2H_5ONa or KOH) in di- or triethylene glycol as a solvent at 180–220°C. Hydrazine hydrate forms the hydrazone of the ketone which gets reduced with the evolution of nitrogen according to the following reaction sequence

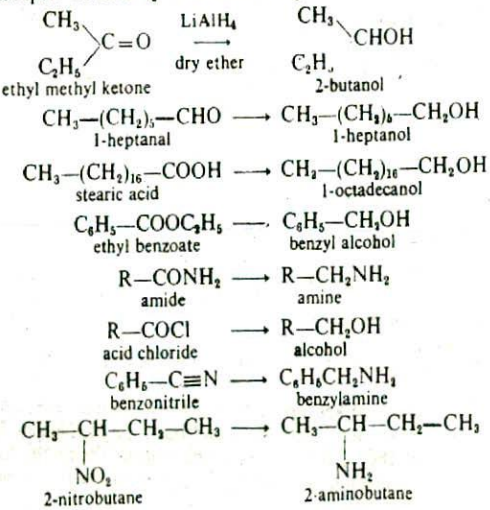


(3) **Lithium aluminium hydride Reductions** Carbonyl compounds are reduced to alcohols by a variety of reagents. Catalytic hydrogenation is not normally used because it is a slow process. $LiAlH_4$ has proved to be a very effective reducing agent for almost all the classes of organic compounds. $NaBH_4$ (sodium borohydride) has also been used. $LiAlH_4$ gives hydride ions which reduce the carbonyl compounds according to the following sequence.



Thus each of the four hydrogen atoms in $LiAlH_4$ is available for transfer to the carbonyl groups.

Some more examples of $LiAlH_4$ reductions are given below.

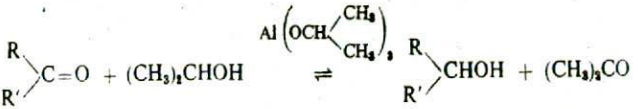


(4) Nitrocompounds on reduction with tin and hydrochloric acid give primary amines.

$$\underset{\text{nitroethane}}{C_2H_5NO_2} + 6H \xrightarrow{Sn/HCl} \underset{\text{ethylamine}}{C_2H_5NH_2} + 2H_2O$$

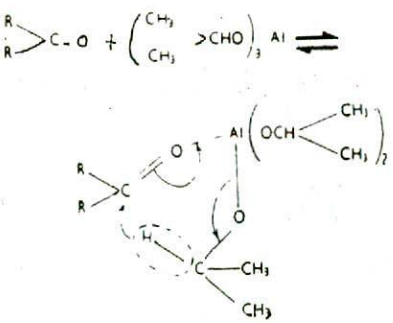
Nitrobenzene yields a variety of reduction products, depending upon the nature of the reducing agent.

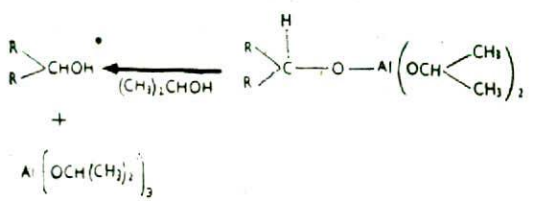
(5) **Meerwein-Ponndorf-Verley Reduction**. This is a specific method for the reduction of ketones into alcohols. The reduction is carried out with aluminium isopropoxide in isopropanol. This is also a hydride ion transfer reaction. Thus,



The acetone so formed, is removed by slow distillation and hence the reaction proceeds only in the forward direction.

MECHANISM





Examples of Oxidation. (1) Unsaturated hydrocarbons on oxidation under different conditions yield different products. This is illustrated by the following examples.

(*a*) With a strong oxidising agent like conc. HNO_3, ethylene is oxidised to carbon dioxide and water.

$$\underset{\text{ethylene}}{C_2H_4} + 6\,[O] \longrightarrow 2CO_2 + 2H_2O$$

(*b*) Mild oxidising agent such as $KMnO_4$, causes a splitting of the molecule at the double bond.

$$\underset{\text{butene}}{CH_3-CH_2-CH=CH_2} + 4\,[O] \longrightarrow \underset{\text{propionic acid}}{CH_3-CH_2-COOH} + \underset{\text{formic acid}}{HCOOH}$$

(c) Very mild oxidising agent like alkaline $KMnO_4$ yields a glycol.

$$\underset{\text{ethene}}{CH_2 \| CH_2} + H_2O + [O] \longrightarrow \underset{\text{glycol}}{CH_2OH | CH_2OH}$$

(2) Alcohols and aldehydes when oxidised with a mixture of potassium dichromate and sulphuric acid, ultimately yield fatty acids. The nature of oxidation products largely depends upon whether the alcohol is primary, secondary or tertiary.

$$\underset{\text{ethyl alcohol}}{CH_3CH_2OH} + [O] \longrightarrow \underset{\text{acetaldehyde}}{CH_3CHO} + H_2O$$

$$CH_3CHO + [O] \longrightarrow \underset{\text{acetic acid}}{CH_3COOH}$$

(3) **Oppenauer Oxidation.** This reaction is reverse of Meerwein-Ponndorf-Verley reduction and is used for the oxidation of alcohols to ketones in the presence of aluminium tertiary butoxide in benzene or toluene solution. A large excess of a ketone, (acetone or cyclohexanone) is generally used to make the reaction proceed in the desired direction.

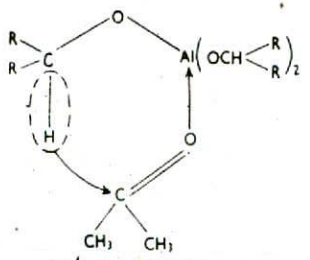
$$\begin{matrix} R \\ R \end{matrix}\!\!>\!CHOH + CH_3\!-\!\underset{\underset{O}{\|}}{C}\!-\!CH_3 \overset{Al[OC(CH_3)_3]}{\rightleftharpoons} \begin{matrix} R \\ R \end{matrix}\!\!>\!C{=}O + (CH_3)_2CHOH$$

This reaction also involves the transfer of a hydride ion *via* a cyclic complex as represented below.

$$3\begin{matrix} R \\ R \end{matrix}\!\!>\!CHOH + Al\left[O\!-\!C\!<\!\begin{matrix} CH_3 \\ CH_3 \\ CH_3 \end{matrix}\right]_3 \rightleftharpoons \left[\begin{matrix} R \\ R \end{matrix}\!\!>\!CHO\right]_3 Al + 3(CH_3)_3COH$$

alcohol — aluminium tert. butoxide — tert. butyl alcohol

$$\left[\begin{matrix} R \\ R \end{matrix}\!\!>\!CHO\right]_3 Al + CH_3COCH_3 \rightleftharpoons$$



CYCLIC COMPLEX

$$\longrightarrow (CH_3)_3C\!-\!O\!-\!Al(OCHR_2)_2 + \begin{matrix} R \\ R \end{matrix}\!\!>\!C{=}O$$

ketone

QUESTIONS

1. What are the major types of organic reactions ? Define each type and illustrate by one example.

2. Describe what you understand by : (*i*) Substitution reactions, (*ii*) Addition reactions, (*iii*) Elimination reactions, and (*iv*) Rearrangement reactions. Give one example of each.

3. What do you mean by the terms : (*a*) substrate, (*b*) attacking reagent, and (*c*) intermediates. Apply these terms to a substitution reaction.

4. Describe homolytic and heterolytic fission of covalent bonds. How do these lead to the formation of carbonium ions and carbanions ?

5. Classify the two types of attacking reagents giving at least four examples of each type. How do they react ?

6. Give an account of the mode of formation of carbonium ions and carbanions. What determines their relative stabilities.

7. Explain inductive effect. Why does it die down as the length of the chain increases ? What is meant by $+I$ effect and $-$ Ieffect ?

8. "Unlike inductive effect, the electromeric effect is not a permanent polarization effect." Elaborate the statement.

9. Define : (*i*) Inductive, and (*ii*) Electromeric effects. Give examples to illustrate these.

10. What do you understand by mechanism of an organic reaction ? Describe the various types of eaction mechanisms.

11. Give a brief account of the free radical mechanism of substitution and polymerization reactions.

12. (*a*) What causes the inductive effect ?
(*b*) Why tertiary carbonium ions are more stable than primary carbonium ions ?
(*c*) Illustrate electromeric effect ? *(Osmania BSc, 1994)*

13. Explain the following terms :
(*a*) Carbonium ions (*b*) Carbanions
(*c*) Electrophiles (*d*) Nucleophiles
(Agra BSc, 1993 ; Bangalore BSc, 1994 ; Indore BSc, 1994)

14. Write notes on : (*a*) Inductive effect, and (*b*) Carbanions. *(Saugar BSc III, 1993)*

15. Write a note on : Stability of Carbonium ions. *(Madurai BSc, 1994)*

16. Write a note on : Stability of Carbanions. *(Delhi BSc, 1993)*

17. Write notes on :
(*a*) Inductive effect (*b*) Electromeric effect
(*c*) Nucleophiles (*d*) Electrophiles
(Magadh BSc Hons. 1993 ; Berhampur BSc, 1993 ; Rajasthan BSc, 1994 ; Vikram BSc, 1994)

18. Which of the following is the stable carbonium ion ?

(*a*) $\overset{+}{C}H_3$ (*b*) $CH_3\overset{+}{C}H_2$

(*c*) $CH_3\overset{+}{C}HCH_3$ (*d*) $(CH_3)_3\overset{+}{C}$ *(Kakatiya BSc, 1993)*

Answer. (*a*)

19. Write a note on : Mesomeric effect. *(North Bengal BSc, 1993)*

20. Explain SN_1 and SN_2 reactions with suitable examples. *(Cochin BSc, 1993)*

21. Discuss the mechanisms of E_2 and E_1 elimination reactions. *(Jiwaji BSc, 1993 ; Karnataka BSc, 1994)*

22. Discuss SN_1 and SN_2 mechanisms by taking the examples of alkaline hydrolysis of methyl bromide and *t*-butyl bromide. *(Delhi BSc, 1993 ; Nagpur BSc, 1994)*

Chapter 7

Isomerism

In the study of Organic chemistry we come across many cases when two or more compounds are made of equal number of like atoms. *These compounds possess the same molecular formula but differ from each other in physical or chemical properties, and are called* **Isomers** and the phenomenon is termed **Isomerism** (Greek, *isos*=equal ; *meros*=parts). Since isomers have the same molecular formula, the difference in their properties must be due to different modes of combination or arrangement of atoms within the molecule. Broadly speaking, isomerism is of two types :

(*i*) *Structural Isomerism* ; and (*ii*) *Stereoisomerism*.

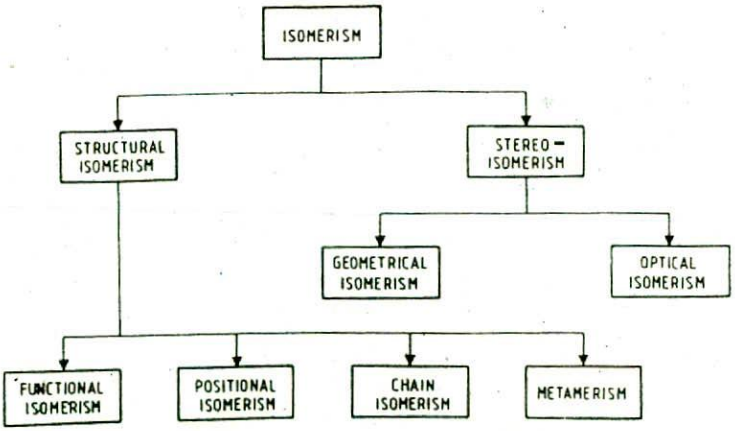
Structural Isomerism. *When the isomerism is simply due to difference in the arrangement of atoms within the molecule without any reference to space*, the phenomenon is termed **Structural Isomerism**. In other words, the structural isomers while they have the same molecular formulas, possess different structural formulas. This type of isomerism which arises from difference in the structure of molecules, includes :

(*a*) *Chain or Nuclear Isomerism* ;
(*b*) *Positional Isomerism* ;
(*c*) *Functional Isomerism*; and
(*d*) *Metamerism.*

Stereoisomerism. *When isomerism is caused by the different arrangements of atoms or groups in space*, the phenomenon is called *Stereoisomerism* (Greek, *Stereos*=occupying space). The stereoisomers have the same structural formulas but differ in the spatial arrangement of atoms or groups in the molecule. In other words, stereoisomerism is exhibited by such compounds which have identical molecular structure but different *configurations*.

Stereoisomerism is of two types :
(*a*) *Geometrical or Cis-Trans isomerism* ; and
(*b*) *Optical Isomerism.*

Thus various types of isomerism could be summarised as follows.



CHAIN OR NUCLEAR ISOMERISM

This type of isomerism arises from the difference in the structure of carbon chain which forms the nucleus of the molecule. It is, therefore, named as **Chain** or **Nuclear Isomerism**. For example, there are known two butanes which have the same molecular formula (C_4H_{10}) but differ in the structure of the carbon chains in their molecules.

$CH_3-CH_2-CH_2-CH_3$
n-butane

$H_3C-CH(CH_3)-CH_3$
isobutane

While n butane has a continuous chain of four carbon atoms, isobutane has a branched chain. These chain isomers have somewhat different physical and chemical properties, n-butane boiling at $-0{\cdot}5°$ and isobutane at $-10{\cdot}2°$. This kind of isomerism is also shown by other classes of compounds. Thus n-butyl alcohol and isobutyl alcohol having the same molecular formula C_4H_9OH are chain isomers.

$CH_3-CH_2-CH_2-CH_2OH$
n-butyl alcohol

$CH_3-CH(CH_3)-CH_2OH$
isobutyl alcohol

It may be understood clearly that the molecules of chain isomers differ only in respect of the linking of the carbon atoms in the alkanes or in the alkyl radicals present in other compounds.

POSITIONAL ISOMERISM

When two or more compounds have structural formulas which differ only in the position of the substituent atom or group on the carbon chain, these are called **Position isomers** and the phenomenon is termed **Positional isomerism**. Thus n-propyl alcohol and isopropyl alcohol offer an example of positional isomerism. They possess the same molecular formula (C_3H_7OH) and their molecules are made of a chain of three carbon atoms. In n-propyl alcohol, the OH group is on the end carbon atom while in isopropyl alcohol it is on the middle carbon atom.

$CH_3-CH_2-CH_2(OH)$
n-propyl alcohol

$CH_3-CH(OH)-CH_3$
isopropyl alcohol

The positional isomerism may also be extended to alkanes and alkynes which differ only in the position of the double or triple bond in their molecules. Thus the molecular formula C_4H_8 stands for two butenes,

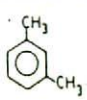
$CH_2=CH-CH_2-CH_3$
1-butene

$CH_3-CH=CH-CH_3$
2-butene

in which the position of the double bond is different.

In the aromatic series, the disubstitution products of benzene also exhibit positional isomerism due to different relative positions occupied by the two substituents on the benzene ring. Thus xylene, $C_6H_4(CH_3)_2$, exists in the following three forms which are positional isomers


o-XYLENE
(ortho)


m-XYLENE
(meta)


p-XYLENE
(para)

FUNCTIONAL ISOMERISM

When any two compounds have the same molecular formula but possess different functional groups, they are called **Functional isomers** and the phenomenon is termed **Functional isomerism**. In other words substances with the same molecular formula but belonging to different classes of compounds exhibit functional isomerism. Thus,

(1) Diethyl ether and butyl alcohol both have the molecular formula $C_4H_{10}O$, but contain different functional groups.

$C_2H_5-O-C_2H_5$
diethyl ether

C_4H_9-OH
butyl alcohol

The functional group in diethyl ether is (—O—), while in butyl alcohol it is (—OH).

(2) Acetone and Propionaldehyde both with the molecular formula C_3H_6O are functional isomers.

$CH_3—CO—CH_3$ (acetone) $\qquad$ $CH_3—CH_2—CHO$ (acetaldehyde)

In acetone the functional group is (—CO—), while in acetaldehyde it is (—CHO).

METAMERISM

This type of isomerism is due to the unequal distribution of carbon atoms on either side of the functional group in the molecule of compounds belonging to the same class. For example, methyl propyl ether and diethyl ether both have the molecular formula $C_4H_{10}O$. The number of carbon atoms attached to the ethereal group —O—,

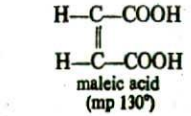
$CH_3—O—C_3H_7$ (methyl propyl ether) $\qquad$ $C_2H_5—O—C_2H_5$ (diethyl ether)

in methyl propyl ether is 1 and 3, while in diethyl ether it is 2 and 2. This isomerism known as **Metamerism** is shown by members of classes such as ethers, ketones and amines where the central functional group is flanked by two chains. The individual isomers are known as **Metamers.**

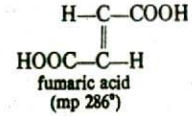
GEOMETRICAL ISOMERISM

We have discussed above the various types of isomerism arising from difference in the structure of compounds having the same molecular formula. Now we will study a new type of isomerism where the isomers possess the same structural formula containing a double bond and differ only in respect of the arrangement of atoms or groups about the double bond. The simple examples of this kind of isomerism are :

(*i*)

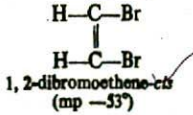


maleic acid (mp 130°)

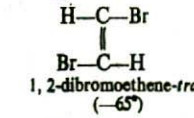


fumaric acid (mp 286°)

(*ii*)

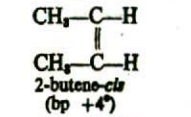


1, 2-dibromoethene-*cis* (mp —53°)

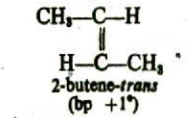


1, 2-dibromoethene-*trans* (—65°)

(*iii*)

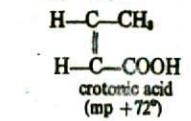


2-butene-*cis* (bp +4°)

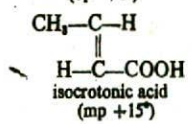


2-butene-*trans* (bp +1°)

(*iv*)

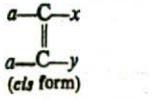


crotonic acid (mp +72°)

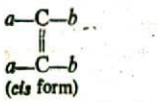


isocrotonic acid (mp +15°)

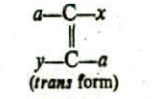
It may be noticed that in all the above examples, the doubly bound carbon atoms are linked to two different groups, so that in general we could say that **Geometrical isomerism** *is shown by alkenes or their derivatives in which two different atoms or groups are attached to each carbon containing the double bond.* Thus the compounds having the formula $abC=Cxy$ or the simple structure $abC=Cab$ occur in two forms and exhibit geometrical isomerism.



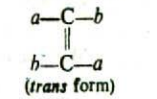
(*cis* form)



(*cis* form)

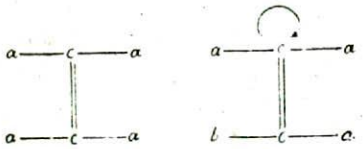


(*trans* form)



(*trans* form)

If the two atoms or groups linked to the same doubly linked carbon are similar as in the molecule $aaC{=}Cab$, the compound does not show geometrical isomerism. Here the two possible configurations are, in fact, the same.



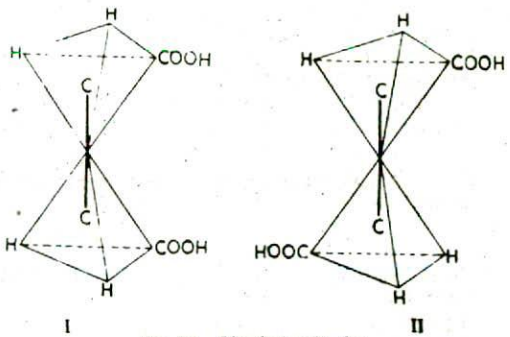
I II

The structure II when rotated 180° through the axis of the double bond, can be superimposed over structure I.

The geometrical isomerism is also shown by compounds containing C=N or a cyclic ring structure in their molecules.

Explanation and Definition of Geometrical Isomerism. To understand the cause of geometrical isomerism we must return to the fundamental conception of the tetrahedral nature of the carbon atom.

According to Le Bel and van't Hoff (1874), the valencies of the carbon atom are distributed symmetrically in space. They may be pictured as directed towards the four corners of a regular tetrahedron constructed round the carbon atom as the centre. According to this theory, a derivative of ethane, say succinic acid, containing two carbon atoms united by a single bond could be represented by two tetrahedra joined corner to corner.



I II

Fig. 7·1. Identical molecules.

If the two tetrahedra were fixed rigidly to each other, the two compounds having the models I and II should be possible. Actually there is only one succinic acid known. The natural conclusion is that the two carbon atoms are able to rotate about the axis formed by the bond between them and can, therefore, assume form I or II. Thus, the possibility of different spatial arrangements in ethane derivatives is ruled out.

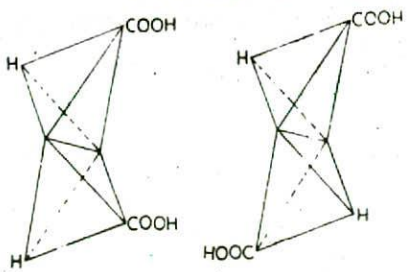
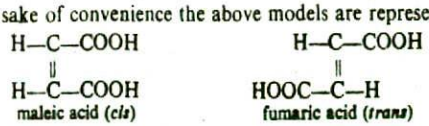


Fig. 7·2. Tetrahedral models of the maleic acid and fumaric acid.

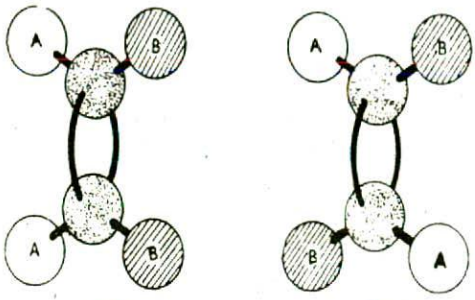
If, however, the two carbon atoms are united by a double bond, the two tetrahedra representing them must necessarily be in contact at two corners. In such a case all free rotation of the tetrahedra ceases and the groups attached to the two carbon atoms are fixed relative to each other. Thus, different spatial arrangements of the groups about the doubly bonded carbon atoms now become possible. For example, the two tetrahedral models representing maleic acid and fumaric acid will be as shown in Fig. 7·2.

For the sake of convenience the above models are represented in a plane as follows :—



maleic acid (*cis*) fumaric acid (*trans*)

It may be noted clearly that meleic acid and fumaric acid have quite different arrangements of groups about the double bond. While in one case similar groups are on the same side, in the other they lie on opposite sides. *This type of isomerism due to the different geometrical arrangements of the groups about the doubly bonded carbon atoms* is known as **Geometrical isomerism**. When the similar groups lie on the same side as in maleic acid, it is called the **Cis isomer** (Latin, *cis*=on same side). When similar groups are on the opposite sides as in the fumaric acid, it is called the **Trans isomer** (Latin, *trans*=across). Consequently this type of isomerism is often spoken of as **Cis-Trans Isomerism**.



(*Cis*) (*Trans*)

Fig. 7·3. Ball-and-stick models of Geometrical isomers.

The ball-and-stick models of geometrical isomers of an organic compound are given in Fig. 7·3. Here the two spitted balls (carbon atoms), in each model are joined by two spring-rods and are thus 'fixed' and are incapable of free rotation. The balls A and B (representing different atoms or groups) could be arranged in two ways about the doubly bonded spitted balls. The first model having similar balls on the same side represents the *cis* isomer, while the second one with similar balls on opposite sides represents the *trans* isomer.

A beautiful illustration of geometrical isomerism becoming possible by a double union between the carbon atoms is given in Fig. 7·4.

In (I) two boards are shown joined by a single nail. Since the boards can rotate independently, the marked ends of the boards cannot be arranged relative to each other. If, however, the boards are fastened by two nails, they are fixed and hence two arrangements (II and III) of the marked ends are possible.



Fig. 7·4. Illustration of Geometrical isomerism.

Explanation Based on Orbital Theory

The modern orbital theory offers a more sophisticated explanation of geometrical isomerism. We have already discussed in the previous chapter that the doubly bonded carbon atoms in ethylene exhibit a trigonal type of hybridization (2*s*, $2p_x$, $2p_y$ hybridized). The three new sp^2 orbitals lie in one plane. Thus the three σ bonds formed by each of these two carbon atoms are coplanar. The unhybridized third p_z orbitals of the doubly bonded carbon atoms which stand at right angles to the trigonal bonds, overlap at two positions to form π orbital. The two types of overlapping results in the formation of *Cis* and *Trans* isomers.

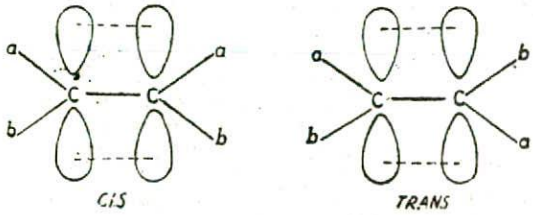
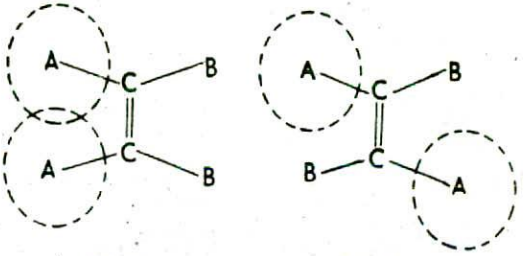


Fig. 7·5.

Stability of Cis, Trans or Geometrical isomers. The *trans* isomers of alkenes are usually more stable than their corresponding *cis* isomers. The reason for this becomes clear if we consider the *cis* and *trans* isomers of the alkene ABC=CAB in which 'A' is a bulky group as compared to 'B' (*e.g.*, CH_3—HC=CH—CH_3). In the *cis* isomer, the two bulky 'A' groups are very close to each other. The repulsion due to the over-lapping of the electron clouds of the two bulky 'A' groups will make this isomer less stable than *trans* isomer in which the bulky 'A' groups are far apart (being on the opposite sides of the double bond).



cis isomer *trans* isomer

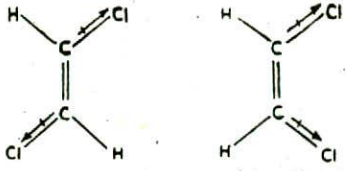
Fig. 7·6. The bulky 'A' groups in the *cis* isomer being very near overlap, while in the *trans* isomer the 'A' groups lie far apart and do not overlap.

Determination of Configuration of Isomers

There is no absolute method for the determination of the configuration of *cis-trans* isomers. Several elementary relationships are, however, helpful to the beginner.

From a study of the Physical properties. The difference in the structure of *cis, and trans* isomers is reflected in their physical properties. Some such properties are illustrated below.

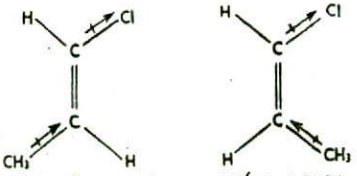
(1) DIPOLE MOMENTS. The *trans* isomers have normally less dipole moments than their corresponding *cis* isomers. The reason for this is clearly understood if we consider the *cis* and *trans* isomers of 1, 2-dichloroethylene. The *trans* isomer has a dipole moment of zero. This is due to the fact that the two bond moments of C—Cl bonds are opposed because of the symmetry of the molecule. On the other hand, the *cis* isomer being non-symmetrical has a finite dipole moment because here the bond moments are not opposed.



TRANS(μ=0·01D) CIS(μ=1·89D)

In such alkenes which have one polar substituent different from the other, the dipole moment will not normally be zero but would be smaller than the corresponding *cis* isomer. If, however, one substituent is electron-donating and the other electron-withdrawing, the bond moments are fully additive in *trans* isomer. Thus the *trans* isomer in this case has a higher dipole moment than the corresponding *cis* isomer.

Thus in 1-chloroprene we have,



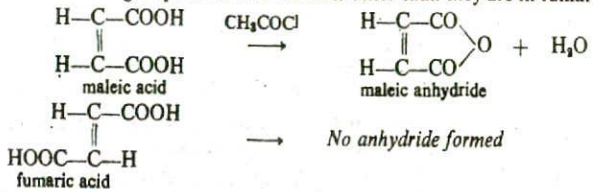
TRANS(μ=1·97D) CIS(μ=1·71D)

Therefore, it is possible to assign configuration to a pair of isomers on the basis of dipole measurements, provided the nature of substituents is known.

(2) MELTING POINTS AND RELATED PHENOMENA. In general, a *trans* isomer nas greater symmetry than the corresponding *cis* isomer. Thus it packs more easily in the crystal lattice and hence has a higher melting point. *Cis* compounds, on the other hand, have low melting points since they being less symmetrical do not pack well in the crystal lattice. Moreover, the poor packing leads to weaker forces of attraction between the molecules in the crystal lattice. The weaker forces of attraction can be easily broken by the dielectric constant of the solvents and hence the *cis* isomers have greater solubilities than their *trans* isomers. *Cis* compounds have also been found to have higher heats of formation and ionization constants as acids. Due to these differences in properties, it is sometimes possible to assign configurations to a pair of geometrical isomers.

(3) BY CHEMICAL METHODS. The formation of a cyclic molecule from an open chain molecule takes place easily only when the reacting groups are close to each other. This fact has been most useful in assigning configuration to *cis-trans* isomers in which the doubly bound carbon atoms carry groups that are capable of reacting with each other. The configuration of maleic and fumaric acids is established on this basis.

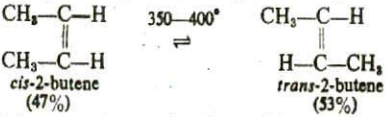
Maleic acid readily forms cyclic anhydride whereas fumaric acid does not. This means that in maleic acid the two groups are nearer to each other than they are in fumaric acid. That is,



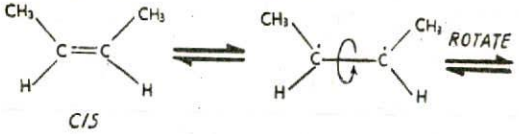
Obviously maleic acid is the *cis* form and fumaric acid the *trans* form.

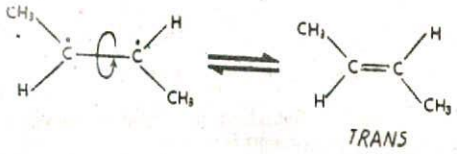
In addition to the methods given above, other physical measurements such as the measurement of the distances between certain atoms by means of X-ravs, measurement of absorption spectra etc., may be of help for deciding upon the configuration in some cases.

Interconversion of Geometrical isomers. Although geometrical isomers are stable at ordinary temperatures one can be converted into the other or to an equilibrium mixture of both by heat, by exposure to ultraviolet light, or by use of catalysts. Thus,



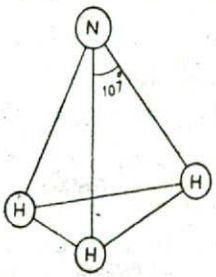
This interconversion of *cis* to *trans* isomer involves the breakage of carbon-carbon π bond. The cleavage of the carbon-carbon π bond requires approximately 40 kcal/mole of energy. At room temperature, only an insufficient proportions of collisions possesses this energy and hence the rate of interconversion is low but can be increased by employing higher temperatures. The interconversion presumably follows the following pathway.



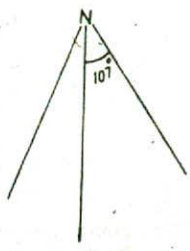


GEOMETRICAL ISOMERISM OF OXIMES

From the dipole moment and the examination of its infrared spectrum, ammonia molecule has been shown to possess a pyramidal shape. The N atom is occupying the top position of the pyramid and the H atoms the corners of the base. Thus the valency bonds of N atom, like those of C atom, are distributed in space, the angle contained by any two bonds being 107°.



Shape of amonia molecule.



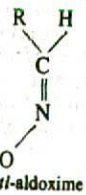
Direction of valency bonds of nitrogen atom.

Fig. 7·7.

Therefore, the compounds such as the oximes of aldehydes, R–CH=N–OH, in which the C-atom is joined to a N-atom by a double bond, are capable of exhibiting geometrical isomerism, since the H and OH groups may be arranged on the same side or the opposite sides of the double bond. The two stereoisomers thus obtained are designated as *syn* (equivalent to *cis*) and *anti* (equivalent to *trans*) respectively. The two geometrical isomers of an aldoxime may be written as :

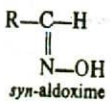


syn-aldoxime

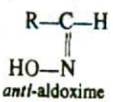


anti-aldoxime

Or simply as :

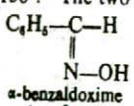


syn-aldoxime

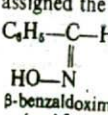


anti-aldoxime

Two bezaldoximes have been actually isolated : (1) α-benzaldoxime, mp 35° , and (2) β-benzaldoxime, mp 130°. The two isomers have been assigned the configurations :

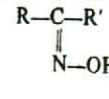


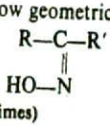
α-benzaldoxime (*syn*-form)



β-benzaldoxime (*anti*-form)

The ketoximes of mixed ketones, R—CO—R′, also show geometrical isomerism. Thus,

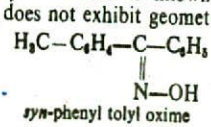




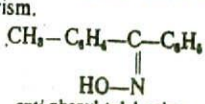
(Two stereoisomers of ketoximes)

No such geometrical isomerism is possible in ketoximes derived from simple ketones in which R and R′ are same.

Phenyl tolyl ketoxime is known to exist in two forms, while benzophenone oxime, $(C_6H_5)_2C$: N.OH, does not exhibit geometrical isomerism.



syn-phenyl tolyl oxime

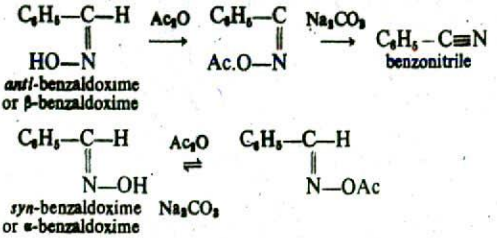


anti-phenyl tolyl oxime

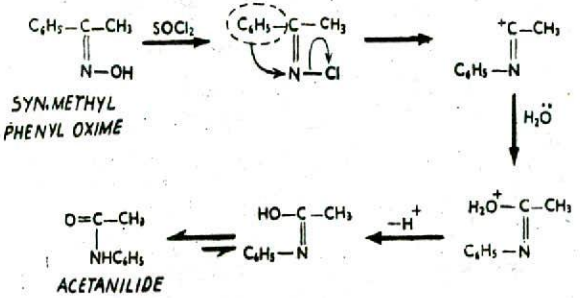
Here the prefixes *syn* and *anti* refer to the relative positions of the OH group and the hydrocarbon radical (attached to doubly bonded C atom) first named.

Determination of Configuration. The configuration of a pair of aldoximes can be established by converting them into their corresponding acetates followed by treatment with

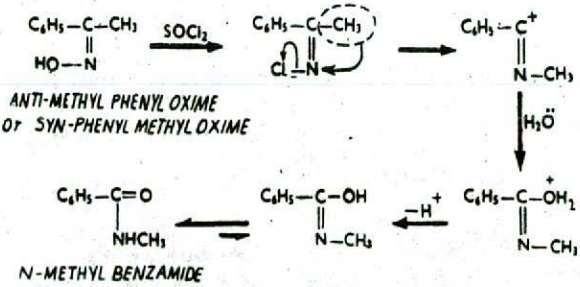
aqueous sodium carbonate. In this way the *anti* isomer eliminates a molecule of acetic acid and is converted into the corresponding nitrile, whereas the *syn* isomer regenerates the original aldoxime.



Since the oximes of ketones cannot be converted into nitriles as above, their configuration cannot be determined by this method. Configurational assignments to a pair of oximes can be successfully made by application of Beckmann rearrangement. In this transformation, the ketoxime is treated with an acidic reagent such as phosphorus pentachloride, thionyl chloride, phosphoric acid or sulphuric acid when it undergoes a molecular rearrangement to give the acid amide. This method of configurational assignment depends upon the fact that it is always the *trans* hydrocarbon group R (with respect to the hydroxyl group attached to N-atom) which migrates in this transformation. Thus by identifying the acid amide (hydrolysis to parent acid and amine) produced after the Beckmann rearrangement, the configuration of the given ketoxime can be determined. Thus *syn*-methyl-phenyl oxime on Beckmann rearrangement gives acetanilide, whereas *anti*-methyl-phenyl oxime gives N-methyl-benzamide.

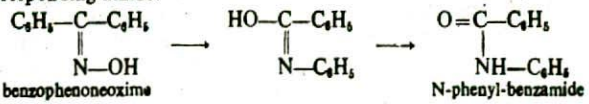


and



Evidently, the identification of the product reveals the configuration of the starting ketoxime.

A simple ketoxime like the benzophenone oxime upon Beckmann transformation would give the corresponding amide.



OPTICAL ISOMERISM

In optical isomerism we have a much more subtle phenomenon than even the geometrical isomerism. While the geometrical isomers differ in physical properties such as melting point, boiling point, density etc., and also in certain chemical properties, the optical isomers will have the same chemical reactions and will be alike in all physical properties mentioned above. They can only be distinguished by their *'action on plane-polarized light'*. This property which is often referred to as the **Optical activity** requires a brief discussion.

What is Optical Activity ? Light is propagated by a vibratory motion of the 'ether' particles present in the atmosphere. Thus in ordinary light vibrations occur in all planes at right angles to the line of propagation. In plane polarized light the vibrations tak place only in one

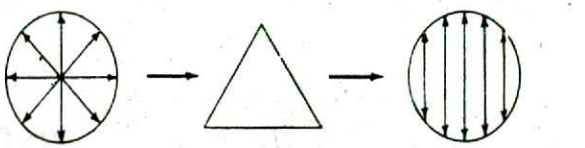


Fig. 7·8



Fig. 7·9

plane, vibrations in other planes being cut off. Plane polarized light can be obtained by passing ordinary light through a *Nicol prism.**

Certain organic compounds, when their solutions are placed in the path of a plane polarized light, have the remarkable property of rotating its plane through a certain angle which may be either to the left or to the right. If the polarized light has its vibrations in the plane XY before entering such a solution, the direction on leaving it will be changed to say X'Y', the plane having been rotated through the angle α (Fig. 7·10). *This property of a substance of rotating the*

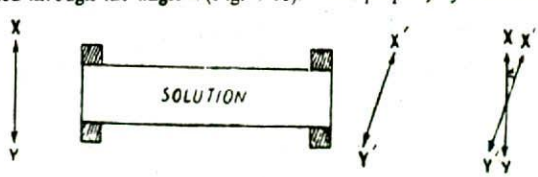


Fig. 7·10. Rotation of the plane of polarized light by a solution. (*Diagrammatic*)

*Nicol Prism : A Nicol prism is constructed of iceland spar, a substance which is doubly refracting. It is so made that light waves vibrating in all directions except one are cut off by refraction to one side of the prism.

plane of polarized light is called **Optical activity** and the substance possessing it is said to be **Optically active.**

The observed rotation of the plane of polarized light (determined with the help of polarimeter) produced by a solution depends on : (*a*) the amount of the substance in tube ; (*b*) on the length of the solution examined ; (*c*) the temperature of the experiment ; and (*d*) the wavelength of the light used.

For the measurement of optical rotations, a term **Specific Rotation** is introduced. This is a physical constant characteristic of a substance as much as the melting point, boiling point, density or its refractive index. It is defined as *the number of degrees of rotation observed when light is passed through 1 decimetre (10 centimetres) of its solution having concentration 1 gram per millilitre.* The specific rotation of a given substance can be calculated by using the following expression.

$$\left[\alpha\right]_D^{t^\circ} = \frac{\alpha_{obs}}{l \times c}$$

where $\left[\alpha\right]_D^{t^\circ}$ stands for specific rotation determined at t°C and using D-line of sodium light ; α_{obs} is the observed angle of rotation ; l is the length of the solution in decimetres ; and c is the concentration of the active compound in grams per millilitre. For example, the specific rotation of amyl alcohol (2-methyl-1-butanol at 25°C for D-line of sodium light is given by

$$\left[\alpha\right]_D^{25^\circ} = -5{\cdot}756^\circ$$

The sign attached with the angle of rotation signifies the direction of rotation. Negative sign (—) indicates that the rotation is toward the left, while positive (+) sign means that the direc- tion of rotation is toward right.

The rotation may be different in different solvents and this needs to be mentioned while reporting the specific rotation. Thus,

$$\left[\alpha\right]_D^{25^\circ} = +24{\cdot}7^\circ \text{ (in chloroform)}$$

Definition and Examples of Optical Isomerism. The simple organic compounds which show optical activity are :

Lactic acid $CH_3—CH(OH)—COOH$

Isoraleri acid $\begin{matrix} CH_3 \\ \diagdown \\ \quad CH—COOH \\ \diagup \\ C_2H_5 \end{matrix}$

Isoamyl alcohol $\begin{matrix} CH_3 \\ \diagdown \\ \quad CH—CH_2OH \\ \diagup \\ C_2H_5 \end{matrix}$

All these substances are known to exist in three forms :

(1) *One rotating the plane of polarized light to the left.* This form is named **Laevorotatory** (Latin, *laevous*=left) or direction (+)— form.

(2) *One rotating the plane of polarized light exactly to the same extent but to the right.* This form is named **Dextrorotatory** (Latin, *dexter*=right) or direction (—)— form.

(3) *An inactive from which does not rotate the plane of polarized light at all.* This is a mixture of equal amounts of (+)-and (—)-forms and hence its optical inactivity. It is named **(±)-mixture** or **Racemic mixture** (Latin, *racemic*=mixture of equal components).

Thus three lactic acids are known. They are : (*a*) (+)-lactic acid, (*b*) (—)-lactic acid, and (*c*) (+)-mixture. Since the (±)-acid is only a mixture of (+)-and (—)-forms, in reality lactic acid exis in tw forms, the (+)-lactic acid and the (—)-lactic acid. These two acids are exactly identical in physical and chemical properties but differ in their action on the plane polarized light. They have fferent sign of s *ific rotation.* Such forms of the same compound which differ only in their optical properties are called **Optical isomers** and the phenomenon is termed **Optical isomerism**

Table. *Physical Properties of Lactic Acids*

Name	*M Pt °C*	*Density*	$[\alpha]_D 25°$
(+)-lactic acid	26	1·248	+2·24°
(−)-lactic acid	26	1·248	−2·24°
(±)-lactic acid	26	1·248	0·00°

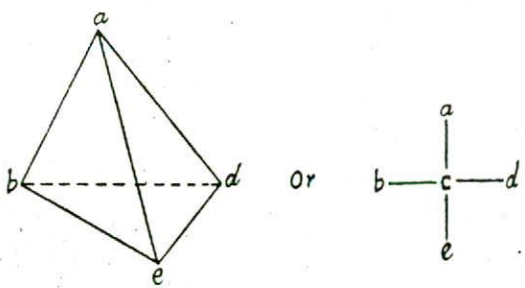
Sometime back a lower case *d* or *l* was used to designate the direction of plane polarised light. Thus *d* is synonymous with (+) and the letter *l* with (−). The three optical isomers of lactic acid, for example, could be represented as :

d-lactic acid instead of (+)−lactic acid ; *l*-lactic acid instead of (−)−acid; and *dl*-lactic acid instead of (±)−lactic acid.

However, it must be clearly understood that lower case *d* and *l* (or + and −) refer to the direction of rotation of plane polarieed light, which is a measured physical constant It is not necessarily related to configuration around asymmetric carbon. Capital *d* and *l* are now used to refer to the absolute configuration around the asymmetric carbon.

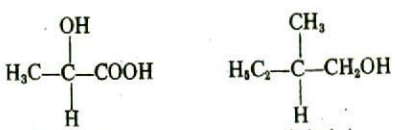
ASYMMETRIC CARBON ATOM

A carbon atom is described as being **asymmetric** when four *different* atoms or groups are bonded to it. Thus it can be represented as



An asymmetric carbon in formula is usually indicated by an asterisk (*) placed near it.

All organic compounds containing one asymmetric carbon atom (lactic acid, amyl alcohol, etc.) are optically active.



lactic acid (*Optically active*) amyl alcohol (*Optically active*)

ASYMMETRIC OR DISSYMMETRIC MOLECULES

Those molecules which have asymmetric or dissymmetric molecular structures in tetrahedral perspective, are called *asymmetric molecules*. The two features of such structures are :—

1. **No Plane of Symmetry.** A 'plane of symmetry' is a plane which divides an object in such a way that the part of it on one side of the plane is the mirror image of that on the other side of the plane. Thus a ball is symmetrical while a hand is asymmetric.

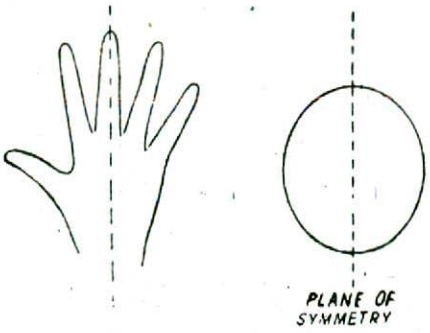
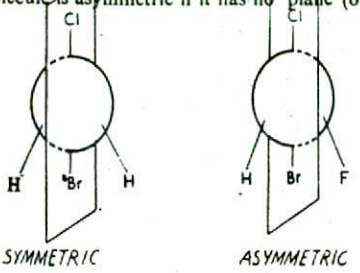


Fig. 7·11. Asymmetric and symmetric objects.

Similarly, an organic molecule is asymmetric if it has no plane (or centre) of symmetry. For example,



(The central ball in above models is carbon atom)

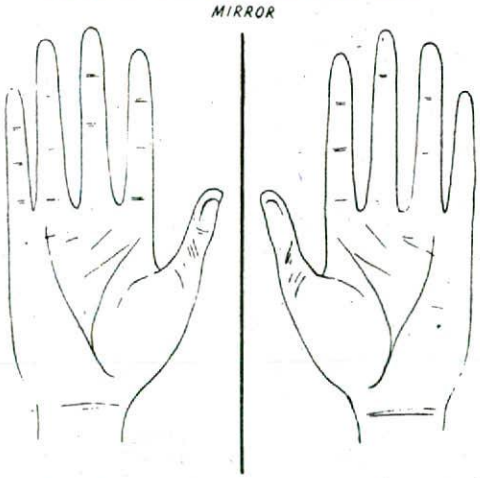
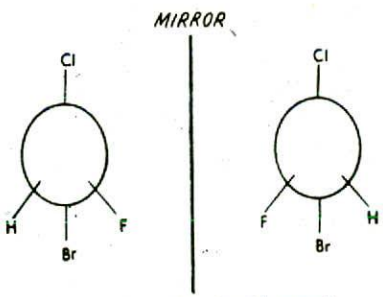


Fig. 7·12. A hand is asymmetric because it cannot superimposed on its mirror image (the other hand

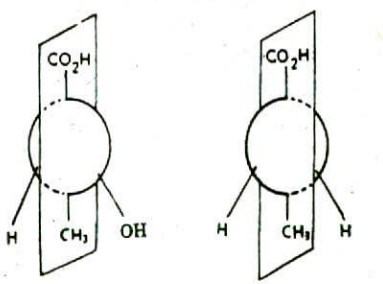
No plane of symmetry can be drawn through the molecule II and hence it is asymmetric.

2. **Nonsuperimposable on its Mirror Image.** An asymmetric object cannot be superimposed on its mirror image. Thus the right hand produces a mirror image which is identical with your left hand. The two hands are nonsuperimposable which is clearly evident if you try to put your right hand in the left-handed glove. On the other hand, a symmetric object like a ball can be superimposed on its mirror image which is another similar ball.

Thus the molecule of bromochlorofluoromethane is asymmetric because it is nonsuperimposable on its mirror image.



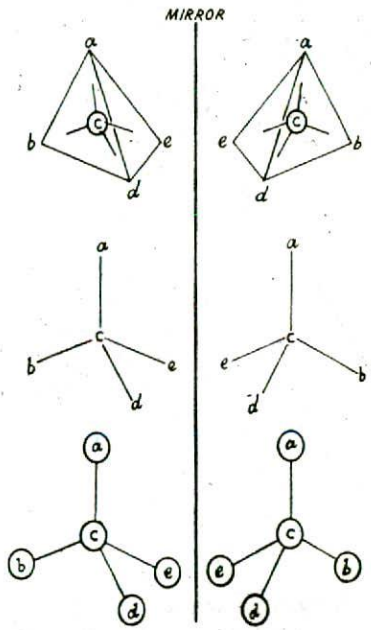
Non superimposable mirror images of bromochlorofluoromethane



Lactic acid has no plane of symmetry.

Propionic acid has a plane of symmetry.

Fig. 7·13 (*a*)



I II

The two forms of a molecule containing one asymmetric carbon represented by (*i*) tetrahedra ; (*ii*) tetrahedral bond direction ; (*iii*) ball-and-stick models.

Fig. 7.13 (*b*)

Chirality. This term has been recently used to describe such molecules as have no elements of symmetry (plane of symmetry or centre of symmetry). Thus asymmetrical molecules are also called **chiral mylecules** and optical activity is attributed to certain **chiral centres** in them. An asymmetrical carbon is a chiral centre.

Chirality is lost when the two atoms bonded to an asymmetric carbon become similar. Thus while lactic acid is optically active, propionic acid is not.

CHIRALITY OR MOLECULAR DISSYMMETRY CAUSE OF OPTICAL ISOMERISM

The necessary condition for a molecule to exhibit optical isomerism is dissymmetry or **Chirality.** Thus all organic compounds which contain an asymmetric carbon (C* *abde*) atom are *chiral* and exist in two tetrahedral forms.

Although the two forms (I and II) shown in Fig. 7·13 (*a*) have the same structure, they have different arrangements of groups *a*, *b*, *d*, *e* about the asymmetric carbon. In fact, they represent asymmetric molecules. They do not have a plane of symmetry. They are related to each other as an object to its mirror image and are nonsuperimposable.

The two models or structures (I and II) actually stand for dexto or (−) and laevo or (+) isomers. Since they are related to each other as mirror images, they are commonly called

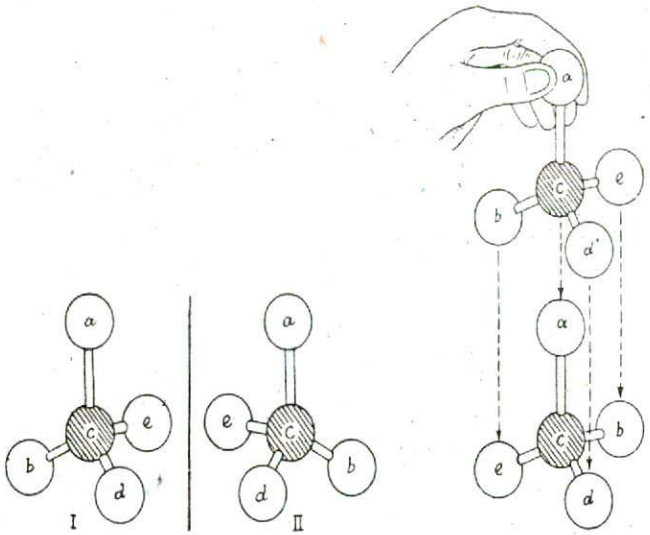
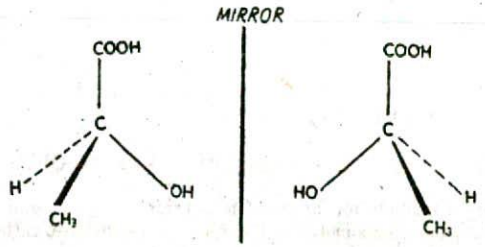


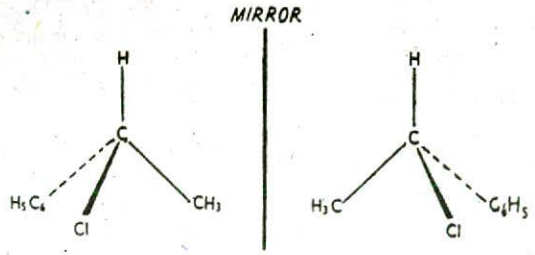
Fig. 7·14. Two ball-and-stick models of form I and II are nonsuperimposable.

Enantiomorphs (Gr., *enantio* = opposite ; *morph* = form) or **Enantiomers**. Thus optical isomerism is now often referred to as **Enantiomerism**.

It is obvious that optical isomers or enantiomers due to the presence of an asymmetric carbon atom in a compound differ only in the arrangement or configuration of groups in tetrahedral perspective. This may be illustrated by taking a few examples of compounds which exist as (+)- and (−)-enantiomers.



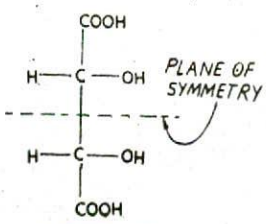
(+)- and (−)-lactic acids



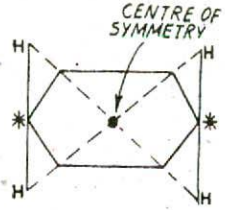
(+)- and (−)-1-chloro-1-phenyl ethane

CRITERION OF ENANTIOMERISM

It is true that most of the compounds which contain one or more asymmetric carbon atoms show enantiomerism. But it is not always so. There are known compounds which have asymmetric carbons but being non-dissymmetric do not show enantiomerism. Thus *meso* tartaric acid has two asymmetric carbons but is optically inactive. Similarly *trans*-cyclohexane-1, 4-dicarboxylic acid has asymmetric carbons but since it has a centre of symmetry (indicated by thick dot), the compound is non-dissymmetric and exhibits no enantiomerism.



meso-tartaric acid
(*inactive*)



trans-cyclohexane-1, 4-dicarboxylic acid

On the other hand, there are certain compounds such as allenes, (R—CH=C=CHR), which are dissymmetric but contain no asymmetric carbon and yet they display enantiomerism.



1, 3-dimethylallene
(dotted line implies different plane)

Thus it is evident that it is chirality and not the presence of asymmetric carbon atoms which is the criterion of enantiomerism.

FISCHER PROJECTIONS

When we attempt to depict configurations, we face the problem of representing three-dimensional structures on a two dimensional surface. To overcome this difficulty we use

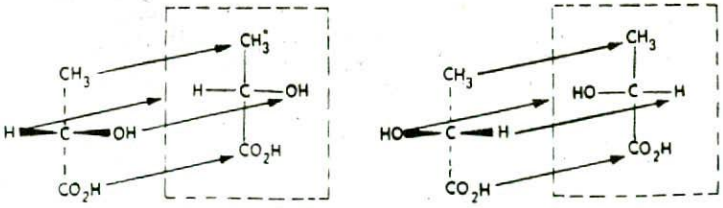


Fig. 7·15. Fischer projection formulas.

the so-called *Fischer projection*. This is the structure of an asymmetric carbon atom drawn in a prescribed orientation and then projected into a planar surface. Thus planar formulas of

the asymmetric carbon are obtained by placing it so that the two substituents are horizontal and project out towards the viewer (shown by thick wedge-like bonds), while the two other substituents are vertical and project away from the viewer (shown by dotted bonds). Hence we may draw the *d* and *e* configurations of lactic acid as in Fig. 7·15.

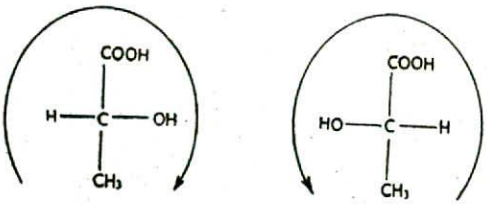
Now the planar representation of two forms of lactic acid may be given as



In these formulas the horizontal bonds *i.e.*, C—OH and C—H project towards us out of the plane of the paper whereas the vertical bonds *i.e.*, C—COOH and C—CH_3 project away from us. Furthermore, since the vertical bonds are actually behind the plane of the paper, the formula may be rotated by an angle of 180° (not by 90° or 270°). Inspection of the models shows that one interchange of a pair of substituents inverts the configuration (changes one enantiomer into its minor image), whereas an even number of such interchanges does not. Thus interchanging of —H for —OH in I gives the enantiomer II while the interchange of CH_3 for —COOH and —H for —OH leaves the configuration unchanged.

ABSOLUTE AND RELATIVE CONFIGURATION

While discussing optical isomerism, we must distinguish between *relative* and *absolute* configuration (arrangement of atoms or groups) about the asymmetric carbon atom. Let us consider a pair of enantiomers, say (+)- and (−)- lactic acids.



We know that they differ from one another in the direction in which they rotate the plane of polarised light. In other words, we know their relative configuration in the sense that one is of opposite configuration to the other. But we have no knowledge of the absolute configuration of the either isomer. That is, we cannot tell as to which of the two possible configurations corresponds to (+)-acid and which to the (−)-acid.

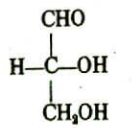
D and L system. The sign of rotation of plane-polarized light by an enantiomer cannot be easily related to either its absolute or relative configuration. Compounds with similar configuration at the asymmetric carbon atom may have opposite sign of rotations and compounds with different configuration may have same sign of rotation. Thus *d*-lactic acid with a specific rotation +3·82° gives *l*-methyl lactate with a specific rotation −8·25, although the configuration (or arrangement) about the asymmetric carbon atom remains the same during the change.

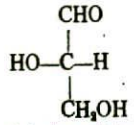


Obviously there appears to be no relation between configuration and sign of rotation.

Thus D-L-system has been used to specify the configuration at the asymmetric carbon atom. In this system, the configuration of an enantiomer is related to a standard, glyceral-

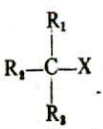
dehyde. The two forms of glyceraldehyde were arbitrarily assigned the absolute configurations as shown below.

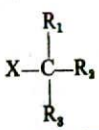

(+)-glyceraldehyde
D configuration


(−)-glyceraldehyde
L configuration

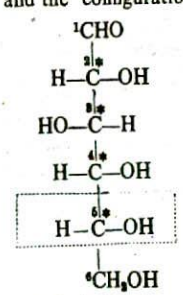
If the configuration at the asymmetric carbon atom of a compound can be related to D (+)-glyceraldehyde, it belongs to D-series ; and if it can be related to L (−)-glyceraldehyde, the compound belongs to L-series. Thus many of the naturally occurring α-amino acids have been correlated with glyceraldehyde by chemical transformations. For example, natural alanine (2-aminopropanoic acid) has been related to L (+)-lactic acid which is related to L(−)-glyceraldehyde. Alanine, therefore, belongs to the L-series.

In general, the absolute configuration of a substituent (X) at the asymmetric centre is specified by writing the projection formula with the carbon chain vertical and the lowest number carbon at the top. The D configuration is then the one that has the substituent 'X' on the bond extending to the 'right' of the asymmetric carbon, whereas the L configuration has the substituent 'X' on the 'left'. Thus,

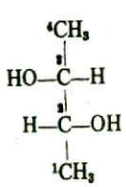

D configuration


L configuration

When there are several asymmetric carbon atoms in a molecule, the configuration at one centre is usually related directly or indirectly to glyceraldehyde, and the configurations at other centres are determined relative to the first. Thus, in natural (+)-glucose there are four asymmetric centres (marked by asterisk). By convention for sugars, the configuration of the highest numbered asymmetric carbon is referred to glyceraldehyde to determine the overall configuration of the molecule. For glucose, this atom is C—5 and, therefore, OH on it is to the right. Hence the naturally occurring glucose belongs to the D-series and is named as D-glucose.


D(+)-glucose

However, the above system of nomenclature based on Fischer projection formulae, has certain disadvantages. Firstly before a name can be assigned to a compound, we must specify how its projection formula is oriented. Secondly, sometimes the two asymmetric carbon atoms having the same kind of arrangements of substituents are assigned opposite configurational symbols. Thus for (−)-2 , 3-butanediol we have


(−)-butane-2-L-3 D-diol

R AND S SYSTEM

This is a newer and more systematic method of specifying absolute configuration to optically active compounds. Since it has been proposed by R.S. Cahn, C.K. Ingold and V. Prelog, this system is also known as **Cahn-Ingold-Prelog system**. This system of designating configuration has been used increasingly since the early 1960s and may eventually replace the DL-system.

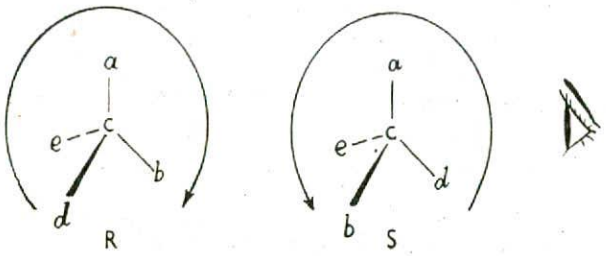
Cahn-Ingold-Prelog system is based on the actual three-dimensional or tetrahedral structure of the compound. In order to specify configuration about an asymmetric carbon *C *abde*, the groups *a*, *b*, *d* and *e* are first assigned and order of priority determined by the 'sequence rules'. These rules will be given later. For the present, let us assign priorities 1, 2, 3, 4 to the groups *a*, *b*, *d*, *e*. Thus the order of priorities may be stated as

a	>	*b*	>	*d*	>	*e*
(1)		(2)		(3)		(4)

Now the tetrahedral model of the molecule is viewed from the direction opposite to the group '*e*' of lowest priority (4). The '**Conversion rule**' says that :

(*i*) If the eye while moving from $a \rightarrow b \rightarrow d$ travels in a clockwise or right-hand direction, the configuration is designated **R** (Latin, *Rectus*=right).

(*ii*) If the eye while moving from $a \rightarrow b \rightarrow d$ travels in counterclockwise or left-hand direction, the configuration is designated **S** (Latin, *Sinister*=left).



The **Sequence Rules** to determine the order of priorities of groups are :

(1) *The atoms or groups directly bonded to the asymmetric carbon are arranged in order of decreasing atomic number and assigned priority 1, 2, 3, 4, accordingly.*

Thus in chlorobromofluorormethane (CHClBrF), the substituents Br (at no=35), Cl (at no =17), F (at no =9) and H (at no =1) give the order of priorities.

Br	>	Cl	>	F	>	H
(1)		(2)		(3)		(4)

(2) *When two or more groups have identical first atoms attached to asymmetric carbon, the priority order is determined by considering the atomic numbers of the second atoms ; and if the second atoms are also identical the third atoms along the chain are examined.*

Let us consider the three groups ·

$-\overset{1}{C}H_2-\overset{2}{H}$	methyl
$-\overset{1}{C}H_2-\overset{2}{C}H_2-\overset{3}{H}$	ethyl
$-\overset{1}{C}H_2-\overset{2}{C}H_2-\overset{3}{C}H_3$	n-propyl

In methyl and ethyl the first atom is carbon and, therefore, atomic numbers of the second atoms H (at no 1) and C (at no 6) decide the priority order, ethyl > methyl. While considering ethyl and *n*-propyl the second atom is also identical (carbon) and hence the third atoms (H, C) give the priority order n-propyl > ethyl

(3) *If the first atoms of the two groups have same substituents of higher atomic number, the one with more substituents takes priority.*

Thus $-CHCl_2$ has a higher priority than $-CH_2Cl$.

(4) *A doubly or triply bonded atom 'A' present in a group appended to assmmetric carbon, is considered equivalent to two or three singly bonded 'A's, respectively.*

Thus,

$=A$ equals $\begin{matrix} A \\ \diagup \\ \diagdown \\ A \end{matrix}$ (A, A)

$\equiv A$ equals $\begin{matrix} A \\ \diagup \\ A \\ \diagdown \\ A \end{matrix}$ (A, A, A)

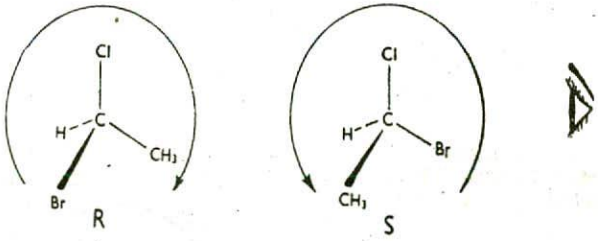
Hence between groups $-\overset{H}{\underset{|}{C}}=O$ (O, O, H) and $-CH_2OH$(O, H, H), the former will have higher priority.

A phenyl group is handled as if it had one of the Kekule structures.



Let us now illustrate the above rules by assigning **R** and **S** configurations to enantiomers of some compounds.

Example 1. *The two enantiomers of 1, 1-chlorobromoethane are* :

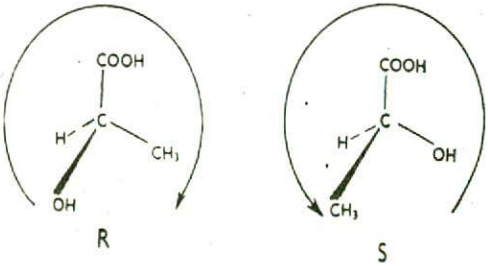


The four atoms directly bonded to asymmetric carbon are Br (atno=35), Cl (at no=17), C (at no=6) and H (at no=1). Hence the priority order is

Br	>	Cl	>	CH_3	>	H
(1)		(2)		(3)		(4)

Now viewing the groups Br, Cl, CH_3 in tetrahedral perspective, the configurations **R** and S are assigned as in Fig. above

Example 2. *The two enantiomers of lactic acid are* :

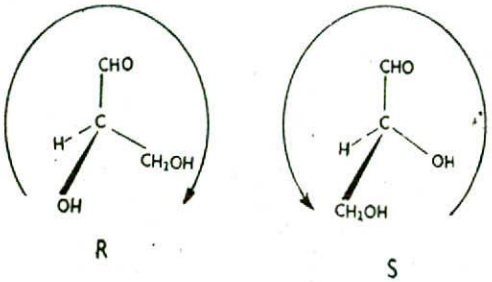


According to the sequence rules described before, the priorities of the four groups are

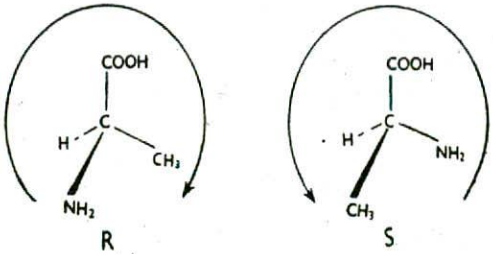
OH	>	CO_2H	>	CH_3	>	H
(1)		(2)		(3)		(4)

and the configurations **R** and **S** as shown in diagram above.

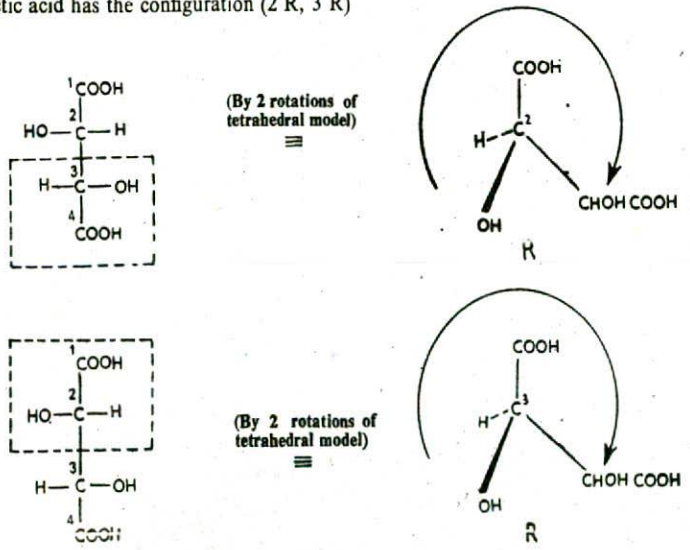
Example 3. *The groups bonded to asymmetric carbon in glyceraldehyde, $CHO.CHOH.CH_2OH$, have the priority order $OH > CHO > CH_2OH > H$. Applying the conversion rule, he configuration of the two enantiomers are assigned as*



Example 4. *Alanine in which the group order is $NH_2 > CO_2H > CH_3 > H$, has the configurations of the two isomers :*



If more than one asymmetric centre is present in a molecule, the configuration at each centre is specified by the symbol R or S together with the number of the asymmetric carbon. Thus L-lactic acid has the configuration (2 R, 3 R)

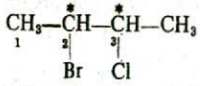


It may be noted that *R* and *S* system is merely a nomenclature device and has nothing to do with the sign and magnitude of optical activity. Thus the complete description of an optically active compound must include both the direction of rotation (+ or −) and the configuration of the compound (R or S). A racemic modification is an equimolecular mixture of two enantiomers and is given the prefix (RS).

OPTICAL ISOMERISM IN COMPOUNDS WITH MORE THAN ONE ASYMMETRIC CARBON ATOM

In the above discussion we have seen that an asymmetric carbon atom can produce molecular asymmetry. Thus the molecules containing an asymmetric carbon exist in two optically active forms, (+)-isomer and (−)-isomer, and an equimolar mixture of the two, (±)-mixture, which is optically inactive. When there are two or more asymmetric carbon atoms in a molecule, the problem is complicated considerably.

An organic compound which contains **two dissimilar asymmetric carbons**, can give four possible stereoisomeric forms. Thus 2-bromo-3-chlorobutane may be written as

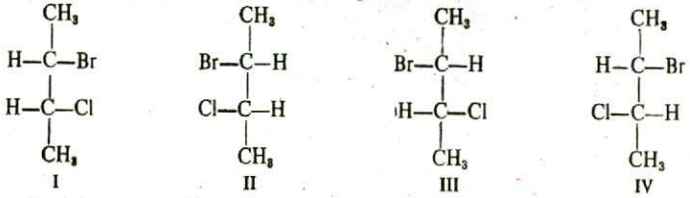


The two asymmetric carbons in its molecule are dissimilar in the sense that the groups attached to each of these are different.

C2 has CH_3, H, Br, $CHClCH_3$

C3 has CH_3, H, Cl, $CHBrCH_3$

Such a substance can be represented in four configurational forms.



The forms I and II are optical enantiomers (related as object and mirror image) and so are forms III and IV. These two pairs of enantiomers will give rise to two possible racemic modifications.

It may be noted that forms I (2 S, 3 S) and III (2 S, 3 R) are not mirror images or enantiomers, and yet they are optically active isomers. Similarly, the other two forms *i.e.*, II (2 R, 3 R) and IV (2 R, 3 S) are also not enantiomers but optically active isomers.

Such stereoisomers which are optically active isomers but not mirror images, are called **Diastereoisomers** or **Diastereomers.**

Diastereoisomers have different physical properties. Thus they have different melting points, boiling points, solubilities in a given solvent, densities, and refractive indices. They also differ in specific rotations ; they may have the same or opposite signs of rotations.

Like geometrical isomers, the diastereoisomers may be separated from each other :—

(*i*) by fractional distillation due to their difference in boiling points ;

(*ii*) by fractional crystallisation due to their difference in solubility ;

(*iii*) by chromatography due to their different molecular shapes and polarity.

NUMBER OF OPTICAL ISOMERS

As has been discussed above, a compound containing two dissimilar carbon atoms can exist in four optically active forms. Reasoning in the same fashion, we will find that a compound containing three such asymmetric carbon atoms can exist in eight different configurations which represent optical isomers. Thus in general, the number of stereoisomers for a compound with *n* distinct asymmetric carbon atoms is 2^n. An important group of compounds containing a number of asymmetric carbon atoms are the carbohydrates which we will study later on.

When an organic compound contains two similar asymmetric carbon atoms in its molecule, *abd* $\overset{*}{C}-\overset{*}{C}$*abd*, the number of optically active isomers decreases. Thus tartaric acid has two asymmetric carbon atoms and exists in three optically active forms only.

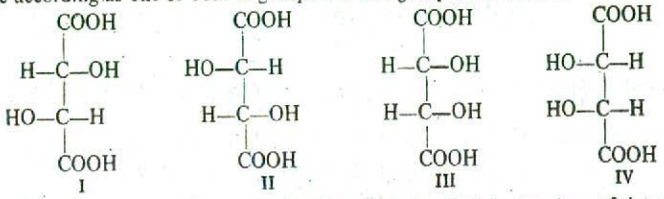
ISOMERISM OF TARTARIC ACID

Let us now proceed to discuss the optical isomerism of tartaric acid which contains two similar asymmetric carbon atoms, in detail.

The two asymmetric carbon atoms in tartaric acid,

*CH(OH)COOH
|
*CH(OH)COOH

are attached to the groups H, OH, COOH, and CH(OH)COOH. Its molecule can be represented by space models of two tetrahedra joined corner to corner but for the sake of convenience we will use the plane formulas. The end groups being identical, in all four arrangements are possible according as one or both H groups and OH groups are on the left or on the right.



Of these, formula IV when rotated through 180° in the plane of the paper becomes identical with formula III. Therefore, for tartaric acid we can have only three different arrangements, *viz* I, II and III.

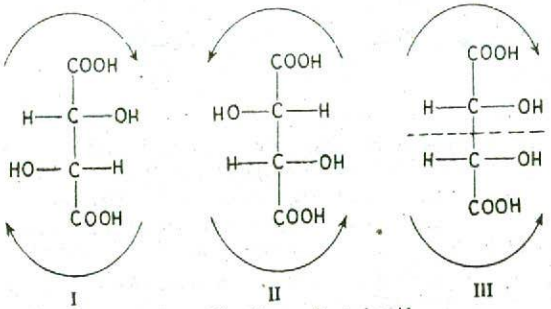


Fig. 7·16. Three forms of tartaric acid.

Now, if the force which rotates the plane of polarised light be directed from H to OH,

(*i*) structure I will rotate the plane of polarised light to the right and will represent (+)-tartaric acid ;

(*ii*) structure II will rotate the plane of polarised light to the left and will represent (−)-tartaric acid ; and

(*iii*) structure III will represent optically inactive tartaric acid, since the rotatory power of the upper half of the molecules is balanced by that of the lower half.

It may also be noted that formulas I and II are mirror images of each other and hence represent (+)- and (−)- isomers Formula III, however, has a plane of symmetry (dotted line) and hence represents an inactive isomer of tartaric acid.

In actual practice, four tartaric acids are known :

(*i*) (+)-Tartaric acid ;

(*ii*) (−)-Tartaric acid ;

(*iii*) Inactive or *i*-Tartaric acid ; this is also known as *meso*-Tartaric acid or *m*-tartaric acid ; and

(*iv*) (±) Tartaric acid ; this form of tartaric acid being a mixture of equal amounts of (+)- and (−)-isomers.

The physical properties of the four tartaric acids are tabulated below :

Table. *Physical properties of Tartaric acids*

Name	M Pt °C	Density	$[\alpha]_D$
(+)-Tartaric acid	179	1·760	+12°
(−)-Tartaric acid	170	1·760	−12°
(±)-Tartaric acid	206	1·697	0°
m-Tartaric acid	140	1·666	0°

The three tartaric acids (+)-, (−)-, *m*-, are all space isomers but *m*-tartaric acid is not a mirror image of either of the active forms. Hence it differs from them in melting point, density and other physical properties.

EXTERNAL AND INTERNAL COMPENSATION

If equimolecular amounts of *d*- and *l*-isomers are mixed in a solvent, the solution is inactive. The rotation of each isomer is balanced or compensated by the equal but opposite rotation of the other. Optical inactivity having this origin is described as due to **External Compensation**. Such mixtures of (+)- and (−)-s isomers (*Racemic mixtures*) can be separated into the active components.

In *meso* tartaric acid the inactivity is due to effects within the molecule and not external. The force of rotation due to one half of the molecule is balanced by the opposite and equal force due to the other half. The optical inactivity so produced is said to be due to **Internal Compensation**. It occurs whenever a compound containing two or more asymmetric carbon atoms has a plane or point of symmetry. Since the optical inactivity of such a compound arises within the molecule, the question of separating it into active components does not arise.

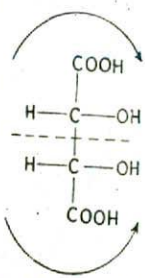
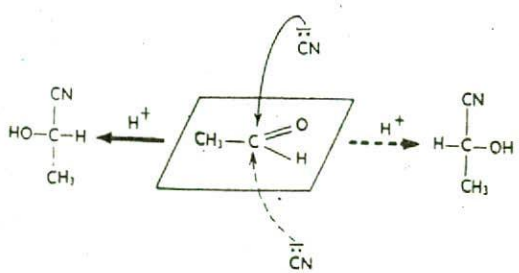


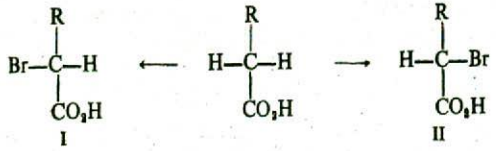
Fig. 7-17. Inactivity of Meso Tartaric acid by Internal Compensation.

LABORATORY SYNTHESIS YIELDS RACEMIC MIXTURE

The synthesis of a dissymmetric or asymmetric structure from a symmetric molecule always results in the formation of a racemic modification, provided that the reaction is carried out in the absence of optically active reagents or asymmetric physical influences such as circularly polarized light. A simple illustration is the formation of lactonitrile by the addition of HCN to acetaldehyde. Approach to either side of the planar carbonyl group is equally likely so that equal number of molecules of (+) and (−) enantiomers result and the product is the racemic modification. Numerous other examples of this type are known.



Asymmetric carbon atoms are also produced by substitution reactions. For example, α-bromination of an aliphatic carboxylic acid, $R—CH_2—CO_2H$, gives the racemic modification, $(\pm)RCHBrCO_2H$, since two α-hydrogens are equivalent so each is replaced at the same rate. Thus,



I II

It should be noted that structures (I) and (II) are related as mirror images of each other and hence if (I) is laevorotatory the other (II) must be dextrorotatory.

RESOLUTION OF RACEMIC MIXTURES

The separation of a racemic mixture into its (+)-*and* (−)-*components* is termed **Resolution.** Since the optical isomers have identical physical properties, they cannot be separated by ordinary methods such as fractional crystallisation or fractional distillation.

(1) **Mechanical Separation** (*Pasteur, 1848*). This method is applicable only to solid substances which form well defined crystals. Frequently the racemic mixtures consist of two types of crystals which have different shapes, being the mirror images of each other. The two varieties of crystals can be separated with the aid of a magnifying lens and a small forceps. Since the crystals of one type are all (±)-isomer and the crystals of the other types are (−)-isomer, their separation leads to the resolution of the racemic mixture. This method is too tedious for practical purposes and is now of historical interest only because it was the first method which Pasteur employed for the separation of the tartaric acids.

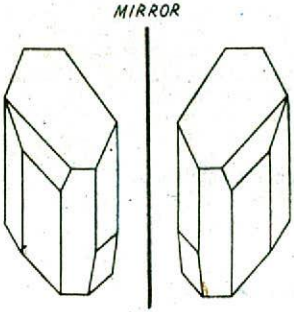


Fig. 7-18. Shapes of crystals of two forms of tartaric acid.

(2) **Biochemical Method** (*Pasteur, 1858*). In this method the resolution is effected by destroying one form (+)-or (−)- by a biochemical process. When certain micro-organisms such as yeast, moulds and bacteria are allowed to grow in the solution of a racemic mixture, they assimilate one form selectively leaving the other in solution. The separation is almost complete so that the form left in solution can be isolated by fractional crystallisation. For example, if ordinary mould, *Penicillium glaucum*, is added to a solution of (−)- tartaric acid, the solution becomes laevorotatory due to the destruction of *dextro* form. The selective consumption of one isomer is believed to be due to the asymmetry and optical activity of the enzyme present in the microorganism.

The method is, no doubt, much more practical than the mechanical separation but it suffers from the following disadvantages.

(*i*) One-half of the material is sacrificed.

(*ii*) It cannot be applied to (±)-mixtures of poisonous substances which are incapable of acting as food for organisms.

(3) **Chemical Method** (*Pasteur, 1858*). This is the most general method of resolution. In this method the (±)-mixture is united with another suitable optically active isomer when the products are no longer mirror image isomers and may be separated by crystallisation.

For example, a solution of racemic lactic acid may be treated with an optically active base such as the alkaloid (−)-Brucine. The resulting product will consist of two salts :

(*i*) (+)- Acid. (−)- Base ; and (*ii*) (−)- Acid. (−)- Base.

The relation of the configurations of the two salts may be explained by the following illustration. Suppose the two enantiomorphic forms of lactic acid are represented by the symbols



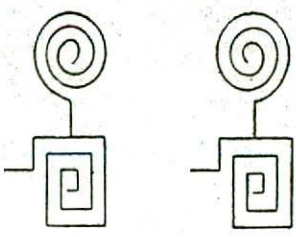
(+)-lactic acid (−)-lactic acid

and the two enantiomorphic forms of brucine by the symbols



(+)- brucine (−)- brucine

Now the two compounds (−)- brucine.(+)-lactate and (−)-brucine. (−)-lactate may be represented as shown below.



(−)-brucine (+)- lactate (−)- brucine (+)-lactate

Inspection of the configurations of the two salts shows that they are not enantiomorphic. Therefore, they have different solubility in water and can be separated by fractional crystallisation. The isolated salts are then treated with dilute sulphuric acid when the optically active acids are regenerated.

Similarly, a racemic mixture of a base can be resolved by combination with an optically active acid such as -(+) tartaric acid. A racemic mixture of alcohols may be resolved by esterification with an optically active acid.

(4) **Kinetic Method** (*Markwald, McKenzie,* 1899). The fact that enantiomers react with an optically active substance at different rates, is used for the separation of racemic mixtures. Thus (−)-menthol (an alcohol) reacts faster with (+)-mandelic acid ($C_6H_5\overset{*}{C}HOHCOOH$) than (−)-mandelic acid to form ester. Therefore, when racemic mandelic acid is esterified with a limited quantity of (−)- menthol, the product is richer in (+). (−)-ester than (−). (−)-ester which upon hydrolysis gives partially resolved mandelic acid.

(5) **Selective Adsorption**. Sometimes 'resolution' may be achieved by passing a solution of the racemate over a column of a finely powdered, optically active adsorbent such as starch, sugar or quartz. The surface of the adsorbent, adsorbs selectively one enantiomer and thus the solution emerging at the bottom is richer in the other enantiomer. In this way partial resolution is effected.

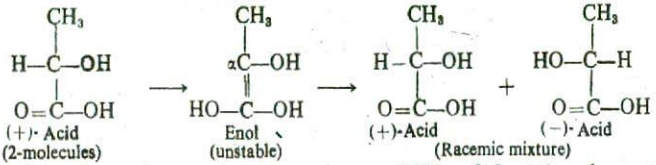
RACEMIZATION

The process of converting an optically active compound (+)- or (−)- into racemic modification (±)- is known as *racemization*. The (+)- and (−)- forms of most of the compounds are capable of racemization under the influence of heat, light or chemical reagents. The process involves the change of half of the active compound to the isomer of the opposite rotation, thus resulting in the racemic mixture.

$$\left.\begin{array}{l} 2\,(+)\text{-A} \longrightarrow (+)\text{-A}.\ (-)\text{-A} \\ \text{or} \quad 2\,(-)\text{-A} \longrightarrow (+)\text{-A}.\ (-)\text{-A} \end{array}\right] \text{ Racemic mixture}$$

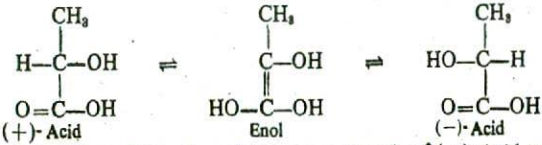
Many theories have been put forward to explain racemization. Owing to the diverse nature of the structures of the various optically active compounds, one cannot expect to find one theory which would explain the racemization of all such compounds. Thus a number of mechanisms have been suggested, each one explaining the racemization of a particular type of compounds.

Racemization takes place readily in the case of optically active hydroxy acids like lactic, malic and tartaric acids in the presence of a base. All these compounds have a carboxyl group adjacent to an asymmetric carbon atom carrying a hydrogen. Thus racemization has been interpreted to take place through the formation of an *enol* which at once changes to the other enantiomer. In case of lactic acid we have :



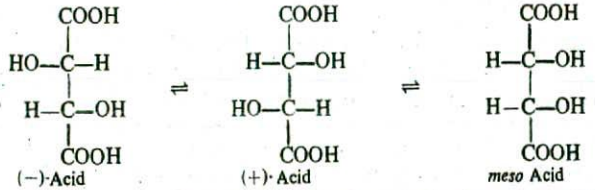
Since the enol is a planar molecule, so the possibility of frontal and rear attachment of H-atom to α-carbon atom (in the enol form) is equally probable. Consequently equal number of molecules of (+)- and (−)- form would result and racemic modification would be produced.

But the changes shown above are reversible and in actual practice we get an equilibrium mixture since one molecule of (+)-Acid remains as if it were unchanged.



The equilibrium mixture thus obtained contains one molecule of (+)- Acid and one molecule of (−)- Acid *i.e.*, the racemic mixture of the acid.

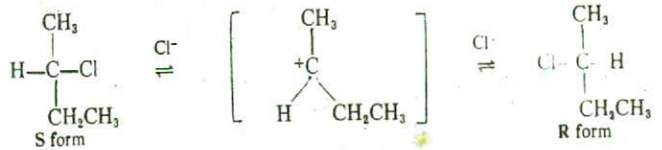
Pasteur found that if a solution of (+)-tartaric acid is heated for some time at 165°C, it loses its optical activity forming the racemic mixture and *meso* acid. This is due to the fact that tartaric acid having two asymmetric carbon atoms may undergo inversion of H and OH only about one carbon or both, yielding *meso* or racemic form respectively.



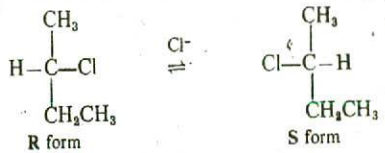
The equilibrium mixture (through the enolic form) in the above case will consist of equal amounts of the (+)- and (−)- isomers.

Optically active substances which cannot enolize because they have no hydrogen atom at α carbon to a carbonyl group, do not in general racemize except under conditions which bring about other chemical changes as well.

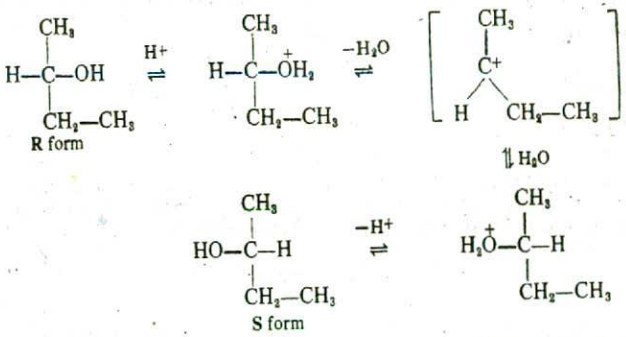
The racemization of optically active halides may take place either by an S_N1 or S_N2 mechanism depending upon the experimental conditions. In polar solvents, *S*-butyl chloride racemizes by S_N1 mechanism. Dissociation of the compound produces planar carbonium ion which can recombine with the anion *i.e.*, Cl^- yielding both *d*- and *l*- forms of the compound.



S-butyl chloride also racemizes in acetone containing dissolved LiCl probably by an S_N2 mechanism. Displacement of chloride ion of the halide by chloride ion (from LiCl) inverts configuration at the carbon atom undergoing substitution. A second such substitution regenerates the original enantiomer. Eventually, this back and forth process produces equal number of **R** and **S** forms ; the substance is then racemic.



Asymmetric alcohols are often racemised by strong acids. Undoubtedly, the process of racemization must involve ionization with the generation of a planar carbonium which then recombines with water to furnish either enantiomer.



Racemization reactions are also known to take place through the intermediacy of carbanions.

ASYMMETRIC SYNTHESIS

We have already seen that when a compound containing an asymmetric carbon atom is synthesised by ordinary laboratory methods from a symmetric compound, the product is a racemic mixture. If, however, such a synthesis is carried under the 'Asymmetric influence' of a suitable opitically active reagent, one of the optically active isomers, (+)-or(−)-, is produced in preference. *This kind of process in which an asymmetric compound is synthesised form a symmetric compound to yield the* (+)- *or* (−)- *isomer directly*, is termed **Asymmetric Synthesis.**

In such asymmetric synthesis, both the active isomers, (+)- and (−)-,are invariably produced simultaneously but one of these is obtained in excess and often (but not always) it has the same sign of rotation as the active reagent employed. An illustration of asymmetric synthesis is offered by the following early example (Mackenzie, 1905).

When pyruvic acid is reduced as such, it yields (±)-lactic acid. However, when pyruvic acid is first combined with an optically active alcohol, ROH, such as (−)-menthol* to form an ester which is then reduced, the product upon hydrolysis yields (−)- lactic acid in excess.

$$CH_3-CO-COOH + \underset{\text{(−)-menthol}}{ROH} \longrightarrow \underset{\text{(−)-menthyl pyruvate}}{CH_3-CO-COOR} + H_2O$$

$$CH_3-\overset{O}{\overset{\|}{C}}-COOR + 2H \longrightarrow \underset{\substack{\text{(−)-menthyl-}l\text{-lactate (excess)}\\ \text{and (+)-menthyl (+)-lactate}}}{CH_3-\underset{OH}{\overset{H}{\overset{|}{\underset{|}{C}}}}-COOR} \xrightarrow{+H_2O} \underset{\substack{\text{(−)-lactic acid (exesss)}\\ \text{and (+)-lactic acid}}}{CH_3-\underset{OH}{\overset{H}{\overset{|}{\underset{|}{C}}}}-COOH} + \underset{\text{(−)-menthol}}{ROH}$$

In nature, numerous optically active substances such as terpenes, alkaloids and proteins are produced by asymmetric synthesis, under the influence of optically active enzymes. These enzymes unite with the substance available in plants and when the synthesis is complete, they separate from the product and are thus again free to combine with more of the parent inactive substance and the endless process continues.

As the things stand today, very little is known about asymmetric synthesis and its mechanism is still a matter of speculation.

WALDEN INVERSION

When an atom or group directly linked to the asymmetric carbon atom is replaced, the reaction may proceed with inversion of configuration. This phenomenon was first of all observed by Walden (1895) and hence the name Walden inversion. Walden inversion may also be defined as *the conversion of the (+)-form to (−)-form or vice versa, without recourse to resolution.* Thus (+)-malic acid may be converted to (−)-malic acid as follows.

$$\underset{\substack{\text{(+)-malic acid}}}{\overset{COOH}{\overset{|}{H-C-OH}}\atop{\overset{|}{CH_2COOH}}} \xrightleftharpoons[KOH]{PCl_5} \underset{\text{(−)-chlorosuccinic acid}}{\overset{COOH}{\overset{|}{Cl-C-H}}\atop{\overset{|}{CH_2COOH}}} \xrightarrow{AgOH} \underset{\text{(−)-malic acid}}{\overset{COOH}{\overset{|}{HO-C-H}}\atop{\overset{|}{CH_2COOH}}}$$

Since S_N2 reactions always proceed with inversion of configuration, Walden inversion is a type of S_N2 reaction. Thus in the above reaction Walden Inversion observed in the reaction of PCl_5 on (+)-malic acid and that of KOH on (−)-chlorosuccinic acid.

QUESTIONS

1. What is Stereoisomerism ? Distinguish between the two types of stereoisomerism you have studied.
2. Write a brief account of optical activity in organic compounds with examples. Explain the terms dextrorotatory, laevorotatory, racemic, and meso as applied to optical isomers.
3. What is metamerism ? Give an example. *(Bangalore BSc III, 1993)*
4. Write a note on : Geometrical isomerism. *(Punjab BSc, 1993)*
5. Discuss the Geometrical isomerism of maleic and fumaric acids. *(Madras BSc, 1993)*
6. Discuss the isomerism of aldoximes and ketoximes.
7. Differentiate between : Enatiomers and Diastereomers. *(Baroda BSc, 1993)*
8. Discuss the methods of resolution of racemic mixtures. *(Nagpur BSc, 1994)*
9. Illustrate sequence rules for assigning *R* and *S* configuration to an optically active compound. *(Annamalai BSc, 1994 ; Vikram BSc, 1994)*
10. Explain the notations *R* and *S* as used in stereochemistry.
11. Write a note on : Geometrical isomerism. *(Shivaji BSc, 1994)*
12. Discuss the Geometrical isomerism of maleic and fumaric acids. *(Gauhati BSc Hons, 1994)*

13. Mention the specific types of isomerism exhibited by each of the following pairs :
    (*a*) Maleic acid and Fumaric acid
    (*b*) *n*-Butyl alcohol and Diethyl ether
    (*c*) Diethyl ether and Methyl propyl ether

Answer. (*a*) Geometrical isomerism ; (*b*) Functional isomerism ; (*c*) Metamerism.

14. Give a brief account of the optical isomerism of Lactic acid. *(Delhi BSc Hons, 1994)*

15. Give a brief account of the optical isomerism of Tartaric acid. *(North Eastern Hill BSc Hons, 1994)*

16. Which one of the following compounds exhibits optical isomerism :
    (*a*) Nitromethane (*b*) Biphenyl
    (*c*) Glyceraldehyde (*d*) Ethylene glycol

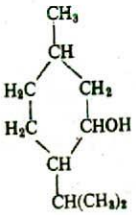
Answer. (*c*).

17. How will you distinguish between Enantiomers and Diastereomers ? *(Pandicherry BSc, 1994)*

18. How can *D* and *L* tartaric acids be obtained in optically active forms from a racemic mixture.

---

*Menthol has the structure



Chapter **8**

Classification and Nomenclature of Organic Compounds

In the early stages of the development of organic chemistry, relatively small number of compounds were known. Therefore, their study did not pose any serious problem. With the passage of time, the number of organic compounds discovered continued to increase. At present there are known as many as about three million organic compounds and their structural formulas established. The study of such a large number of compounds would be well nigh impossible without a systematic classification having 'structural basis'.

PRINCIPAL SERIES

The organic molecules may be made of carbon-carbon open chains or cyclic structures. The cyclic structures may contain only carbon atoms or carbon atoms and another atom (O,N,S). Broadly speaking, the entire population of organic compounds could be embraced by the following *principal series.*

Acyclic Series

The compounds whose molecules contain an open-chain of carbon atoms, are said to constitute the **Acyclic** or **Noncyclic Series.** For example,



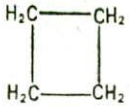
The compounds of this series are also called **Aliphatic Compounds** and the series **Aliphatic Series.** The term aliphatic is derived from the Greek word *aleipher*, meaning 'fatty' since the earliest known compounds of this type were obtained from fats.

Cyclic Series

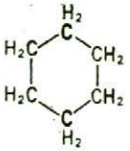
The compounds whose molecules contain ring structures constitute this series. It consists of two types of compounds :

(1) **Carbocylic Compounds** which have a ring made of carbon atoms only. The carbocyclic compounds are again divided into two categories.

(*a*) **Alicyclic compounds** which contain a cyclic structure made of atoms only joined by single covalent bonds. They behave like *ali*phatic compounds and are hence named as *alicyclic.* Example are :

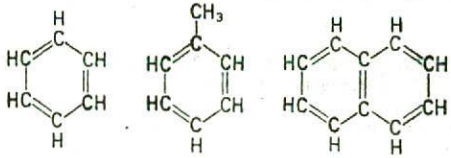


CYCLOBUTANE



CYCLOHEXANE

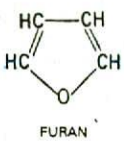
(*b*) **Aromatic Compounds** (Greek *aroma* = fragrant smell) which contain one or more benzenoid rings. This type of compounds are said to constitute the **Aromatic Series**. Thus benzene, toluene and naphthalene are examples of aromatic compounds.



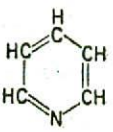
BENZENE TOLUENE NAPHTHALENE

Aromatic comdounds are designated as **monocyclic, bicyclic and tricyclic** according as they contain one, two or three rings.

(2) **Heterocyclic Compounds**. The cyclic compounds which include one or two atoms other than carbon (O,N,S) in the ring, are cali d heterocyclic compounds or **Heterocycles** (*hetero*, meaning different). Thus furan and pyridine are heterocyclic compounds.



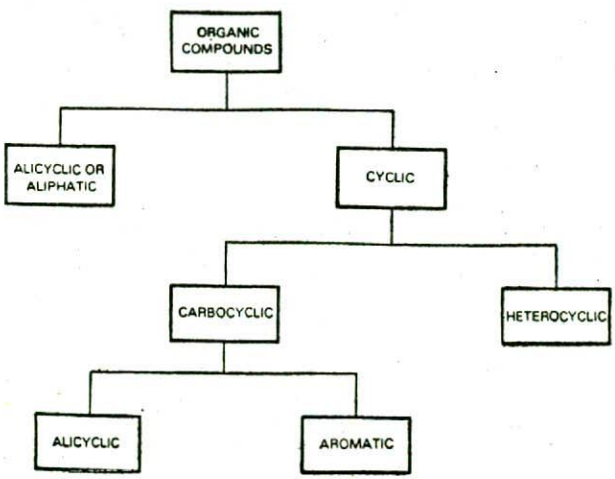
FURAN



PYRIDINE

The heterocyclic compounds with five and six atoms in the ring are referred to as *five-membered* and *six-membered heterocycles* respectively.

A complete **genealogical table** given below indicates the broad classification of organic compounds into the principal series.



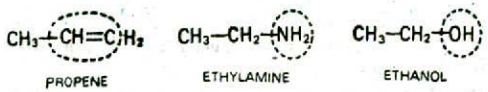
The division of organic compounds into *aliphatic series* and *aromatic series* is particularly useful. These embrace the various types of compounds belonging to all the other series stated above. The basic structural differences between the compounds of the two series are reflected in their chemical reactions. Hence a separate study of aliphatic and aromatic compounds has been preferred in this text.

FUNCTIONAL GROUPS

The structural formulas of oraganic compounds are made of a carbon-hydrogen framework which is relatively chemically unreactive. It is the presence of another atom or groups of atoms, or carbon-carbon multiple bonds in the molecule that confer on it chemical reactivity. These sites of reactivity in organic molecules are referred to as functional groups or just **'function'**.

A functional group may be precisely defined as an atom or group of atoms which determines the chemical behaviour of an organic compound.

Examples of functional groups (circled) are :

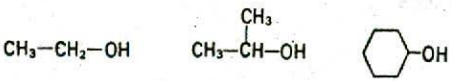


PROPENE ETHYLAMINE ETHANOL

Each functional group gives characteristic reactions which are largely independent of the rest of the molecule. Evidently the reactions of any number of compounds containing a specific functional group are similar. Since there are only a dozen or so functional groups present in simple organic compounds, the study of thousands of organic compounds is made simple. Otherwise, we would have to memorise the chemistry of each individual compound. Table 8·1 lists the most important functional groups encountered in our study.

CLASSES OF ORGANIC COMPOUNDS

A series of compounds that contain the same functional group are said to constitute a **Class** *of organic compounds.* For example, each of the following series of compounds contain a hydroxyl group (—OH). These compounds all belong to the class of compounds called *alcohols.*



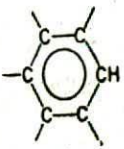
Compounds in the same class undergo similar reactions. This enables us to study a few compounds as representatives of a large number of others. In this manner we can learn the chemical reactions of many thousands of compounds by considering only a few.

Because of the similar reactions among compounds with the same functional group, it is convenient to use a general formula for a class of compounds. If R— representats an alkyl group (a group that contains C and H only), we may represent alcohol as R OH. Smilarly, the compounds containing the functional group $-NH_2$ constitute a class called *amines.* These have the general formula $R—NH_2$. In Table 8.1 are listed the important functional groups and classes of compounds with general formula.

HOMOLOGOUS SERIES

When members of a class of compounds having similar structures are arranged in order of increasing molecular weight, they are said to constitute a **Homologous Series.** Each member of such a series is referred to as a **Homologue** of its immediate neighbour. For example, the following sequence of straight chain alcohols forms a homologous series.

Table 8·1. Common Classes of Organic Compounds

General Formula	Name	Functional Group	
R—H	Alkanes	None	
$RCH=CH_2$	Alkenes		double bond
R–C≡C–H	Alkynes	–C≡C–	triple bond
ArH	Arenes		aromatic ring
R–X	Alkyl halides	–F	fluoro group
		–Cl	chloro group
		–Br	bromo group
		–I	iodo group
R–OH	Alcohols	–OH	hydroxy group
R–O–R′	Ethers	–O–	ether group
$R-NH_2$	Amines	$-NH_2$	amino group
R–SH	Thiols	–SH	sulphdryl group
R–S–R	Sulphides	–S–	sulphide group
	Aldehydes		aldehyde group
	Ketones		ketonic group
	Carboxylic acids		carboxyl group
	Esters		ester group
	Amides		amide group
R—C≡N	Nitriles	—C≡N	nitrile group
$R-NO_2$	Nitro compounds	$-NO_2$	nitro group
$R-SO_2-OH$	Sulphonic acids	$-SO_2-OH$	sulphonic acid

CH_3-OH	Methyl alcohol
CH_3-CH_2-OH	Ethyl alcohol
$CH_3-CH_2-CH_2-OH$	Propyl alcohol
$CH_3-CH_2-CH_2-CH_2-OH$	Butyl alcohol, etc.

Characteristics of a Homologous Series

(1) Any member of the series differs from the next by the unit $-CH_2-$ (methylene group).

(2) The series may be represented by a general formula. The general formula for alcohols is $C_nH_{2n+1}OH$ which gives the molecular formulas of the members by putting $n=1, 2, 3$, etc.

(3) The chemical properties of the members of a homologous series are similar, though in some series the first member shows different behaviour.

(4) The physical properties such as density, melting point and boiling point show a gradation in a rather semi-regular fashion.

The organisation of organic compounds into homologous series makes the study of organic chemistry particularly interesting and useful. This allows to learn about many compounds while only having to remember the trends applicable to a specific series. The existence of these series is of great importance on account of their predictive value. As we learn about one homologous series, much of the information would be applicable to the other similar homologous series.

A SURVEY OF ORGANIC NOMENCLATURE

In the middle of the 19th century, many compounds were known and used without any knowledge of their structures. Since these compounds had to be called something, names were given to them. These names often reflected the properties or the origins of the compounds. In some cases, compounds were named after friends or relatives of chemists who first discovered them. For example, ethane (C_2H_6) is quite inflammable and its name was derived from the Greek word *aithen*, meaning to kindle or blaze. Formic acid (HCOOH) was so named because it was obtained by the distillation of red ants (Latin *formica*=ants). Barbituric acid was named after a lady friend of the German chemist who discovered the compound.

A name assigned to an organic compound by the discoverer as he thought appropriate and not having any structural bearing, is referred to as the **Common name** *or the* **Trivial name.**

It was not long before that chemists around the world realised the futility of the haphazard **Common Nomenclature** (system of assigning common or trivial names). It was ridiculous to have different names of the same compound in different countries. And, then to remember such quaint names of thousands of organic compounds (now about three million) would be a mad man's job. Therefore, the chemists felt the need of a **Systematic Nomenclature** which could assign a logical name to each known organic compound on the basis of molecular structure.

The rational name of an organic compound derived from its structure, is called the **Systematic Name.**

The systematic nomenclature which has been developed and is used in modern practice, is the **IUPAC Nomenclature.** The names assigned according to this system are referred to as the **IUPAC Names.** Although the older common names are now obsolete, some of these are still used as 'nick names' because they are so handy.

In our study of organic chemistry, we will be using *systematic names* in general and *common names* that have been adopted on account of long usage. Let us recapitulate that :

(1) A COMMON NAME *is whimsy and has no structural relevance.* These names have been accepted for continued use through years.

(2) A SYSTEMATIC NAME *is based on the structural formula of a compound and is unambigous.* That is each name stands for one compound and one structure.

THE IUPAC SYSTEM OF NOMENCLATURE

In 1892, an assembly of chemists from different countries met in Geneva, Switzerland, to devise a rational system of naming organic compounds. This international body was eventually formalised as the International Union of Pure and Applied Chemistry (**IUPAC**). The primary nomenclature formulated by IUPAC was adopted unanimously at a meeting in Paris in 1957. This official system of naming organic compounds is referred to as the **IUPAC System of Nomenclature** or simply **IUPAC** ("you-pack") **Nomenclature**. The IUPAC organisation is responsible for further development and constant revision of the systematic organic nomenclature so as to keep it up to date.

The IUPAC system provides set rules for assigning names to all the known about three million organic compounds and to many more yet to be synthesised. The rules are so simple that a student of chemistry familiar with them can write the name of any organic compound whose structure is given. In the same way, one is also able to derive the structure of a compound from its IUPAC name.

Now we proceed to discuss the systematic naming of continuous-chain or straight-chain alkanes and the other classes of compounds derived from them. This will be followed by a study of the IUPAC rules for assigning names to branched-chain hydrocarbons and compounds containing the various common functional groups stated earlier.

A. Alkanes

The compounds composed of carbon and hydrogen only are called hydrocarbons. The hydrocarbons whose molecules contain carbon atoms joined to each other by single bonds can add no more hydrogen atoms. These are referred to as **Saturated hydrocarbons**, meaning saturated with hydrogen.

The open-chain saturated hydrocarbons as a class are named **Alkanes** according to the IUPAC system. The IUPAC name of saturated hydrocarbons with a cyclic carbon-structure is **Cycloalkanes.**

The alkanes whose molecules are made of continuous or straight carbon-chains, are referred to as **Continuous-chain** or **Straight-chain Alkanes.** The foundations of the IUPAC system are the names of the continuous-chain alkanes. The structures and names of the first ten continuous-chain alkanes are listed in Table 8·2.

Table 8·2. The structural formulas and names of the First Ten Continuous-Chain Alkanes.

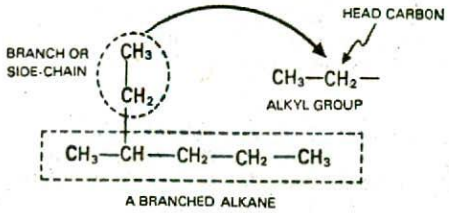
Structural formula	*No of Carbon atoms in chain*	*IUPAC Name*
CH_4	1	methane
CH_3-CH_3	2	ethane
$CH_3-CH_2-CH_3$	3	propane
$CH_3\ CH_2-CH_2-CH_3$	4	butane
$CH_3-CH_2-CH_2-CH_2-CH_3$	5	pentane
$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$	6	hexane
$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$	7	heptane
$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$	8	octane
$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2\ CH_2-CH_3$	9	nonane
$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$	10	decane

The names of alkanes in Table 8·2, end in **-ane**, which is the IUPAC ending for a saturated hydrocarbon. The first part of the name of the first four alkanes (methane to butane) is derived from the trivial name of the respective alkane. For higher alkanes (pentane on), the first part of the alkane name is derived from the Greek word for the number of carbon atoms in the molecule. For example, the prefix "pent" comes from the Greek word *penta*, meaning five. Thus the prefix *pent* in 'pentane' indicates that the alkane contains 5 carbons and the ending *-ane* denotes that it is a saturated hydrocarbon.

Use of prefix *n*-. The alkanes with a continuous carbon-chain or normal carbon-chain are referred to as **normal alkanes**. For clarity, the prefix **n-** is sometimes added to the alkane name to indicate that it contains a continuous carbon-chain. For example, $CH_3—CH_2—CH_2—CH_3$ is named as *n*-butane. ***But the prefix n- is not strictly necessary in the IUPAC system.*** Thus the name butane (without prefix *n*-) denotes C_4H_{10} containing a continuous C-chain.

Branched Alkanes

When an alkane has a shorter side-chain attached to the continuous-chain, it is designated as a **Branched alkane**. The continuous chain is called the **root** or **parent**, while the side-chain the **alkyl group**. The carbon of the alkyl group bonded directly to the parent chain is referred to as the **head carbon**.



Nomenclature of Alkyl groups

The hydrocarbon units derived by removal of one H of an alkane, are called **Alkyl groups**. The IUPAC name of an alkyl group is obtained by replacing the ending **-ane** of the parent alkane with **-yl** (alkane—ane+yl=alkyl). Thus CH_3CH_3 is ethane and $CH_3CH_2—$ is named as ethyl group.

Normal or **Continuous-chain Alkyl groups.** The alkyl groups obtained by dropping the terminal H atom of a *normal* or *continuous-chain* alkane, are referred to as **normal** or **n-alkyl groups**. However, in the IUPAC system the use of the prefix *n*- is redundant since the absence of a prefix implies a continuous chain. The names of the first five continuous-chain alkyl groups are listed in Table 8·3.

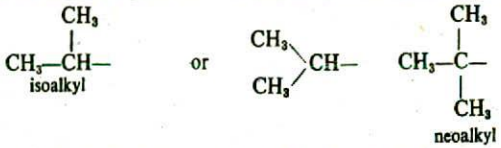
Table 8·3. IUPAC names of the First five Continuous-chain Alkyl groups.

Structure	*IUPAC Name*
$CH_3—$	methyl
$CH_3—CH_2—$ or $C_2H_5—$	ethyl
$CH_3—CH_2—CH_2—$	propyl
$CH_3—CH_2—CH_2—CH_2—$	butyl (or *n*-butyl)
$CH_3—CH_2—CH_2—CH_2—CH_2—$	pentyl (or *n*-pentyl)

Branched-chain Alkyl groups. These are derived by dropping a hydrogen on a middle carbon of alkane chain. The stem name of a branched alkyl group is determined by the number of carbons they contain. Thus propyl has 3 carbons, butyl 4 and pentyl 5. This type of

branched-chain is indicated by a specific prefix added to the stem name. The common prefixes used are :

(1) **iso** indicates the presence of a CH_3 branch at the end of the chain



(2) **neo** indicates the presence of two CH_3 branches at the end of the chain.

(3) **secondary** or **sec-** indicates the presence of two carbons attached to the head carbon.

(4) **tertiary-** or **tert-** or **t-** indicates the presence of three carbons attached to the head carbon.

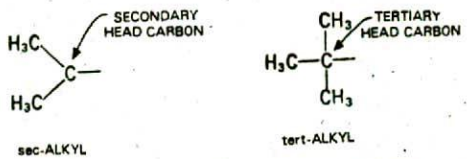
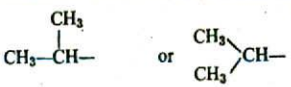
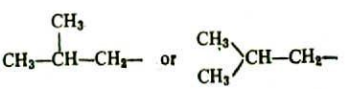
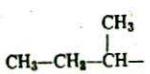
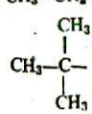
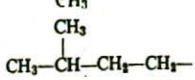
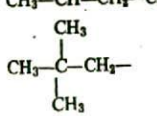
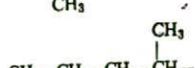
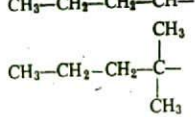
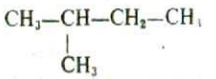


Table 8·4. Branched-chain Alkyl groups having 3, 4, 5 carbon atoms.

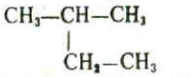
Structure	*Name*
	isopropyl
	isobutyl
	*sec*-butyl (or *s*-butyl)
	*tert*-butyl (or *t*-butyl)
	isopentyl
	neopentyl
	*sec*-pentyl (or *s*-pentyl)
	*tert*-pentyl (or *t*-pentyl)

IUPAC Rules for Naming Branched Alkanes.

1. *Select the longest continuous carbon-chain and name the branched alkane as alkyl derivative of the parent alkane containing this chain.* It is not necessary that the longest chain be written in a straight line ; it may be straight or zig-zag. Thus the longest continuous chain in the following molecules contains four carbons and the name of the parent alkane in both cases is butane.

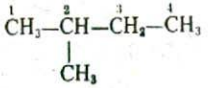


(straight four-carbon chain)

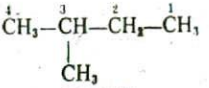


(zig-zag four-carbon chain)

2. *The parent-chain carbon atoms are numbered 1, 2, 3, 4, etc., beginning with the end nearest to the branch (alkyl group).* This gives the lowest number to the carbon to which the alkyl group is attached.



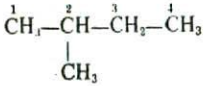
(RIGHT)



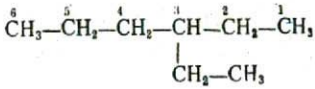
(WRONG)

The position of the alkyl group on the parent chain is indicated by the number of the carbon which carries it. This is referred to as its **Position number** (or **Locator number**). *The position number is mentioned before the name of alkyl group from which it is separated by a hyphen* (-). Thus, if a methyl group is on carbon 2, it is written as 2-methyl.

3. *The complete name of the branched alkane is written as one word by prefixing the name of the alkyl group to the name of the parent alkane.* For example,

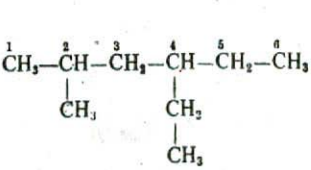


2-methylbutane

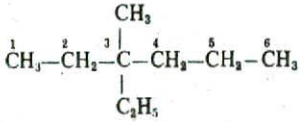


3-ethylhexane

4. *When two or more different alkyl groups are present on the parent chain, assign position-number to each and list them alphabetically with a hyphen in between.*

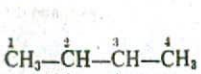


4-ethyl-2-methylhexane

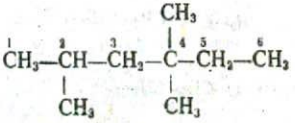


3-ethyl-3-methylhexane

5. *When two or more identical groups are present, indicate this by the use of the prefixes di, tri, tetra, etc., immediately before the alkyl group.* Commas are used to separate position-numbers from each other.

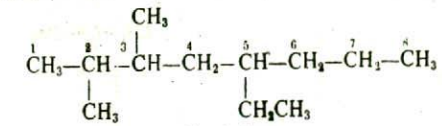


2, 3-dimethylbutane



2, 4, 4-trimethylhexane

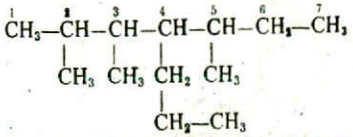
While determining the alphabetic order, the prefixes *di*, *tri*, etc., are ignored. Thus,



5-ethyl-2, 3-dimethyloctane

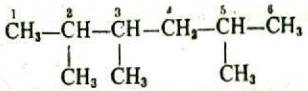
Here the prefix *di* is disregarded while determining the alphabetic order.

6. *When there are two longest chains having equal member of carbons, select the one with the greater member of branches (alkyl groups) as the parent chain.*



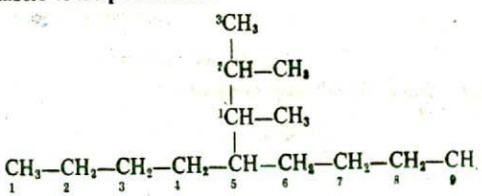
2, 3, 5-trimethyl-4-propylheptane (4 alkyl groups)
NOT 4-*sec*-butyl-2, 3-dimethylheptane (3 alkyl groups)

7. *When branching occurs at an equal distance from either end of the longest chain, choose the name that gives the lower number at the first point of difference.*



2, 3, 5-trimethylhexane (first point of difference : 3)
NOT 2, 4, 5-trimethylhexane (first point of difference : 4)

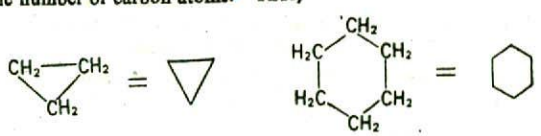
9. *In case the substituent on the parent chain is a complex one (containing more than 4 carbons), name it as a substituted alkyl group whose carbon chain is numbered from the carbon attached to the main chain.* **The name of the complex substituent is given in brackets to avoid confusion with the numbers of the parent chain.**



5-(1, 2-dimethylpropyl) nonane

Naming of Cycloalkanes

Cycloalkanes are saturated hydrocarbons with a ring of carbon atoms in the molecule. Their IUPAC names are derived by prefixing **cyclo** to the names of continuous-chain alkanes containing the same number of carbon atoms. Thus,



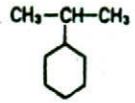
CYCLOPROPANE CYCLOHEXANE

Substituted Cycloalkanes. These are named according to the following rules.

1. The name of the alkyl side-chain is prefixed to the name of the parent cycloalkane.

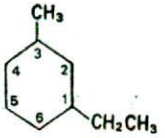


METHYLCYCLOHEXANE

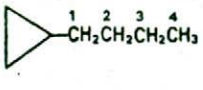


ISOPROPYLCYCLOHEXANE

2. *When more than one side-chain is present, we number the ring beginning with one side-chain so that the next side-chain gets the lower number possible.*



1-ETHYL-3-METHYLCYCLOHEXANE

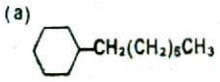


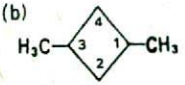
1-CYCLOPROPYLBUTANE

NOT 1-ethyl-5-methylcyclohexane *NOT* butylcyclopropane

3. If the alkane chain has a greater number of carbons than the ring, we designate the ring as the substituent. (*See above*)

Example 1. *Give the names of the following substituted cycloalkanes.*





Solution :

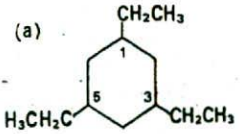
(*a*) The side-chain has 7 carbons, while the ring has 6. Therefore, it will be named as a substituted alkane :

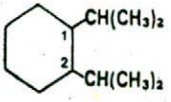
hexylheptane.

(*b*) There are two methyl substituents in positions 1 and 3 on a four-carbon ring. Therefore, it will be named as :

1, 3-dimethylcyclobutane

Example 2. *Name the following compounds* :





Solution :

(*a*) There are three ethyl groups (C_2H_5) on a cyclohexane ring in 1, 3, 5 positions. Thus its name is

1, 3, 5-triethylcyclohexane

(*b*) There are two isopropyl, $(CH_3)_2CH$, substituents in 1, 2 positions. Thus its full name is

1, 2-diisopropylcyclohexane

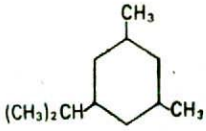
Example 3. *Write the structure of 5-isopropyl-1, 3-dimethylcyclohexane.*

Solution :

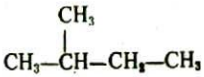
(*a*) Since it is cyclohexane, the ring structure may be written as



(b) Attaching isopropyl, $(CH_3)_2CH$, in posltion 5 and methyl (CH_3) in positions 1, 3 we get the desired structure.



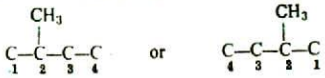
Example 1. *Name the following structure. Say why the prefix number is not needed in this name.*



Solution :

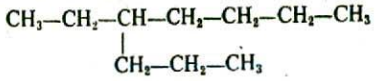
(*i*) Longest chain : 4 carbons
Parent alkane : *butane*

(*ii*) Number the chain near to the branch (CH_3) :



(*iii*) The prefix number is not needed because there is only one methylbutane as evident from (*ii*). The only other place to attach the CH_3 group would be the carbon 1 or 4 but this compound is pentane (5 carbons in a continuous chain) and not methylbutane.

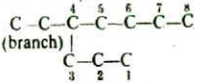
Example 2. *Name the following branched alkane,*



Solution :

(*i*) The longest chain : eight carbons
∴ The parent alkane *is octane.*

(*ii*) Number from end closer to branch,



(*iii*) Alkyl group : ethyl (CH_3CH_2) at carbon 4
∴ Name of alkyl group : 4-ethyl

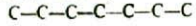
(*iv*) Name of branched alkane : 4-ethyloctane

Example 3. *Write the structure of the compound whose IUPAC name is*

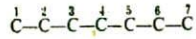
5-ethyl-2, 2-dimethylheptane

Solution :

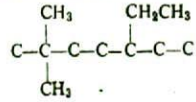
(*i*) Write the parent chain (heptane : 7 carbons) :



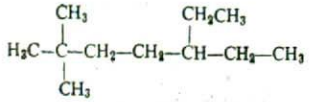
(*ii*) Number the carbons :



(*iii*) Attach ethyl (CH_3CH_2) to carbon 5 ; two methyls (CH_3) to carbon 3 :



(iv) Add hydrogens so that each carbon has four bonds :



B. Alkenes

A hydrocarbon with one double bond (C=C) is called an *alkene*. The IUPAC name of a particular alkene is derived by changing the **ane** of the corresponding alkane (same number of carbons) to **ene**. That is,

$$\text{alkane} - \text{ane} + \text{ene} \longrightarrow \text{alkene}$$

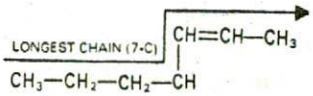
The functional group of alkenes is C=C, which is designated by the suffix *ene*. The IUPAC names and trivial names of some simple unbranched alkenes are listed in Table 8·5.

Table 8·5. Names of some Unbranched Alkenes

Structure	*IUPAC Name*	*Trivial Name*
$CH_2=CH_2$	ethene	ethylene
$CH_3CH=CH_2$	propene	propylene
$CH_3CH_2CH=CH_2$	1-butene	butylene
$CH_3CH=CHCH_3$	2-butene	
$CH_2=CHCH_2CH_2CH_3$	1-pentene	
$CH_3CH_2CH=CHCH_2CH_3$	3-hexene	

IUPAC Rules for Naming Alkenes. The alkenes containing four or more carbons are named by the following rules.

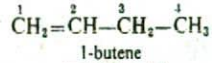
1. *Select the longest continuous chain that contains both carbons of the double bond and change the name of the corresponding alkane name from* **ane** *to* **ene.** This gives the parent name



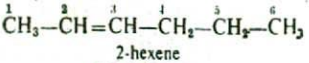
of the alkene. The compound has 7-carbon chain containing the double bond. Therefore, the corresponding alkane is heptane and the parent alkene heptene.

NOTE. It may be noted that the above selected chain may or may not be the longest continuous chain in the structure.

2. *Number the parent chain beginning at the end nearer the double bond and indicate the position of the double bond by using the number of the first carbon of the double bond as prefix.* For example,

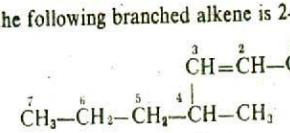


1-butene
(not 3-butene)



2-hexene
(not 4-hexene)

The parent name in the following branched alkene is 2-heptene

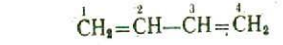


3. *Name and indicate the position of any substituent group as for the alkanes.*

In the above branched alkene, the substituent group is methyl and its position number is 4 on the main chain. Thus the complete name of the alkene is

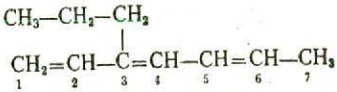
4-methyl-2-heptene

4. *When there are two or more double bonds in a continuous-chain alkene, it is named as* **Alkadiene, Alkatriene,** *and the locator numbers of the double bonds are prefixed.* Thus the compound



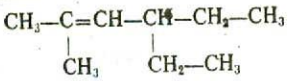
is named as 1, 3-butadiene.

5. In a branched alkene with several double bonds, the parent chain is the longest continuous chain that contains the maximum number of double bonds. Thus,



3-propyl-1, 3, 5-heptatriene

Example 1. *Name the alkene* :

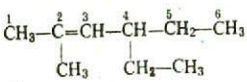


Solution :

(*i*) Longest chain containing C=C is 7 carbons

(*ii*) Parent name : *hexene*

(*iii*) Number the chain from left to right and prefix locator number of double bond.



This gives the basic name : 2-hexene

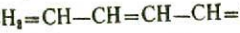
(*iv*) Name the substituent groups : CH_3 and CH_2CH_3, with locator numbers indicated before them.

2-methyl 4-ethyl

(*v*) Hence complete IUPAC name of the alkene is :

4-ethyl-2-methylhexene

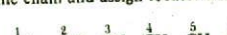
Example 2. *Name the compound*



Solution :

(*i*) The six-carbon chain has three double bonds. The basic name is *hexatriene*.

(*ii*) Number the carbons of the chain and assign locator numbers to double bonds.



As evident, the locator numbers of double bonds are : 1, 3, 5.

(*iii*) Prefixing the locator numbers to the basic name, the complete IUPAC name is :

1, 3, 5-hexatriene

Example 3. *Write the structure for 5-methyl-1-hexene.*

Solution :

(*i*) Parent name hexene shows the presence of a 6-carbon chain.

(*ii*) Position of double bond on the chain being 1, we have

$$\overset{1}{C}=\overset{2}{C}-\overset{3}{C}-\overset{4}{C}-\overset{5}{C}-\overset{6}{C}$$

(*iii*) Attach methyl (CH_3) to carbon 5 :

$$C=C-C-C-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-C$$

(*iv*) Supply requisite hydrogens to get the complete structure :

$$H_2C=CH-CH_2-CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}H-CH_3$$

Alkenyl groups. The groups derived by removing a hydrogen atom from an alkene molecule, are called *alkenyl groups*. The IUPAC name of an individual such group is obtained by dropping *-e* of the corresponding alkene and adding the suffix *-yl*. The numbering of the group-chain starts with the carbon attached directly to the parent chain. A few alkenyl groups have trivial names which are commonly used. The IUPAC and trivial names of some alkenyl groups are listed in table 8·6.

Table 8·6. Names of some Alkenyl groups.

Structure	*IUPAC Name*	*Trivial Name*
$CH_2=CH-$	ethenyl	vinyl
$\overset{3}{C}H_2=\overset{2}{C}H-\overset{1}{C}H_2-$	2-propenyl	allyl
$CH_2=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{\overset{2}{C}}}-$	1-methylethenyl	isopropenyl
$\overset{4}{C}H_3-\overset{3}{C}H=\overset{2}{C}H-\overset{1}{C}H_2-$	2-butenyl	
$\overset{4}{C}H_2=\overset{3}{C}H-\overset{2}{C}H_2-\overset{1}{C}H_2-$	3-butenyl	

IUPAC Rules for Naming Cycloalkenes. They are named in a manner similar to cycloalkanes

1. Assign name to a simple cycloalkene by replacing *ane* of the corresponding cycloalkane by *ene*. Thus,



CYCLOPENTENE

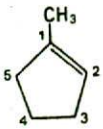


CYCLOHEXENE

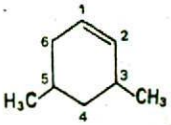


CYCLOBUTENE

2. Number substituted cycloalkenes in the direction around the ring that gives the position 1, 2 to the double bond, and the lowest numbers to the substituent groups. Note that this rule often makes it unnecessary to give the position of the double bond because it is always 1, 2. For example,



1-methylcyclopentene
(*NOT* 2-methylcyclopentene)



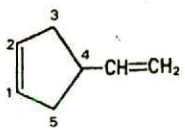
3, 5-dimethylcyclohexene
(*NOT* 4, 6-dimethylcyclohexene)

3. The common names of the following substituents are generally used :

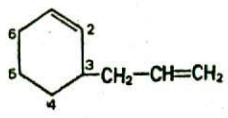
$CH_2=CH-$ vinyl

$CH_2=CH-CH_2-$ allyl

For example,

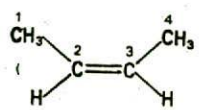


4-VINYLCYCLOPENTENE

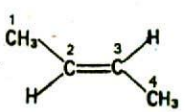


3-ALLYLCYCLOHEXENE

Designation of Configuration. When there are the same two-different atoms or groups attached to each double-bond carbon, two space arrangements of the alkene molecule are possible. These arrangements or configurations are designated as **cis** and **trans** according as the identical groups are on the same side or opposite sides of the double bond. The two molecules with *cis* and *trans* configuration are called **Geometrical isomers.** For example, 2-butene exists in two forms :



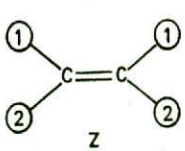
cis-2-BUTENE



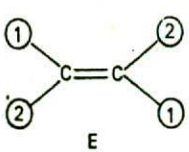
trans-2-BUTENE

(E) and (Z) System. When there are three or four different groups attached to double-bond carbons, it is sometimes difficult to assign *cis* or *trans* designation to the isomers. Thus a new system of isomer assignment has been adopted in place of the older *cis-trans* system. This is called (*E*) and (*Z*) system.

The (*E*) and (*Z*) system is based on assignment of '*priorities*' 1 and 2 to the atoms or groups attached to each carbon of the double bond. If the higher priority atoms or groups are on the same side of the double bond, the isomer is designated as Z (German : *Zusammen*= together). If these groups are on opposite sides of the double bond, the isomer is E (German : *Entgegen*=across).



Z

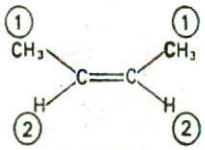


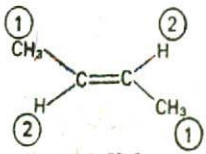
E

According to the priority rules developed by **Cahn-Ingold-Prelog system,** the basis of assigning priorities to substituents is atomic number.

(1) *An atom with higher atomic number has higher priority.* For example, in isomers of 2-butene the carbon atom of each CH_3 group receives first priority and the H attached to the

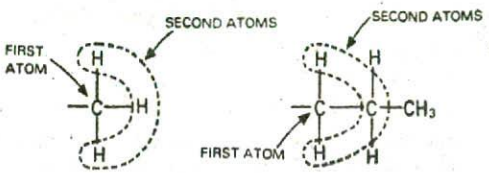
double-bond carbons has second priority. Thus *cis*-2-butene becomes *Z*-2-butene and *trans*-2-butene becomes *E*-2-butene.





(2) *When atoms directly attached to a double-bond carbon have the same priority, precedence is given to the group with the second atom of the higher atomic number.*

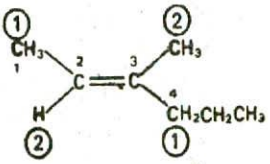
For example, 3-methyl-2-hexene has a CH_3— group and a $CH_3CH_2CH_2$— (propyl) group attached to carbon 3. In each case, the first atom is carbon and hence no priority can be assigned according to *Rule 1*.

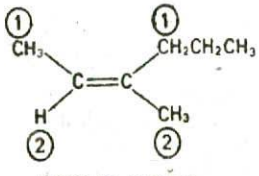


The methyl group has three H's as second atom.

The propyl group has two H's and one C as second atoms.

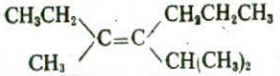
The second atoms of CH_3 (methyl) are three H's. For the propyl group, the second atoms are two H's and one C. The carbon atom takes precedence over any number of hydrogen atoms. Hence propyl receives priority 1, while methyl gets priority 2. Applying Rule 1 to CH_3 and H attached to carbon 2, CH_3 receives priority 1 (at. no. of C=6), while H (at. no.=1) gets priority 2. Thus the two geometrical isomers of 3-methyl-2-hexene may be written as





It may be noted that in this case *cis-trans* designation will be ambiguous.

Example. *Provide a name, including Z and E designation, for the following compound :*

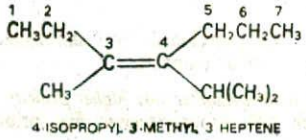


Solution :

(*i*) Longest chain containing double bond = 7 carbons

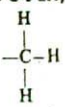
∴ Basic name : heptene

(*ii*) Number the chain and name the substituents ; derive IUPAC name of compound.



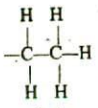
(*iii*) Assignment of designation :

(*a*) Groups attached to C-3 are,



methyl

(Second atoms : 3 H's)

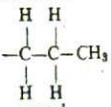


ethyl

(Second atoms : 2 H's and 1 C)

Since first atom in two cases is same, the priority is determined by the second atoms. We find that ethyl group is of higher priority.

(*b*) Groups attached to C-4 are :



propyl

(Second atoms : 2 H's and 1 C)

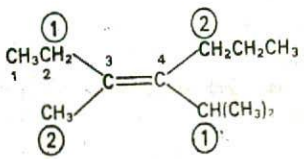


isopropyl

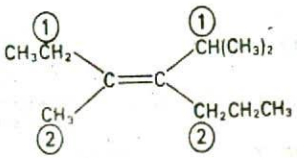
(Second atoms : 1 H and 2 C)

Since first atom in both cases is carbon, the priority will be determined by the second atoms. Evidently isopropyl group has a higher priority.

(*iv*) Providing *Z* and *E* designations, the two isomers are :



Z-4-ISOPROPYL-3-METHYL-3-HEPTENE



E-4-ISOPROPYL-3-METHYL-3-HEPTENE

C. Alkynes

The hydrocarbons with the carbon-carbon triple bond (C≡C) are called *alkynes*. The IUPAC name of an individual alkyne is derived by changing the **-ane** of the corresponding alkane to **-yne**. That is,

$$\text{alkane} - \text{ane} + \text{yne} \longrightarrow \text{alkyne}$$

The functional group of alkynes is C≡C which is designated by the suffix '*yne*'. The alkynes are named in much the same way as alkenes.

Table 8·7. Names of some unbranched alkynes

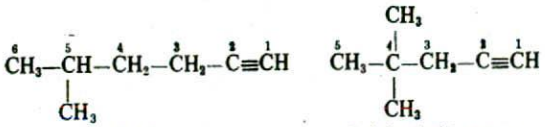
Structure	*IUPAC Name*	*Trivial Name*
$HC{\equiv}CH$	ethyne or acetylene	acetylene
$CH_3C{\equiv}CH$	propyne	methylacetylene
$CH_3CH_2C{\equiv}CH$	1-butyne	ethylacetylene
$CH_3C{\equiv}CCH_3$	2-butyne	dimethylacetylene
$CH_3CH_2CH_2C{\equiv}CH$	1-pentyne	propylacetylene
$CH_3CH_2C{\equiv}CCH_3$	2-pentyne	ethylmethylacetylene

Rules for Naming Branched Alkynes. These are the same as for alkenes with modifications listed below.

1. Select the longest chain containing both carbons of the triple bond as the parent chain. *This may not be necessarily the longest continuous chain in the molecule.*

2. Number the chain at the end nearer the triple bond. Indicate the position of the triple bond by prefixing number of the first carbon of the triple bond.

3. The names of substituents with locator numbers are given as for branched alkanes. Thus,



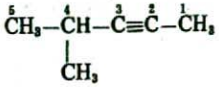
5-methyl-1-hexyne 4, 4-dimethyl-1-pentyne

4. When there are two or more triple bonds in a molecule, it is named as **Alkadiyne, Alkatriyne**, etc. The Chain containing the maximum number of triple bonds is selected and numbered so as to give lowest possible numbers to the triple bonds.



5-ethyl-1, 3, 5-hexatriyne

Example 1. *Assign IUPAC name for the following branched alkyne* :



Solution :

(*i*) Longest chain containing triple bond = 5 carbons

∴ Basic name : pentyne

(*ii*) Number the chain ; prefix triple-bond locator number with basic name :

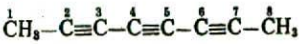
2-pentyne

(*iii*) Name of substituent : 4-methyl

(*iv*) IUPAC name of the hydrocarbon :

4-methyl-2-pentyne

Example 2. *Provide systematic name for*



Solution :

(*i*) Continuous chain = 8 carbons

Number of triple bonds = 3

Therefore, basic name : Octatriyne

(*ii*) Prefix locator number of triple bonds on the chain numbered as above. Thus systematic name is :

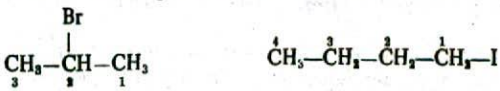
2, 4, 6-Octatriyne

D. Alkyl halides

In the IUPAC system, alkyl halides (RX) are named as halogen substituted alkanes (**Haloalkanes**). Thus the name of a halogen compound is given by prefixing *fluoro, chloro, bromo* and *iodo* to that of the alkane. CH_3Cl is chloromethane and CH_3CH_2Br is bromoethane. For naming complex halogen compounds, the same IUPAC rules as for branched alkanes are applied.

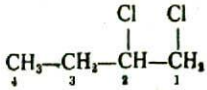
(1) The longest continuous carbon chain bearing the halogen atom is numbered from the end nearer to the halogen and the parent alkane named.

(2) The name of the halogen substituent is prefixed to the alkane name. For example,

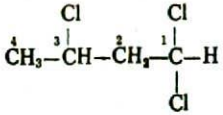


2-bromopropane 1-iodobutane

(3) When there are two or more halogens, the appropriate prefix is used : *di-*, *tri-*, *tetra-*, *and so on.*

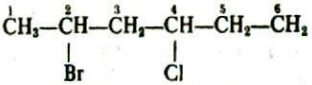


1, 2-dichlorobutane



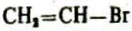
1, 1, 3-trichlorobutane

(4) If the halogens are different, they are named in alphabetic order.



2-bromo-4-chlorohexane

(5) Halogen-substituted alkenes are named as **Haloalkenes.**

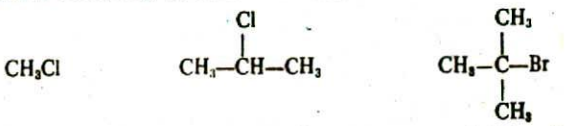


bromoethene
(vinyl bromide)



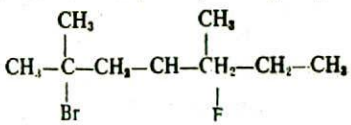
1-iodo-2-propene
(allyl iodide)

Many common alkyl halides have **Trivial names.** In these names, the name of the alkyl group is given which is followed by the name of the halide.



methyl chloride | isopropyl chloride | *tert*-butyl bromide

Example. *Provide IUPAC name for the following compound* :

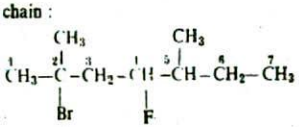


Solution :

(*i*) Number of carbons in longest chain = 7 carbons

Therefore, basic name of alkane = heptane

(*ii*) Numbering the parent chain :



(*iii*) IUPAC name of the compound :

2-bromo-4-fluoro-2, 5-dimethylheptane

E. Alcohols

The IUPAC name of alcohols is **Alkanols.** The name of an individual alcohol is obtained by dropping **e** of the corresponding alkane and adding **ol,**

alkane − e + ol ⟶ alkanol

The functional group of alcohols is −OH (hydroxy) which is represented by the ending *ol.*

IUPAC Rules for Naming Alcohols :

1. *Select the longest chain to which the OH group is directly attached.* Change **e** of the alkane corresponding to this chain to *ol.* This gives the basic name of the alcohol.

2. Number the above chain so as to give the carbon bearing the OH group the lowest possible number. Indicate the position of the OH group by using this number.



2-pentanol
(*NOT* 4-pentanol)

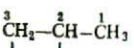
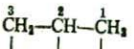
The numbering of the chain is done as above irrespective of whether a double or triple bond is or is not a part of the parent chain.

3. Prefix the names of alkyl substituents with locator numbers as for alkanes. Thus,



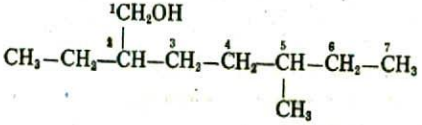
2-methyl-3-hexanol

4. Molecules containing more than one OH group are referred to as **diols** (2OH), **triols** (3OH), etc., in the IUPAC system. Thus :

Structure	*IUPAC Name*	*Trivial*
	1, 2-ethanediol	ethylene glycol
	1, 2-propanediol	propylene glycol
	1, 2, 3-propanetriol	glycerine (glycerol)

It may be noted that while naming diols and triols, *e* of the parent name is retained because the suffix *diol* or *triol* does not begin with a vowel.

Example 1. Provide IUPAC name for the following *alcohol* :



Solution :

(*i*) The longest chain bearing OH = 7 carbons

∴ Basic name : heptanol

(*ii*) Number the chain as above and write names of substituent alkyl groups :

2-ethyl and 5-methyl

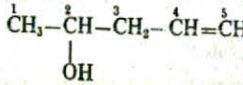
(*iii*) Provide position number of OH to the basic name :

1-heptanol

(*iv*) Prefix the names of substituents to get complete IUPAC name :

2-ethyl-5-methyl-1-heptanol

Example 2. *Assign systematic name to the following compound* :



Solution :

(*i*) The longest chain bearing OH = 5 carbons

∴ Basic name : pentenol

(*ii*) Number the chain and prefix position number of double bond

4-pentenol

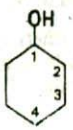
(*iii*) Insert position number of OH :

4-penten-2-ol

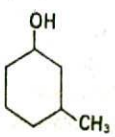
Example 3. *Give the structure for 3-methyl-1-cyclohexanol.*

Solution :

(*i*) Since OH has position number 1, the structure of the basic alcohol is



(*ii*) Providing substituent methyl CH_3, at position 3 :

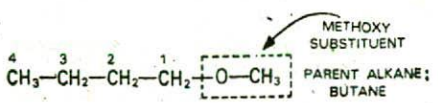


F. . Ethers

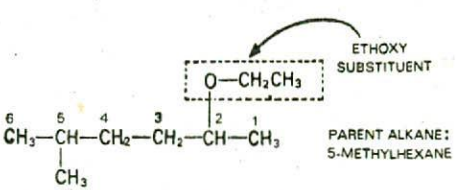
In IUPAC system of naming ethers (R—O—R'), the smaller group R plus O atom are said to form an alkoxy group (RO—) which is regarded as a substituent. Thus we have the substituents :

CH_3O-	CH_3CH_2O-	$CH_3CH_2CH_2O-$
methoxy	ethoxy	propoxy

and so on. The alkoxy substituent is considered to be attached to the parent-alkane chain at carbon number 1. Thus ethers are named as **alkoxyalkanes**. For example,



IUPAC NAME : 1-METHOXYBUTANE



IUPAC NAME : 2-ETHOXY-5-METHYLHEXANE

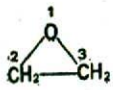
However, simple ethers are often named by the trivial names. These are written by listing the names of the two hydrocarbon groups attached to O atom followed by the word 'ether'.

The IUPAC and trivial names of some ethers are given below :

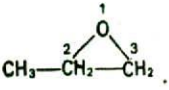
Structure	*IUPAC Name*	*Trivial Name*
CH_3-O-CH_3	methoxymethane	methyl ether (dimethyl ether)
$CH_3CH_2-O-CH_3$	methoxyethane	ethyl methyl ether
$CH_3CH_2-O-CH_2CH_3$	ethoxyethane	ethyl ether (diethyl ether)
$(CH_3CH_2CH_2CH_2)_2O$	butoxybutane	butyl ether

It may be noted that if both alkyl groups are the same, the name of the group is mentioned only once. The groups are assumed to be the same without the use of the prefix *di-*.

Epoxides. Epoxides are cyclic ethers with three-membered rings. In IUPAC nomenclature epoxides are called **Oxiranes.** While assigning systematic names to substituted oxiranes, we give number 1 to the O atom in the ring. The trivial name for epoxides is **Alkene oxides.** Thus :



IUPAC name : oxirane
Trivial name : ethylene oxide



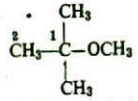
IUPA name : 2-methyloxirane
Trivial name : propylene oxide

Example. *Assign both IUPAC and common names to the following ethers* :

(a) $(CH_3)_3COCH_3$ (b) $(CH_3)_2CHO-C_6H_4-CH_3$

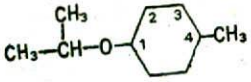
Solution :

(*a*) The structure of ether may be written as below and the name assigned :



IUPAC name : 1-methoxy-1, 1- dimethylethane
Common name : *tert*-butyl methyl ether

(*b*) The structure of ether may be written as below and name assigned :



(*i*) **Basic alkane** : 4-methylcyclohexane

(*ii*) **Substituent alkoxy group** : isopropoxy

(*iii*) Complete IUPAC Name : 1-isopropoxy-4-methylcyclohexane.

(*iv*) Common Name : isopopyl methyl ether

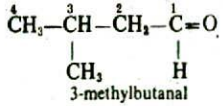
G. Aldehydes

The IUPAC name for aldehydes (RCHO) is **Alkanals.** For naming an individual aldehyde, the final e of the parent alkane is replaced with **al,**

alkane — e + ol ⟶ alkanal

Since the functional group CHO is always present at the end of the parent chain, it is not necessary to

designate its position. When other substituents are present, the parent chain including the CHO group is numbered with carbon of CHO as number1. For example,



3-methylbutanal

The IUPAC and trivial names of some aldehydes are listed in table below.

Table 8·8. Names of some aldehydes

Structure	*IUPAC Name*	*Trivial Name*
HCHO	Methanal	formaldehyde
CH_3CHO	ethanal	acetaldehyde
CH_3CH_2CHO	propanal	propionaldehyde
$CH_3CH_2CH_2CHO$	butanal	*n*-butyraldehyde
$(CH_3)_2CHCHO$	2-methylpropanal	isobutyraldehyde
$CH_3CH=CHCHO$	2-butenal	crotonaldehyde

H. Ketones

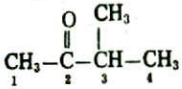
The IUPAC name of ketones (R—CO—R') is **Alkanones** and the functional group —CO— is referred to as *carbonyl group*. The name of an individual ketone is obtained by replacing the final e of the corresponding alkane (containing same number of carbons) with **one,**

$$\text{alkane} - \text{e} + \text{one} \longrightarrow \text{alkanone}$$

For naming higher ketones :

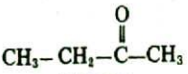
(1) Select the longest chain containing the —CO— group and write the basic name after the parent alkane as shown above.

(2) Number the chain from the end that gives the —CO— group the lowest possible number. This is the locator number of carbonyl group on the parent chain.



3-methyl-2-butanone

When the carbonyl group can be positioned only in one way, numbering the chain is unnecessary.



butanone

(3) If the structure contains a double bond, name the ketone as **Alkenone** and insert position numbers.



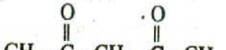
3-buten-2-one

The *trivial names of* ketones are obtained by naming the two hydrocarbon group, attached to $-CO-$ group and adding the word 'ketone'. The IUPAC and trivial names of some ketones are listed in Table 8·9.

Table 8·9. Names of some ketones

Structure	*IUPAC Name*	*Trivial Name*
$CH_3-CO-CH_3$	Propanone	acetone, dimethyl ketone
$CH_3CH_2-CO-CH_3$	butanone	methyl ethyl ketone
$\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2-\overset{2}{C}O-\overset{1}{C}H_3$	2-pentanone	methyl *n*-propyl ketone
$\overset{1}{C}H_3\overset{2}{C}H_2-\overset{3}{C}O-\overset{4}{C}H_2\overset{5}{C}H_3$	3-pentanone	diethyl ketone
$\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2-\overset{2}{C}O-\overset{1}{C}H_3$	2-hexanone	methyl *n*-butyl ketone

(4) When there are present two carbonyl groups in a saturated parent chain, the compound is named as **Alkanedione** with position numbers prefixed to it.



2, 4-pentanedione

I. Carboxylic Acids

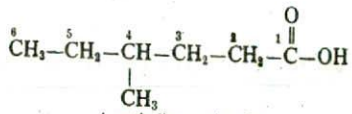
The IUPAC name of aliphatic carboxylic acids (RCOOH) is **Alkanoic acids**, while the functional group COOH is referred to as *carboxyl group*. The name of a particular, carboxylic acid is obtained by replacing the final e with **oic acid**,

$$\text{alkane} - \text{e} + \text{oic acid} \longrightarrow \text{alkanoic acid}$$

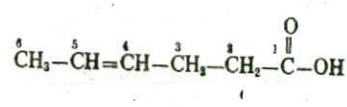
For naming higher carboxylic acids :

(1) The longest chain containing COOH is selected and the basic name is derived by changing *ane* of the corresponding alkane to *oic acid.*

(2) The chain is numbered starting with carboxyl carbon as 1. Thus it is unnecessary to give the number of COOH. For example,

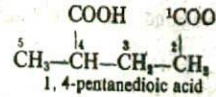


4-methylhexanoic acid



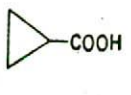
4-hexenoic acid

(3) A dicarboxylic acid is named as **Alkanedioic acid** with position numbers of COOH groups prefixed with it.

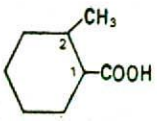


1, 4-pentanedioic acid

(4) When the COOH group is attached to a cyclic structure,—carboxylic acid becomes appropriate suffix.



CYCLOPROPANE–CARBOXYLIC ACID



2-METHYLCYCLOHEXANE-CARBOXYLIC ACID

The IUPAC and trivial names of some carboxylic acids are listed in Table 8·10.

Table 8·10. Names of some Carboxylic acids

Structure	*IUPAC Name*	*Trivial Name*
$HCOOH$	methanoic acid	formic acid
CH_3COOH	ethanoic acid	acetic acid
CH_3CH_2COOH	propanoic acid	propionic acid
$CH_3CH_2CH_2COOH$	butanoic acid	butyric acid
$CH_2{=}CHCOOH$	propenoic acid	acrylic acid

The trivial names for the first few carboxylic acids are accepted by the IUPAC.

J. Carboxylic acid Derivatives

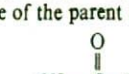
The functional derivatives of carboxylic acids have various atoms or groups (Z) in place of OH of COOH.



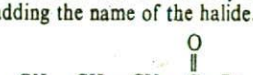
The important acid (or acyl) derivatives are listed below.

Structure	*Name*	
$R-\overset{O}{\overset{\|}{C}}-X$	acid or (acyl) halide	$R-\overset{O}{\overset{\|}{C}}-NH_2$
$R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$	acid anhydride	$R-\overset{O}{\overset{\|}{C}}-NHR'$ } amides
$R-\overset{O}{\overset{\|}{C}}-OR'$	ester	$R-\overset{O}{\overset{\|}{C}}-NR'_2$

(1) **Acid halides**. Both IUPAC and trivial names are obtained by replacing *-ic* of the respective name of the parent acid with *-yl*, and adding the name of the halide. Thus,

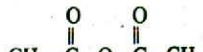


IUPAC : ethanoyl chloride
Trivial : acetyl chloride



IUPAC : butanoyl bromide
Trivial : *n*-butyryl bromide

Carboxylic Anhydrides. Both IUPAC and trivial names of carboxylic anhydrides (or acid anhydrides) are derived by dropping the word *acid* from the name of the parent carboxylic acid and then adding the word *anhydride*.

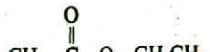


IUPAC : ethanoic anhydride
Trivial : acetic anhydride



IUPAC : propanoic anhydride
Trivial : propionic anhydride

Esters. The names of esters are derived by naming the alkyl group of the corresponding alcohol followed by the name of the acid part with the ending *-ic* changed to *-ate*. Thus,



IUPAC : ethyl ethanoate
Trivial : ethyl acetate



IUPAC : *tert*-butyl propanoate
Trivial : *tert*-butyl propionate

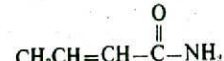
Amides. These are named by dropping *-ic acid* from the trivial name of the acid or *-oic acid* from the IUPAC name and then adding *-amide*.



IUPAC : ethanamide
Trivial : acetamide



IUPAC : propanamide
Trivial : propionamide

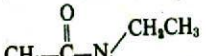


IUPAC : 2-butenamide
Trivial : crotonamide

Substituted amides ($RCONHR'$, $RCONR_2'$) are named by prefixing the name of the alkyl groups attached to nitrogen atom prefaced by *N*- or *N, N*- to the name of the parent amide. Thus,



N-methylacetamide

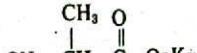


N, N-diethylacetamide

Carboxylic Salts. These are named by replacing *-ic acid* of the carboxylic acid with *-ate*. This applies to IUPAC as well as to trivial names. Thus,



IUPAC : sodium ethanoate
Trivial : sodium acetate



IUPAC : potassium 2-methyl propanoate
Trivial : potassium isobutyrate

K. Sulphonic Acids

The functional group in sulphonic acids ($R-SO_3H$) is the *sulphonic acid group* which may be written as $-SO_3H$ or SO_2OH. The sulphonic acids are named by adding the ending *-sulphonic acid* to the name of the parent hydrocarbon.

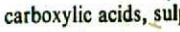


ethanesulphonic acid

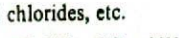


4-methyl pentanesulphonic acid

Like carboxylic acids, sulphonic acids form acid chlorides, etc.



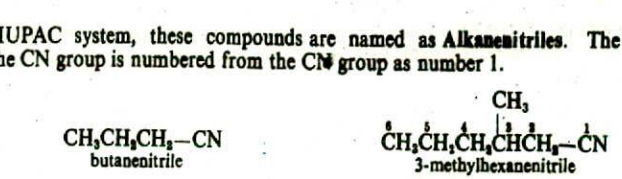
ethanesulphonyl chloride



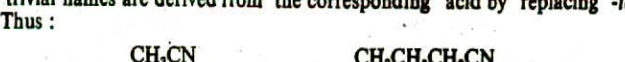
ethanesulphonamide

L. Nitriles

In IUPAC system, these compounds are named as **Alkanenitriles**. The longest chain containing the CN group is numbered from the CN group as number 1.



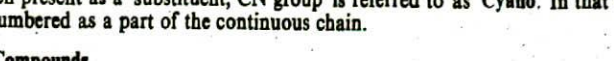
The trivial names are derived from the corresponding acid by replacing *-ic* or *-oic* by —onitrile. Thus :



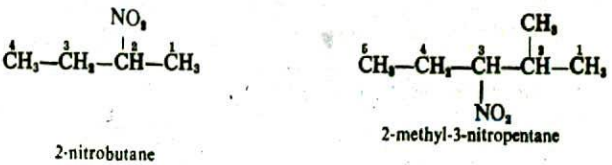
When present as a substituent, CN group is referred to as Cyano. In that case carbon of CN is not numbered as a part of the continuous chain.

M. Nitro Compounds

The alkanes containing a nitro group (NO_2) are named as **Nitroalkanes**.

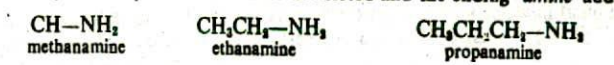


When NO_2 group is present on a continuous carbon chain, it is always treated as a substituent along with others. The position numbers are provided to the substituents which are stated in alphabetic order.

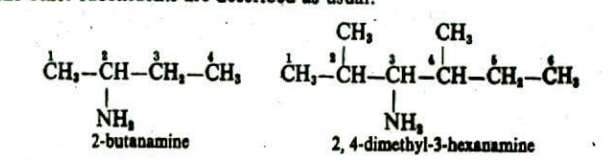


N. Amines

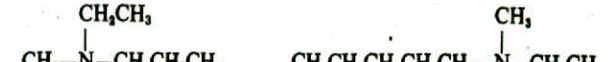
In the IUPAC system this class of compounds are named as **Alkanamines**. To name a particular amine '*e*, of the hydrocarbon name in deleted and the ending *-amine* added.



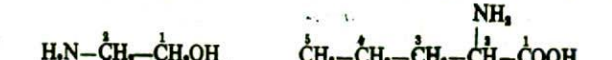
For naming **Substituted amines**, the longest chain bearing NH_2 group is numbered and the position of the amino group prefixed to the basic name of the amine. The names with locator numbers of the other substituents are described as usual.



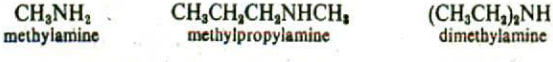
A substituent on nitrogen atom is designated by capital *N*.



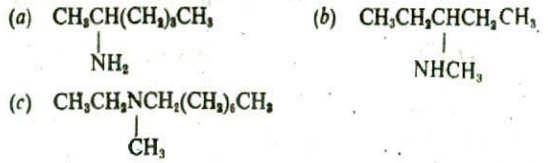
When present in molecules as a substituent, amino group is designated as **amino**.



Simple amines are usually named by the **Common System** which is permitted by IUPAC. Here the alkyl group or groups are named and the ending *-amine* is added. The largest alkyl group is made the base name.



Example. *Name the following by IUPAC System :*



Solution :

(*a*) Longest chain bearing NH_2 = 6 carbons
Position of NH_2 = 2
∴ IUPAC name : 2-hexanamine

(*b*) Longest chain bearing NH_2 = 5 carbons
Position number of NH_2 = 3
Substituent on N : N-methyl
∴ IUPAC name : *N*-methyl-3-pentanamine

(*c*) Longest chain bearing amino group = 8 carbons
Position number of amino group = 1
Substituents on N :
N-ethyl and *N*-methyl
∴ IUPAC name : *N*-ethyl-*N*-methyl- 1-octanamine

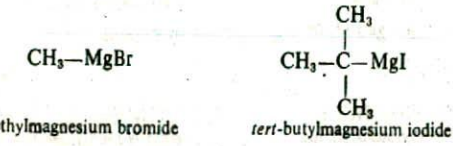
O. Organometallic Compounds

A compound in which alkyl groups are directly bonded to a metallic atom (Li, Zn, Mg) or to a metalloid (B, Si), is referred to as an organometallic compound. These are named in two ways :

(1) **As Alkylmetals**



If the metal is bonded to an alkyl group as well as an inorganic anion, the compound is named as an *alkyl derivative* of inorganic salt.



(2) **As Derivatives of Hydrides.** The organometallic compounds of boron and silicon are named as derivatives of the hydrides of these elements : borane (BH_3), Silane (SiH_4).



NOMENCLATURE PRIORITY OF FUNCTIONAL GROUPS

If a structure contains one functional group only, this group determines the class (or family) of the compound. But when there are two or more functional groups or functions in a molecule, question arises as to which one of these would determine the class of the compound. *The group which determines the class of a multifunction compound is referred to as the* **Principal function**. All the remaining groups are treated as subsidiary functions or **Substituents**.

For example, the molecule $CH_3-CH=CH-CH_2OH$ contains one carbon-carbon double bond (C=C) and one OH group. This could be named as an *alkene* or an *alcohol*. As to which of these groups is the principal function, is found from the Nomenclature Priority Table given by IUPAC. A function which is placed higher in the table takes precedence over others lying below and is designated as the principal function. Thus the class name of the compound :

$$CH_3-CH=CH-CH_2-OH$$

will be alcohol and not alkene since the OH group occurs higher than C=C group in the Nomenclature Priority Table.

Nomenclature Priority for Citation as Principal Function (IUPAC)

(Highest Priority is at the top)

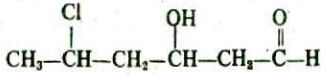
Class Name	*Functional Group*	**Denoted by** **Prefix**	**Suffix**
Carboxylic acid	$-COOH$	—	-oic acid
Sulphonic acid	$-SO_3H$	—	-sulphonic acid
Acid halide	$-COX$	—	-oyl chloride
Amide	$-CONH_2$	Amido-	-amide
Nitrile	$-C\equiv N$	Cyano-	-nitrile
Aldehyde	$-\overset{O}{\overset{\|\|}{C}}-H$ or $-CHO$	Alkanoyl-	-al
Ketone	$-\overset{O}{\overset{\|\|}{C}}-$	Oxo-	-one
Thiol	$-SH$	Mercapto-	-thiol
Amine	$-NH_2$	Amino	-amine
Alkene	$>C=C<$	—	-ene
Alkyne	$-C\equiv C-$	—	-yne
Alkane	$-\overset{\|}{\underset{\|}{C}}-\overset{\|}{\underset{\|}{C}}-$	—	-ane
Ether	$-OR$	Alkoxy	—
Halides	$-F$, $-Cl$, $-Br$, $-I$	Halo-	—
Nitro	$-NO_2$	Nitro-	—
Alkyl	$-R$	Alkyl	—

Note. The groups —OR, —F, —Cl, —Br, —I, $-NO_2$ and —R are denoted only by prefixes. They are regarded as substituents on the hydrocarbon chain.

It may be noted from the table that **the groups —X (—F, —Cl, —Br, and —I) and $-NO_2$ never play the part of Principal function.** These groups are then substituent groups for which we use the prefix halo (fluoro, chloro, bromo, and iodo) and nitro respectively.

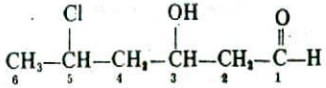
IUPAC RULES FOR NAMING MULTIFUNCTION COMPOUNDS

1. Note the functional groups present in the given structure and then find out from the Priority Table as to which of these stands nearest to the top. This is the principal function and determines the *family* or *class* of the compound. For example, the compound



has one —Cl group, one —OH group and one —CHO group. Have a look at the priority table and you will find that —CHO ranks the highest. Therefore, the compound is an aldehyde and has the class name *alkanal.*

2. The longest continuous chain containing or bearing the principal function is numbered so that this group has the lowest possible position number (or locator number). The carbon that is a part of the principal function (as in —CHO or —COOH) is always assigned number 1. Thus,



Note. When carbon is a part of a substituent group, it is not numbered as a part of the continuous parent chain.

3. The basic or stem name of the compound (here alkanal) is derived from the name of the alkane corresponding to the parent chain, numbered in step 2. Here the parent chain contains six carbons and hence the stem name is *hexanal.*

4. The subsidiary groups (—Cl, —OH) are assigned names as shown in the priority table and arranged in alphabetic order. The substituents are then provided numbers and prefixed to the stem name. The locator numbers are set off by hyphens from the name of the substituents Thus in the example cited above in step 2, we have

5-chloro 3-hydroxy

5. The names of the substituents with locator numbers are fixed to the stem name of the compound. Thus the IUPAC name of the compound under consideration is

5-chloro-3-hydroxyhexanal

6. In numbering a carbon chain of a multifunction compound, lowest numbers are given preferentially in the following order :

(*i*) groups in the priority table named by suffixes;

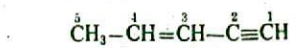
(*ii*) carbon-carbon double bonds;

(*iii*) carbon-carbon triple bond; and

(*iv*) groups named by prefixes.

For illustration, should the name for $ClCH_2CH{=}CH_2$ be 1-chloro-2-propene or 3-chloro-1-propene. We see from the priority table that a double bond is higher in priority than —Cl. Therefore, we give the double bond the lowest possible number and the correct name is 3-chloro-1-propene.

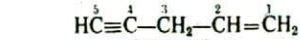
7. When both a double and triple bond are present in a hydrocarbon, its IUPAC name is derived by changing the *-ane* of the parent alkane to *-enyne*. Thus the systematic name for the hydrocarbon would be **Alkenyne**. The chain is numbered to give the multiple bonds (regardless of double or triple bond) the lowest possible numbers. The locator numbers of double and triple bonds are then inserted in the alkenyl name. For example,



3-penten-1-yne

NOT 2-penten-4-yne, which would have higher numbers for the multiple bonds

When there is a choice, double bond is given the lower number



1-penten-4-yne

NOT 4-penten-1-yne, which would have higher number for double bond

8. The molecules with double and triple bonds also having another principal function, are named by dropping *e* of the corresponding *alkenyne* and adding the suffix for the class. Thus if the principal function present is —CO— (class suffix, *one*), the compound is named as *alkenynone* (alkenyne — e + one). The locator numbers are inserted before *alken* (double bond), *yn* (triple bond) and *one* (carbonyl). Thus,



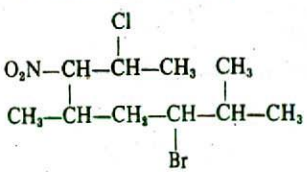
5-hexen-3-yn-2-one

The IUPAC Rules given above may be elucidated by considering the following cases.

CASE 1. When a structure has only substituents and no principal function.

As already discussed, the groups —F, - Cl, —Br, —I and —NO_2 are always treated as substituents while naming complex molecules. Thus a compound containing these functions has no principal function.

Example 1. *Assign IUPAC name to the structure*

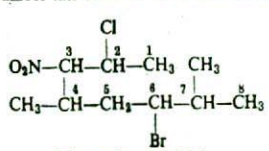


Solution :

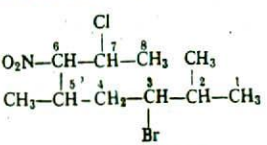
(*i*) Longest carbon-chain contains = 8 carbons

∴ Basic name : octane

(*ii*) Number this chain so that the scheme gives the lower number at the first point of difference.



Scheme I : 2,3,4,6,7



Scheme II : 2,3,5,6,7

In the two schemes the locator numbers at the first two points are identical, while they differ at the third point. Since at the first point of difference, scheme I gives number 4 and scheme II gives number 5, the first scheme is chosen.

(*iii*) Now prefix the names of substituents with locator numbers in alphabetic order to the basic name, octane. Thus the IUPAC name of the given structure is

6-bromo-2-chloro-4, 7-dimethyl-3-nitrooctane.

Example 2. *Write the systematic name of the compound* :

$$CH_3-CHF-CHCl-CH_3$$

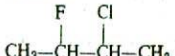
Solution :

(*i*) The chain contains = 4 carbons

∴ Basic name : butane

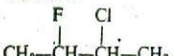
(*ii*) The chain may be numbered by two schemes :

Scheme I



Locants : 2,3

Scheme II



Locants : 2,3

Both schemes give identical locants of substituents. Here the scheme chosen is that which gives the lower number to the substituent whose name comes earlier in alphabetic order. Thus the scheme II is accepted as it gives lower number to chloro(Cl) which occurs earlier than fluoro(F) in alphabetic order.

(*iii*) Prefixing the names of the substituents carrying locator numbers, to the basic name, we can write the systematic name as

2-chloro-3-fluorobutane

CASE II. When the structure contains both a double bond and a triple bond.

Here the basic name is **Alkenyl** with locator numbers prefixed with *alken* (double bond) and *yl* (triple bond). The continuous carbon chain is numbered so as to give a lower number to double bond. The locator numbers are set off by dashes.

Example 1. *Give IUPAC name of the structure* :

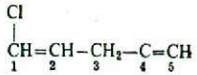


Solution :

(*i*) The continuous carbon chain = 5 carbons

∴ Basic name : pentenyl

(*ii*) Number the chain from left as it gives lower locator number to double bond.



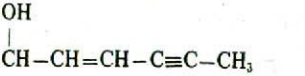
(*iii*) Prefix locator numbers

1-alken-4-yne

(*iv*) Add the name of substituent Cl,

1-chloro-1-alken-4-yne

Example 2. *Assign systematic name to the compound* :

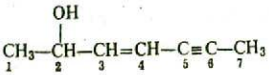


Solution :

Here OH ranks higher than double and triple bond in the priority table and takes precedence over the latter groups and determines class name.

(*i*) The continuous carbon chain bearing OH = 7 carbons.

(*ii*) Number from the end which gives lower locator number to OH.



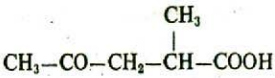
(*iii*) Insert locator numbers of double bond (3), triple bond (5) and OH(2) in the basic name.

3-hepten-5-yl-2-ol

CASE III. When the principal function —COOH is present along with other subsidiary functions.

The —COOH occupies the top position in the priority table and takes precedence over all other functions. The compound gets the class name *Alkanoic acids*.

Example 1. *Provide IUPAC name for the compound* :

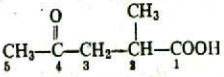


Solution :

(*i*) The continuous carbon chain = 5 carbons

∴ basic name : pentanoic acid

(*ii*) Number the chain with carbon of COOH as 1.



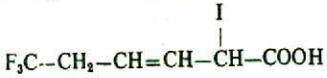
(*iii*) The substituents with locator numbers :

2-methyl 4-oxo

(*iv*) The IUPAC name :

2-methyl-4-oxo-pentanoic acid

Example 2. *Name the compound having structural formula* :

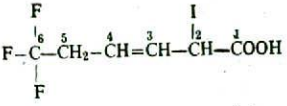


Solution :

(*i*) The continuous chain containing a double bond and COOH as the principal function = 6 carbons

∴ basic name = hexenoic acid

(*ii*) Number the chain with carbon of COOH as number 1.



(*iii*) Substituents with locator numbers arranged in alphabetic order :

6-fluoro 6-fluoro 6-fluoro 2-iodo

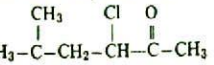
(*iv*) Prefix the substituent names to basic name and provide locator number to double bond.

6,6,6-trifluoro-2-iodo-2-pentenoic acid

Case IV. When principal function —CO— is present along with other substituents placed below in the priority table.

Here the class name is **Akanone** and the names of other substituents with locator numbers are prefixed in alphabetic order.

Example 1. *Assign IUPAC name to the compound* :

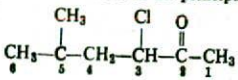


Solution :

(*i*) Longest carbon chain containing —CO— = 6 carbons

∴ basic name : hexanone

(*ii*) Number the chain so as to give lower number to the principal function —CO —.



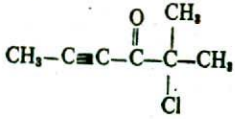
(*iii*) Substituents in alphabetic order :

3-chloro 5-methyl

(*iv*) Prefix substuents with basic name :

3-chloro-5-methyl-2-hexanone

Example 2. *Name the following compound according to IUPAC system* :

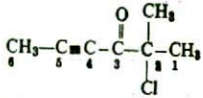


Solution :

(*i*) The continuous carbon chain containing principal function —CO— and a triple bond = 6 carbons :

∴ basic name : hexynone

(*ii*) Number the chain so that —CO— gets lower number,



(*iii*) Substituents with locator numbers in alphabetic order :

2-chloro 2-methyl

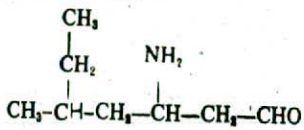
(*iv*) Prefix names of substituents to basic name and provide numbers for suffix names to get complete IUPAC name :

2-chloro-2-methyl-4-hexyn-3-one

Case V. When principal function —CHO is present along with another function below in the Priority table.

Here —CHO takes precedence over other functions lying below and determines the class name. The other functions are treated as substituents.

Example. *Assign name to the structure* :

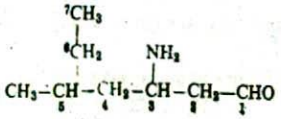


Solution :

(*i*) Longest continuous chain containing —CHO = 7 carbons

∴ basic name : heptanal

(*ii*) Number the parent chain with carbon of —CHO as number 1.



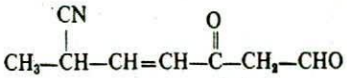
(*iii*) Substituents with locator numbers in alphabetic order :

3-amino 5-methyl

(*iv*) Prefix the substituent names to the basic name to get the IUPAC name :

3-amino-5-methyl-heptanal

Example 2. *Assign IUPAC name to the structure* :



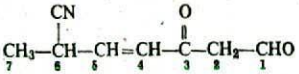
Solution :

—CHO group lies higher than —CN and C=O groups in the priority table and hence determines the class name, alkanal.

(*i*) The continuous carbon chain containing a double bond and —CHO = 7 carbons

∴ basic name : heptenal

(*ii*) Number the chain with CHO carbon as number 1.



(*iii*) Substituents :

6-cyano 3-oxo

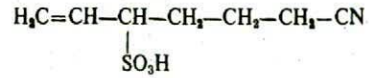
(*iv*) Adding substituents to basic name to get complete IUPAC name of the structure :

3-cyano-3-oxo-4-heptenal

Case VI. When the principal function $-SO_3H$ is present along with a —CN group and a double bond.

Here the class name will be derived from **Alkanesulphonic acid**. While numbering the continuous chain, the carbon of —CN is left out.

Example. *Provide the IUPAC name for the structure* :

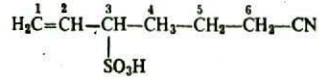


Solution :

(*i*) The longest chain containing a double bond and bearing $-SO_3H$ = 6 carbons

∴ basic name : hexenesulphonic acid

(*ii*) Number the chain to give lower number for $-SO_3H$:



The carbon of —CN is not counted as it is a substituent.

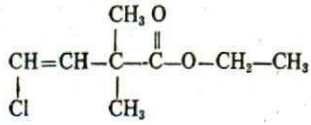
(*iii*) Writing prefix 6-cyano and inserting locator numbers :

6-cyano-1-alkene-3-sulphonic acid

Case VII. When the principal function is an ester group (RCOO—) or acyl halide (—COX)

While naming an ester (RCOOR'), the parent acid (RCOOH) should be first assigned IUPAC name and then the ester named as **Alkyl alkanoate**. In case of acyl halide also, the acid should be named and then the substance called as **Alkanoyl halide**.

Example. *While the systematic name for*



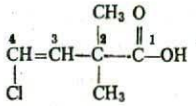
Solution :

(*a*) Naming the parent acid :

(*i*) longest continuous chain containing double bond and COOH = 4 carbons

∴ basic name : butenoic acid

(*ii*) Number the chain with COOH as No. 1,



(*iii*) Substituents :

4-chloro 2-methyl 2-methyl

(*iv*) Adding substituents and indicating the locator number of double bond, we get IUPAC name of the parent acid :

4-chloro-2, 2-dimethyl-butenoic acid

(*b*) The name of the ester is derived as alkyl alkanoate.

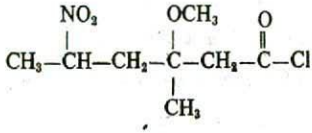
alkyl = ethyl

alkanoate = 4-chloro-2, 2-dimethyl-butanoate

Hence complete systematic name of ester is :

ethyl 4-chloro-2, 2-dimethyl-butanoate

Example 2. *Assign IUPAC name to the compound*



Solution :

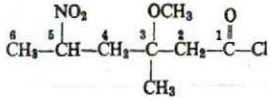
The compound contains —COCl as the principal function and is to be named as *Alkanoyl Chloride*.

(*a*) Name the parent acid :

(*i*) longest continuous chain containing —COOH group = 6 carbons

∴ basic name = hexanoic acid

(*ii*) Number the chain with carbon of COOH as 1.



(*iii*) Substituents with locator numbers and alphabeticised :

5-nitro 3-methoxy 3-methyl

(*iv*) Add substituent names to basic name from (*i*) :

5-nitro-3-methoxy-3-methylhexanoic acid

(*b*) Derive the name of alkanoyl chloride from the name of the corresponding acid as obtained in (*a*).

(*i*) Replace *ic* of acid name by *yl*

(*ii*) Delete '*acid*' and add chloride.

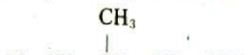
Thus we have

5-nitro-3-methoxy-3-methylhexanoyl chloride

CASE VIII. When NH_2 is the principal function along with other substituents.

When the hydrocarbon groups are too complex, the longest hydrocarbon chain bearing the amino group is named as **Alkanamine** and the other substituents are treated as before.

Example 1. *Name the following amine by the IUPAC System :*

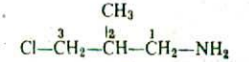


Solution :

(*i*) Longest continuous chain bearing NH_2 = 3 carbons

∴ parent name : propanamine

(*ii*) Number the chain giving lower number to NH_2.



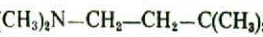
(*iii*) Substituents :

3-chloro 2-methyl

(*iv*) IUPAC name :

3-chloro-2-methylpropanamine

Example 2. Provide IUPAC name for the amine :

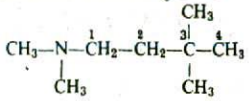


Solution :

(*i*) Longest chain bearing amine group = 4 carbons

∴ parent name : butanamine

(*ii*) Number the chain giving lower number to amine group.



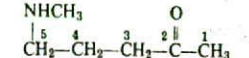
(*iii*) Substituents with locator numbers :

two *N*-methyl two 3-methyl

(*iv*) Prefixing locator number for each of the four CH_3 substituents,

3, 3, *N*, *N*-tetramethylbutanamine

Note. Of the major functional groups, amines have the lowest priority. **Thus amino group when present along with groups as COOH, CHO, OH, etc., it is named as a substituent.**



5-methylaminopentanone

NOMENCLATURE OF AROMATIC COMPOUNDS

In this chapter, we have considered the nomenclature of aliphatic compounds only. The systematic names of aromatic compounds are also based on our knowledge of naming aliphatic compounds.

The detailed nomenclature of aromatic compounds will be discussed in different chapters dealing with various classes of these compounds.

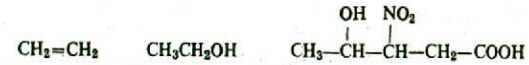
QUESTIONS

1. Name the principal series of organic compounds. Give two compounds belonging to each series.

2. Give a genealogical table listing the broad classification of organic compounds into principal series.

Define what you mean by aliphatic and aromatic series of compounds. Why it is thought convenient to study these separately.

3. Give a precise definition of 'functional group'. Indicate the functional groups in the following compounds.



4. What do you understand by a family or class ? Write the general formulas and functional groups in the following classes of organic compounds :

ethers, thiols, aldehydes, ketones, amides, selphonic acids, nitriles, amides.

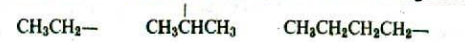
5. Give the meaning of the term 'Homologous Series'. What are the characteristics of such a series ? Illustrate your answer by taking example of alkanes, alcohols or carboxylic acids.

6. Define : (*a*) Common Name ; (*b*) Systematic Name. Why a common name is superior to a systematic name ?

7. What does IUPAC imply ? Give a short historical development of the IUPAC system of nomenclature.

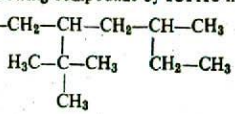
8. Define the terms : Alkanes, Cycloalkanes, Alkenes and Alkynes. Name a normal hydrocarbon of each type containing six carbons.

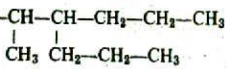
9. What are branched alkanes ? Give the IUPAC names of the following structures :

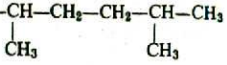


10. Discuss IUPAC rules for naming branched alkanes. Illustrate with examples.

11. Name the following compounds by IUPAC nomenclature :

(*a*) 

(*b*) 

(*c*) 

12. Draw the structure of the compounds :

(*a*) 3-ethyl-4-propyloctane

(*b*) 4-ethyl-2-methylhexane

(*c*) 2, 2-dimethylpentane.

13. Define the term 'locator numbers ? What are the locator number of the following substituents :

3-methyl 4-amino 2, 3-dibromo

14. What is meant by a Principal function ? Give the rank in the Priority table of the following functions :

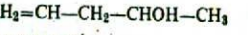


15. Write the condensed line formulas of the following compounds :

(*a*) 3-chloro-2-propene (*b*) 1-bromo-3-pentanone

(*c*) 3, 4-dimethylpentanol (*d*) 4-methyl-3-pentyne

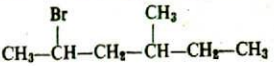
16. (*i*) Write the IUPAC names of the compound :

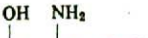


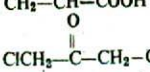
(*ii*) Write the formula of the compound :

2, 5-dibromo-4-ethyl-4-nonene

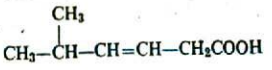
17. Write the IUPAC names for the following :

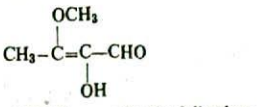




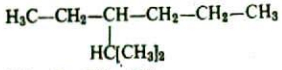


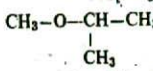
18. Write structural formulae for the following :
    (*i*) 2, 2-Dimethyl-1, 4-diethylheptane
    (*ii*) Pentane-2, 4-dione
    (*iii*) 2,2-Dimethyl-1-propanol
    (*iv*) 4-methyl-1-pentene
19. Write down the structural formulae of :
    (*i*) Pent-2, 4-dione
    (*ii*) 3-Methyl-2-chlorobutanoic acid
    (*iii*) Butane-2-sulphonic acid
    (*iv*) 3-Ethyl-2, 5-dimethylhexane.
20. (*a*) Write the structural formulae of the following compounds :
    (*i*) 2, 5, 5-Dimethyl-3-hexynoic acid
    (*ii*) 2, 4, 4-Trimethyl-3-isopropyl-1-pentene
    (*iii*) Methyl 2-chloro-3-cyano-3-hydroxypentanoate.
    (*b*) Write names of the following :

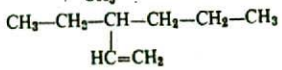




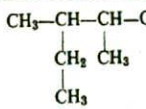
21. Give IUPAC names for the following :
    (*i*) $CH_3-CO-CH_2-COOH$
    (*ii*) $CH_3-CH=CH-COOH$

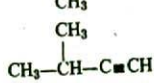


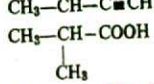




22. Write the IUPAC names of :







(*iv*) $CH_3-CH_2-CH_2-CO-CH_3$

23. Write the IUPAC names of the following compounds :

(*i*) $HOH_2C-C\equiv C-CH_2OH$

(*ii*) $CH_3-\underset{\displaystyle CHO}{\underset{|}{CH}}-CH_2-\underset{\displaystyle CH_2-CH_3}{\underset{|}{CH}}-CH_3$

(*iii*) $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH-CH_2-\underset{\displaystyle CH_2-CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3$

24. Write the graphic formulae of the following :

(*a*) 1-Hexene-3-yn-5-ol

(*b*) 2-nitro-1, 3-propenediol

(*c*) 1-bromo-2, 2-dimethylpropene.

25. (*a*) Write the structural formulae of :

(*i*) 2, 4-dimethyl-4-ethylheptane

(*ii*) 4-methyl-2-pentene.

(*b*) Write IUPAC names of :

(*i*) $CH_3-C\equiv C-CH(CH_3)_2$

(*ii*) $CH_2=CH-CH=CH_2$

26. Write the structural formulae for the following :

(*i*) 2-methylbuta-1, 3-diene

(*ii*) 2, 3-dimethylbutane.

27. Give the structures of :

(*i*) 1-Chloro-2-propanol

(*ii*) 2-Hydroxypentanoic acid

(*iii*) 4-methylpent-2-yne

(*iv*) 2, 3-Dimethyl-1, 3-butadiene.

28. Write the structural formulae of the following compounds :

(*i*) Hept-1-en-4-yne

(*ii*) 1-Amino-4-methylpentan-2-one

(*iii*) Pent-3-en-1-oic acid.

29. Write the IUPAC names of the following compounds :

(*i*) CH_3-CN

(*ii*) $CH_3-CHOH-\underset{\displaystyle CH_2-CH_2OH}{\underset{|}{CH}}-CH_2-COOH$

(*iii*) $H_2C=CH-C\equiv CH$

(*iv*) $H_2C-NH-CH_2-CH_2-CH_2OH$

30. Write the structural formulae of the following :

(*i*) Hex-4-yn-2-one

(*ii*) Hepta-1, 5-dien-3-ol

(*iii*) Methyl 2-bromo-5-cyano-3-hydroxypentanoate.

(*iv*) Isopropyldimethylamine.

31. (*a*) Give IUPAC names :—

(*i*) $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}CH_2\underset{\displaystyle C_2H_5}{\underset{|}{C}}HCH_2CH_3$

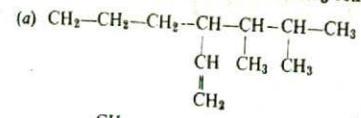
(*ii*) $CH_3CH=CHCH_2CH_3$

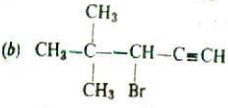
(*b*) Write the structural formulae for the following :—

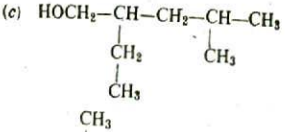
(*i*) 2-methylbuta-1, 3-diene

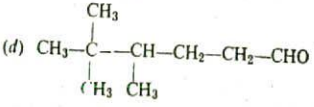
(*ii*) 2, 3-dimethylbutane.

32. Write the IUPAC names for the following compounds :

(*a*) 

(*b*) 

(*c*) 

(*d*) 

33. Write the structural formulae of :
   (*a*) 2-Methyl-1,3-butadiene
   (*b*) 2-Bromo-1-pentanol

34. Give the IUPAC names of the following compounds : *(Dibrugarh BSc, 1994)*
   (*a*) Glycerol (*b*) Oxalic acid
   (*c*) Methyl cyanide (*d*) Allyl bromide

35. Write the structural formulae of : *(Agra BSc, 1993)*
   (*a*) 4-Methyl-2-pentene
   (*b*) 2,3-Dimethylbutanoic acid

36. Write the structural formulae of the following compounds : *(Punjab BSc, 1993)*
   (*a*) 2,4-Pentadiene
   (*b*) 2-Methyl-3-propyl-2-pentanol
   (*c*) 4-Amino-2-ethyl-2-pentanal

37. Write the structural formulae of : *(Sambalpur BSc, 1994)*
   (a) 1,2,3-Propanetriol
   (*b*) 1-Ethoxy-1-propanol

38. Write the structural formulae of the following compounds : *(Saugar BSc, 1994)*
   (*a*) 1-Methylcyclohexene
   (*b*) 4-Methyl-2-pentyne
   (*c*) 2-Chloro-3,5-dimethylhexane
   (*d*) 2-Methyl 4-nitro-2-pentanol *(Bangalore BSc, 1994)*

ALIPHATIC COMPOUNDS

Chapter **9**

Alkanes

Alkanes are the simplest class of organic compounds. They are made of carbon and hydrogen atoms only and contain two types of bonds, carbon-hydrogen (C—H) and carbon-carbon (C—C) single covalent bonds. They do not have functional groups.

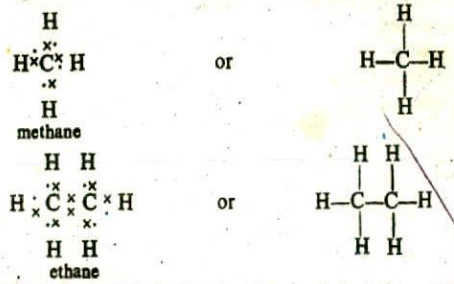
Alkanes form a homologous series with the general formula C_nH_{2n+2}, where n is the number of carbon atoms in the molecule. The first member of the family has the molecular formula CH_4 ($n=1$) and is commonly known as methane and the second member with molecular formula C_2H_6 ($n=2$) is called ethane.

These compounds are also known as the **Saturated hydrocarbons**. This name is more descriptive than the present-day term 'alkane' because it indicates both their composition (carbon and hydrogen) and the fact that the four single covalent bonds of each carbon in their molecules are fully satisfied or 'saturated'.

The name **Alkane** is the generic name for this class of compounds in the IUPAC system of nomenclature. These hydrocarbons are relatively unreactive under ordinary laboratory conditions, but they can be forced to undergo reactions by drastic treatment. It is for this reason that they were named **Paraffins** (Latin *parum* affinis = little activity).

STRUCTURE

As indicated above, the molecules of alkanes are made of carbon atoms joined each to each by single covalent bonds, while the remaining valency bonds of carbons are linked to hydrogen atoms. Thus the simple electronic formulae of methane and ethane could be written as



According to the modern orbital theory, the excited carbon atom has the electronic configuration

C (ground state) $1s^2\ 2s^2\ 2p^1_x\ 2p^1_y\ 2p^0_z$

C (excited state) $1s^2\ 2s^1\ 2p^1_x\ 2p^1_y\ 2p^1_z$

The 2*s* and three 2*p* orbitals in the excited state are hybridised to give four sp^3 orbitals.

The four new sp^3 orbitals are arranged in space in such a way that their axes are directed towards the corners of a regular tetrahedron. In the formation of a methane molecule, the sp^3 orbitals overlap with 1*s* orbitals of four hydrogen atoms to form four *s*-sp^3 sigma bonds.

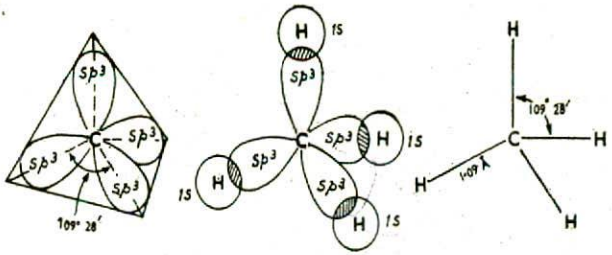


Fig. 9·1. Structure of methane

In ethane molecule, sp^3 orbital of one carbon overlaps with sp^3 orbital of the other carbon The remaining three sp^3 orbitals of each of the two carbons overlap with the 1*s* orbitals of H-atoms to form *s*-sp^3 sigma bonds.

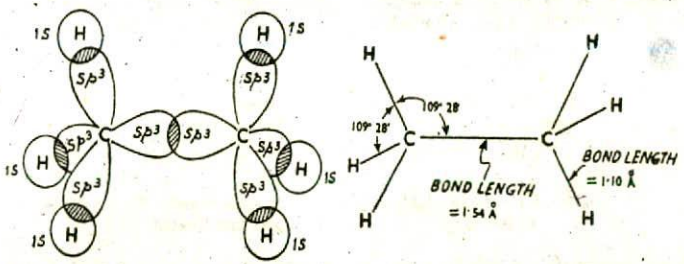


Fig. 9·2. Structure of ethane

Electron diffraction and spectroscopic studies have given the following measurements for the molecule of ethane; H—C—H and H—C—C bond angles are 109° 28′, C—H bond length is 1·10Å and C—C bond length is 1·54Å.

In all higher alkanes the carbon atoms are joined each to each by sp^3-sp^3 σ bonds and to hydrogen atoms by *s*-sp^3 σ bonds, since these σ bonds are remarkably strong, the alkanes are chemically unreactive.

Electron diffraction and spectroscopic studies have also shown that methane has a tetrahedral structure and all the C—H bonds in it are identical. They have the same bond length (1·09 Å). The energy required to break any of the bonds is the same (102 kcal). The angle between any pair of bonds is the tetrahedral angle *i.e.*, 109° 28′.

NOMENCLATURE

Alkanes form a homologous series having the general formula C_nH_{2n+2} and their type formula is RH. The molecular formulae of the various members can be obtained by putting $n = 1, 2, 3, 4$, etc. in the general formula. There are two systems of naming these hydrocarbons.

(1) **The Common System.** The first four members of the series are called by their trivial or common names : Methane, Ethane, Propane and Butane. From the fifth onwards, alkanes are named by prefixing the Greek numerals *pent* (5), *hex* (6), *hept* (7), *oct* (8), etc. indicating the number of carbon atoms in the molecule, to the terminal *-ane*. Thus the name of an individual alkane is a one-word name. The names of first twelve alkanes are given below.

CH_4	Methane	C_7H_{16}	Heptane
C_2H_6	Ethane	C_8H_{18}	Octane
C_3H_8	Propane	C_9H_{20}	Nonane
C_4H_{10}	Butane	$C_{10}H_{22}$	Decane
C_5H_{12}	Pentane	$C_{11}H_{24}$	Undecane
C_6H_{14}	Hexane	$C_{12}H_{26}$	Dodecane

There is one methane, one ethane and one propane known. Further alkanes containing four or more carbon atoms exist in two or more isomeric forms depending on the structure of the carbon skeleton. The alkanes having a straight or normal chain are called **normal** (or 'n-') **hydrocarbons**. This is indicated by prefixing n- to the name of the alkane. Thus :

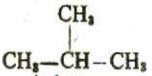
$CH_3CH_2CH_2CH_3$
n-butane

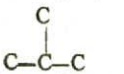
C—C—C—C
(normal chain)

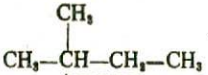
$CH_3CH_2CH_2CH_2CH_3$
n-pentane

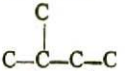
C—C—C—C—C
(normal chain)

The alkanes in which the carbon chain has branches are called **branched chain hydrocarbons**. Such alkanes as possess a one-carbon branch on the second carbon of the normal or basic chain, are referred to as **Iso hydrocarbons** (Greek, *isos* = equal). Thus,

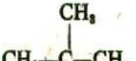

isobutane

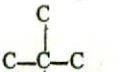

isobutane skeleton

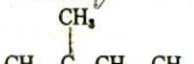

isopentane

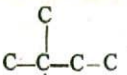

isopentane skeleton

From pentane (C5) onwards, when the normal carbon chain present in the molecule has two one-carbon branches on the second carbon from the end, the alkane is referred to as **Neo hydrocarbon** (Greek, *neos* = new). Thus :

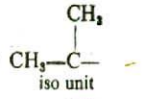

neopentane


neopentane skeleton

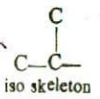

neohexane


neohexane skeleton

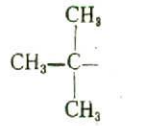
From an examination of the above structures ou will note that branched chain alkanes in general are characterised by the following structural units.



iso unit



iso skeleton



neo unit



neo skeleton

In modern practice, the symbols *n*-, *iso*- and *neo*- are not to be written in italics as was done earlier.

Types of Carbons atoms in Alkanes

The structural formulas of alkanes and their derivatives contain four types of carbon atoms.

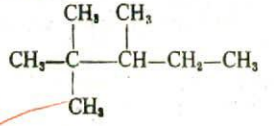
(1) **Primary (1°) carbon** atom which is bonded to one or no other carbon atom.

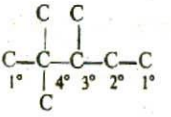
(2) **Secondary (2°) carbon** atom which is bonded to two other carbon atoms.

(3) **Tertiary (3°) carbon** atom which is bonded to three other carbon atoms.

(4) **Quaternary (4°) carbon** atom which is bonded to four carbon atoms.

Thus in the following structure beginning from the left, the first carbon is primary (1°), the second quaternary (4°), the third tertiary (3°), the fourth secondary (2°) and the fifth one again primary (1°).





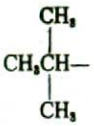
Naming of Alkyl radicals

A group of atoms that has an unused valency (represented by dash) is called a *radical*. The radicals derived from alkanes (R—H) by removal of one H atom are called **Alkyl radicals** (R—). The names of the alkyl radicals corresponding to normal and isoalkanes are obtained by simply changing the suffix *-ane* to *-yl*. In case of normal alkanes the hydrogen atom is removed from the end of the carbon chain while in isoalkanes it comes from the end opposite to the branched or 'iso' end. Thus,

Structure	Name	Abbreviation
CH_3—	Methyl	Me
CH_3CH_2—	Ethyl	Et
$CH_3CH_2CH_2$—	n-propyl	Pr^n
CH_3—CH(—CH_3)	Isopropyl	Pr^i
$CH_3CH_2CH_2CH_2$—	n-Butyl	B^n
CH_3—CH(—CH_3)—CH_2—	Isobutyl	B^i

In more complex cases, the name of the alkyl radical depends on whether the hydrogen is removed from a primary, secondary or a tertiary carbon atom of the hydrocarbon structure. Thus,

$CH_3CH_2CH_2CH_2$—	n-Butyl	B^n
CH_3CH_2CH(—)	ec-Butyl s-Butyl	B^s

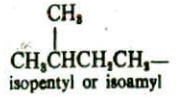


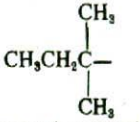
tert-Butyl
t-Butyl

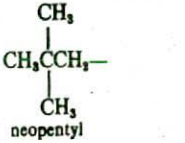
B¹

Proceeding similarly pentane (C_5H_{12}) forms the following radicals.


n-pentyl or n-amyl


isopentyl or isoamyl


tert-amyl or t-amyl


neopentyl

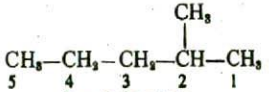
(2) **The IUPAC System** retains the common names for the first ten (C_1 to C_{10}) alkanes as also for the simple alkyl radicals described earlier. This modern system of nomenclature is indispensable for naming branched chain alkanes. We have already discussed how a complex hydrocarbon can be assigned IUPAC name. The rules used for the purpose will be mentioned again by way of recapitulation.

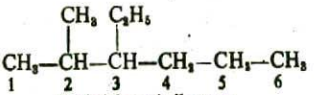
(*i*) The longest carbon chain present in the molecule is selected and the complex hydrocarbon is regarded as alkyl derivative of the parent alkane containing this chain.

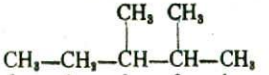
(*ii*) The positions of the substituents (alkyl radicals) attached to the parent chain are determined by numbering this chain from the end which puts them on carbons having the lowest numbers.

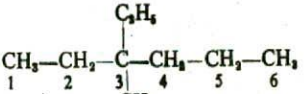
(*iii*) To write the IUPAC name of the complex hydrocarbon the names of the substituents with position numbers indicated in front of them and arranged in alphabetical order, are prefixed to the name of the parent alkane. The substituent names are hyphened on either side except the last one which is merged with the name of the alkane.

(*vi*) If the same substituent appears on the parent chain more than once, the positional numbers are set off by commas and the prefixes *di*, *tri*, *tetra*, etc. are used to indicate the number of times it appears. Thus,


2-methylpentane

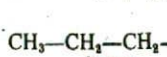

3-ethyl-2-methylhexane


2, 3-dimethylpentane


3-ethyl-3-methylhexane

ISOMERISM IN ALKANES

The alkanes offer for study an excellent example of *Chain Isomerism*. The first three hydrocarbons of the series *viz.*, methane, ethane and propane do not exhibit isomerism. The next hydrocarbon butane (C_4H_{10}) exists in two isomeric forms :


butane

and


isobutane

All higher hydrocarbons show chain isomerism and the number of isomers goes on increasing rapidly with the increase in the number of carbon atoms. Thus,

	C_5H_{10}	C_6H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}
No. of Isomers	2	3	5	9	18

Prediction of Isomers according to theory. Since isomerism in hydrocarbons depends on the different structures of the carbon chains, the number of isomeric forms of a particular hydrocarbon can be worked out by building up the possible carbon chains of that hydrocarbon. Starting from the first hydrocarbon methane which contains only one carbon atom, the chain of ethane can be constructed in a simple way by adding to it another carbon atom.

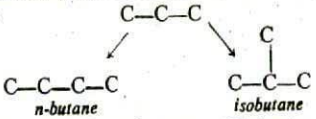
$$\underset{\textit{methane}}{C} \longrightarrow \underset{\textit{ethane}}{C{-}C}$$

Similarly, the carbon chain of propane can be obtained by adding a new carbon atom to the chain of ethane.

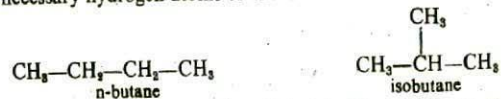
$$\underset{\textit{ethane}}{C{-}C} \longrightarrow \underset{\textit{propane}}{C{-}C{-}C}$$

So far it is all simple, as the addition of the new carbon atom to the previous chain can be done only in one way and the resulting carbon chain has only one structure. Hence, methane, ethane, and propane are incapable of exhibiting isomerism. However, carbon chains of higher hydrocarbons built in this way can have two or more different structures and, therefore, show chain isomerism.

Isomeric Butanes, C_4H_{10}. The C-chain of butane can be obtained from that of propane by the addition of a new C-atom to it. Since the C-chain of propane contains two types of C-atoms (the middle C-atom being different from the side ones), this can be done in two ways :



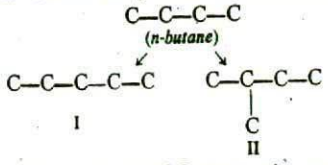
Thus theory predicts the existence of two butanes. Their structural formulae can be written by supplying the necessary hydrogen atoms to the C-atoms in the above chains.



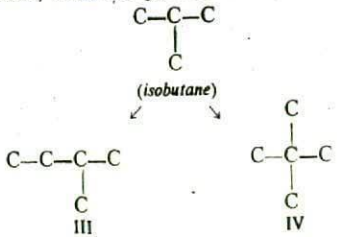
Both these hydrocarbons are actually known. Their boiling points are 1° and —10·2° respectively.

Isomeric Pentanes, C_5H_{12}. Carbon chains of pentanes can be built up from those of butanes by the addition of another C-atom.

The C-chain of n-butane has two types of C-atoms, those in the middle being different from those at the ends. Thus it will give rise to two chains of five carbon atoms.



Isobutane has again two types of C-atoms, the central atom being different from the remaining three. Therefore, it can also give rise to two chains of five C-atoms.



Of the four possible chains derived for pentane, II and III are identical. Hence according to theory there should exist three isomeric pentanes. Supplying the necessary hydrogen atoms to C-chains I, II and IV, the full formulae of the three pentanes may be written. All these hydrocarbons are actually known. They are :

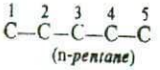
(*i*) $CH_3-CH_2-CH_2-CH_2-CH_3$ n-pentane

(*ii*) $CH_3-CH(CH_3)-CH_2-CH_3$ isopentane or 2-methylbutane

(*iii*) $CH_3-C(CH_3)_2-CH_3$ neopentane or 2,dimethylpropane

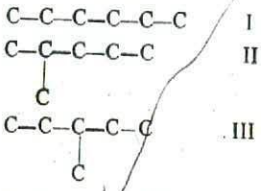
Isomeric Hexanes, C_6H_{14}. Carbon chains of hexanes can be obtained by adding a carbon atom to the chains of three pentanes.

The C-chain of n-pentane has three types of C-atoms,

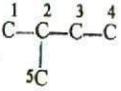


(n-*pentane*)

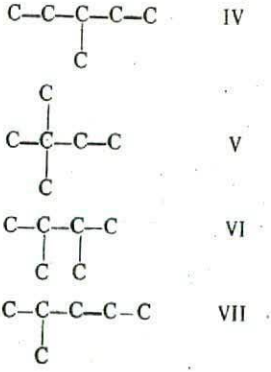
C-atom 1 is similar to 5, and 2 is similar to 4, while 3 is differently linked than all these. Thus, it can give rise to three chains of six carbon atoms.



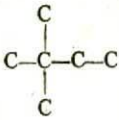
In the C-chain of isopentane only the C-atoms 1 and 5 are similarly linked, hence there are only



four ways of adding the next C-atom. Thus we have four possible chains of six C-atoms.

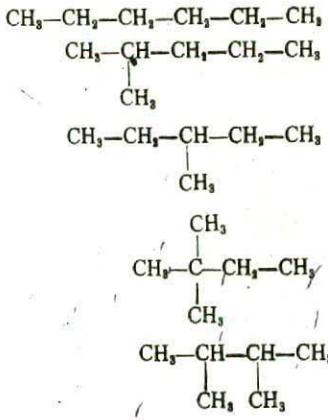


In neo-pentane chain all the four available C-atoms are similarly linked and it can, therefore, give rise to only one chain of six C-atoms.



VIII

Now, of the eight chains of six carbon atoms II and VII, III and IV, V and VIII are identical. This reduces the number of possible C-chains of hexanes to only five. All the five hexanes predicted by theory are known. They are :



n-hexane

2-methylpentane

3-methylpentane

2, 2-dimethylbutane

2. 3-dimethylbutane

Proceeding in a similar way the number of isomeric forms of any higher alkane can be theoretically predicted.

OCCURRENCE

Alkanes are highly widespread in nature. Natural gas given off in petroleum regions contains about 80 % methane and 10 % ethane, the remaining 10 % being a mixture of higher hydrocarbons. Crude petroleum is a mixture of almost unlimited quantities of liquid alkanes and higher solid hydrocarbons. *Ozokerite* found in large deposits in petroleum areas is a mixture of higher solid alkanes.

GENERAL METHODS OF PREPARATION

The first five members of the alkane series can be obtained in the pure form by the fractional distilllation of petroleum and natural gas. As we go higher up in the series, the differences in the boiling points of various members are very small. Consequiently, it is not practical to isolate pure higher alkanes from petroleum fractions. The alkanes can be prepared by the following synthetic methods.

(1) **Hydrogenation of Alkenes and Alkynes**. Alkanes are formed by passing a mixture of an unsaturated hydrocarbon and hydrogen over finely divided nickel at 200—300°C (*Sabatier and Senderens Reaction*). Alkane produced has the same member of carbon atoms as the original unsaturated hydrocarbon.

(*i*) $\underset{\text{alkene}}{R-CH=CH_2} + H_2 \xrightarrow[200-300^\circ]{Ni} \underset{\text{alkane}}{RCH_2CH_3}$

$\underset{\text{ethene}}{CH_2=CH_2} + H_2 \xrightarrow[200-300^\circ]{Ni} \underset{\text{ethane}}{CH_3CH_3}$

$\underset{\text{propene}}{CH_3CH=CH_2} + H_2 \xrightarrow[200-300^\circ]{Ni} \underset{\text{propane}}{CH_3CH_2CH_3}$

(*ii*) $\underset{\text{alkyne}}{R-C\equiv C-R} + 2H_2 \xrightarrow[200-300^\circ]{Ni} \underset{\text{alkane}}{RCH_2CH_2R}$

$\underset{\text{acetylene}}{HC\equiv CH} + 2H_2 \longrightarrow \underset{\text{ethane}}{CH_3CH_3}$

Other catalysts which can be used are palladium and platinum although they are more expensive than nickel.

Since alkanes and alkynes are obtained in large quantities by the cracking of petroleum, this method is used for the industrial preparation of alkanes.

(2) **Decarboxylation of Carboxylic acids.** When the sodium salt of a carboxylic acid, RCOOH, is heated strongly with sodalime (NaOH + CaO), a molecule of carbon dioxide is split off as carbonate and an alkane is obtained. The alkane so produced contains one carbon less than the original acid.

$$\underset{\text{Sod. salt of a carboxylic acid}}{R\,COONa} + NaO\,H \xrightarrow{\Delta} \underset{\text{alkane}}{RH} + Na_2CO_3$$

$$\underset{\text{sodium acetate}}{CH_3COONa} + NaOH \xrightarrow{\Delta} \underset{\text{methane}}{CH_4} + Na_2CO_3$$

$$\underset{\text{sodium propionate}}{CH_3CH_2COONa} + NaOH \xrightarrow{\Delta} \underset{\text{ethane}}{CH_3CH_3} + Na_2CO_3$$

Taking from the original acid, the above reaction could be represented as

$$RCOOH \longrightarrow \underset{\text{alkane}}{RH} + CO_2$$

such a reaction in which CO_2 is split out from a carboxylic group is called **Decarboxylation reaction** or simply **Decarboxylation**.

(3) **Reduction of Alkyl halides.** When reduced with nascent hydrogen, alkyl halides are converted directly to the corresponding alkanes.

$$\underset{\text{alkyl halide}}{R-X} + 2H \longrightarrow \underset{\text{alkane}}{R-H} + HX$$

$$\underset{\text{methyl iodide}}{CH_3I} + 2H \longrightarrow \underset{\text{methane}}{CH_4} + HI$$

The reaction occurs best with iodides and bromides, chlorides and fluorides being less reactive. The hydrogen for reduction may be obtained by employing any of the following reducing agents : Zn + HCl ; C_2H_5OH + Na ; HI + P ; or $LiAlH_4$. Hydrogen gas and catalyst (Ni, Pt or Pd) may also be used. Reduction in all cases occurs smoothly at room temperature.

This method for the preparation of alkanes is employed when pure hydrocarbons are needed.

(4) **Reduction of Alcohols, Aldehydes, Ketones and Carboxylic acids.** Hot Concentrated hydriodic acid in combination with red phosphorus reduces oxygenated compounds like alcohols, aldehydes, ketones and carboxylic acids to form the respective alkanes.

(*i*) $\underset{\text{alcohol}}{R-OH} + 2HI \xrightarrow[150^\circ]{P} \underset{\text{alkane}}{R-H} + I_2 + H_2O$

$$\underset{\text{methyl alcohol}}{CH_3OH} + 2HI \xrightarrow[150^\circ]{P} \underset{\text{methane}}{CH_4} + I_2 + H_2O$$

(ii) $$R-\underset{\text{aldehyde}}{\overset{O}{\overset{\|}{C}}}-H + 4HI \xrightarrow[150^\circ]{P} \underset{\text{alkane}}{RCH_3} + 2I_2 + H_2O$$

$$\underset{\text{acetaldehyde}}{CH_3-\overset{O}{\overset{\|}{C}}-H} + 4HI \xrightarrow[150^\circ]{P} \underset{\text{ethane}}{CH_3CH_3} + 2I_2 + H_2O$$

(iii) $$R-\underset{\text{ketone}}{\overset{O}{\overset{\|}{C}}}-R' + 4HI \xrightarrow[150^\circ]{P} \underset{\text{alkane}}{RCH_2R'} + 2I_2 + H_2O$$

$$CH_3-\underset{\text{acetone}}{\overset{O}{\overset{\|}{C}}}-CH_3 + 4HI \xrightarrow[150^\circ]{P} \underset{\text{propane}}{CH_3CH_2CH_3} + 2I_2 + H_2O$$

(iv) $$R-\underset{\text{carboxylic acid}}{\overset{O}{\overset{\|}{C}}}-OH + 6HI \xrightarrow[200-250^\circ]{P} \underset{\text{alkane}}{RCH_3} + 3I_2 + 2H_2O$$

$$CH_3-\underset{\text{acetic acid}}{\overset{O}{\overset{\|}{C}}}-OH + 6HI \xrightarrow[200-250^\circ]{P} \underset{\text{ethane}}{CH_3CH_3} + 3I_2 + 2H_2O$$

The effective reducing agent is the hydriodic acid. The red phosphorus merely reacts with iodine produced in the reaction to regenerate HI which is reused.

$$2P + 3I_2 + 6H_2O \longrightarrow 6HI + 2H_3PO_3$$

This method is particularly important for the preparation of higher alkanes from carboxylic acid obtained by the hydrolysis of fats.

(5) Action of Sodium on Alkyl halides ; Wurtz Reaction. Higher alkanes are produced by heating an alkyl halide (RX) with sodium metal in dry ether solution. Two molecules of the alkyl halide lose their halogen atoms as sodium halide (NaX). The result is the joining of their two alkyl groups to give alkane containing twice as many carbon atoms as the original halide molecule.

$$\underset{\text{alkyl halide}}{RX} + 2Na + XR \xrightarrow{\text{dry ether}} \underset{\text{alkane}}{R-R} + 2NaX$$

$$\underset{\text{methyl bromide}}{CH_3Br} + 2Na + BrCH_3 \xrightarrow{\text{dry ether}} \underset{\text{ethane}}{CH_3-CH_3} + 2NaBr$$

MECHANISM. Two types of mechanism are possible for Wurtz reaction.

(i) Free Radical Mechanism. This involves the attack of a sodium atom on, say, methyl bromide to produce sodium bromide and a methyl free radical. Two methyl free radicals then unite with each other to give athane.

$$\underset{\text{methyl bromide}}{CH_3Br} + Na \longrightarrow NaBr + \underset{\text{methyl free radical}}{\cdot CH_3}$$

$$2\,H_3C\cdot \longrightarrow \underset{\text{ethane}}{CH_3-CH_3}$$

(*ii*) *Ionic Mechanism.* This involves the intermediate formation of metal alkyls. Thus methyl bromide reacts with two atoms of sodium to produce methyl sodium (CH_3Na) and sodium and sodium bromide. Methyl sodium then reacts with another molecule of methyl bromide to give ethane and sodium bromide.

$$\underset{\text{METHYL BROMIDE}}{CH_3Br} + Na \longrightarrow \underset{\text{METHYL-SODIUM}}{\bar{C}H_3\overset{+}{N}a} + \overset{+}{N}a\bar{B}r$$

$$\overset{+}{N}a\bar{C}H_3 + CH_3\text{—}\bar{B}r \longrightarrow \underset{\text{ETHANE}}{CH_3\text{—}CH_3} + \overset{+}{N}a\bar{B}r$$

The reaction between two different alkyl halides and sodium produces a mixture of alkanes. For example, methyl bromide and ethyl bromide when treated with sodium yield a propane, along with small amounts of ethane and n-butane. This is due to the fact that the methyl and ethyl radicals in addition to reacting with each other can react with themselves also.

$$CH_3\cdot + \cdot C_2H_5 \longrightarrow \underset{\text{propane}}{CH_3-C_2H_5}$$

$$H_3C\cdot + \cdot CH_3 \longrightarrow \underset{\text{ethane}}{CH_3-CH_3}$$

$$H_5C_2\cdot + \cdot C_2H_5 \longrightarrow \underset{\text{n-butane}}{C_2H_5-C_2H_5}$$

For carrying out Wurtz reaction, the alkyl bromides and iodides may also be used. The order of reactivity of alkyl halides is RCl $<$ RBr $<$ RI. Other metals which can be used in place of sodium are zinc and finely divided silver.

Wurtz reaction is a good method of building up higher alkanes from lower members. The lower alkanes are converted into the corresponding halide and then treated with sodium. Thus methane can be converted into ethane as fallows :

$$CH_4 + Cl_2 \longrightarrow \underset{\text{methyl chloride}}{CH_3Cl} + HCl$$

$$2CH_3Cl + 2Na \xrightarrow{\text{dry ether}} \underset{\text{ethane}}{CH_3\text{—}CH_3} + 2NaCl$$

Limitation. As we have seen, the use of two different alkyl halides in Wurtz reaction invariably leads to a mixture of alkanes. The separation of these alkanes is not always easy because of little difference in their boiling points. The problem of isolating the desired product limits the usefulness of this method to the preparation of only the symmetrical alkanes in which the two alkyl groups joined are the same *i.e.*, of the R-R type.

(6) **Hydrolysis of Grignard Reagents.** Alkylmagnesium halides (Grignard reagents) are obtained by heating alkyl halides with magnesium metal in anhydrous ether. These on treatment with water, decompose to give alkanes containing the same number of carbon atoms as the original alkyl halide.

$$\underset{\text{alkyl halide}}{R-X} + Mg \xrightarrow{\text{dry ether}} \underset{\text{alkylmagnesium halide}}{R-Mg-X}$$

$$R-MgX + \underset{\text{water}}{HO-H} \longrightarrow \underset{\text{alkane}}{R-H} + (MgOH)^{+}\bar{X}$$

e.g.

$$\underset{\text{ethyl bromide}}{CH_3CH_2Br} + Mg \xrightarrow{\text{dry ether}} \underset{\text{ethylmagnesium bromide}}{CH_3CH_2MgBr}$$

$$CH_3CH_2MgBr + H_2O \longrightarrow \underset{\text{ethane}}{CH_3CH_3} + (MgOH)X$$

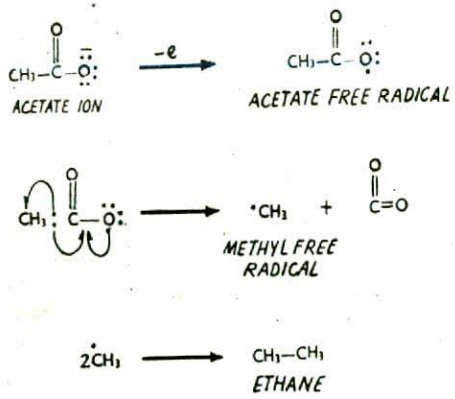
(7) **Electrolysis of salts of Carboxylic acids; The Kolbe's method.** When a concentrated solution of sodium or potassium salt of a carboxylic acid is electrolysed, a higher alkane is formed.

$$\underset{\text{Sod. carboxylate}}{2RCOONa} + 2H_2O \xrightarrow{\text{electrolysis}} \underbrace{R-R}_{\text{alkane}} + \underbrace{2CO_2}_{\text{at anode}} + \underbrace{2NaOH + H_2}_{\text{at cathode}}$$

$$\underset{\text{Sod. acetate}}{2CH_3COONa} + 2H_2O \xrightarrow{\text{electrolysis}} \underbrace{CH_3CH_3}_{\text{ethane}} + \underbrace{2CO_2}_{\text{at anode}} + \underbrace{2NaOH + H_2}_{\text{at cathode}}$$

MACHANISM. When an electric current is passed through a solution of, say, sodium acetate, the acetate ions (CH_3COO^-) migrate to the anode and give up one electron to produce acetate free radical. The acetate free radical in turn decomposes to give a methyl free radical and carbon dioxide. Two of the resulting methyl free radicals then combine to form ethane Thus :

At Anode :



At Cathode :

$$2\overset{+}{Na} \xrightarrow{+2e} 2Na$$

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2\uparrow$$

Thus sodium ions discharge at the cathode producing sodium hydroxide and hydrogen

This method can also be applied to a mixture of alkali salts of two different carboxylic acids, when a mixture of alkanes would be obtained. For this reason, Kolbe's method is useful for the synthesis of symmetrical alkanes only.

This method was first used in 1849 by the German chemist Hermann Kolbe after whom it was named. It provides a good example of doubling up of alkyl free radicals. Methane can not be, obviously, prepared by Kolbe's method.

PHYSICAL PROPERTIES

(1) The first four alkanes (C_1 to C_4) *i.e.*, four methane to butane are gases. The next thirteen members (C_5 to C_{17}) *i.e.*, from pentane to heptadecane are liquids. The higher members (C_{18} onwards) are waxy solids. The gaseous and liquid hydrocarbons have characteristic odours associated with petroleum products. The solid members are generally odourless.

(2) Alkanes have nonpolar molecules and hence are insoluble in water. They are, however, soluble in nonpolar solvents such as benzene and carbon tetrachloride.

(3) The boiling points of *n*-alkanes increase in a smooth manner with increasing molecular weight (Fig. 9·3) whereas the melting points do not increase in such a regular fashion (Fig. 9·4). Except for the very small alkanes, the boiling point rises by 20° to 30° for each carbon that is added to the chain.

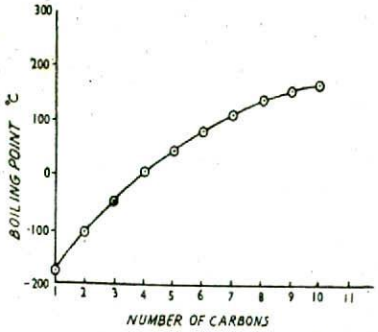


Fig. 9·3. Boiling points of n-alkanes.

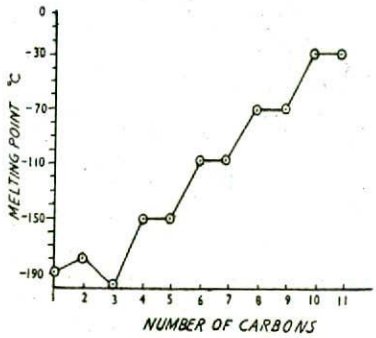


Fig. 9·4. Melting points of n-alkanes.

(4) For alkane which exists in isomeric forms, the branched chain isomer will have a lower boiling point than the corresponding n-isomer. Thus n-butane has a boiling point 0° while isobutane boils at −12°. Furthermore, more numerous the branches, the lower the boiling point. Thus isopentane with one branch chain boils at 28°, while neopentane with two branch chains boils at 9·5°. The fact that branching lowers the boiling is reasonable and can be explained as follows. With branching the shape of the molecule tends to approach that of a sphere and thus the surface area decreases. As a result of the decrease of surface area, the intermolecular forces become weaker and can be overcome at a lower temperature.

(5) The density of alkanes also increases with the size of the molecule and tends to approach a constant value of 0·8 with hexadecane. Thus all the alkanes are lighter than water.

The physical constants of some alkanes are given in the following table.

Table. *Physical Properties of Selected Alkanes*

Compound	*Formula*	*BP (°C)*	*MP (°C)*	*Density (g/ml at 20°)*	*Physical state*
Methane	CH_4	−161·5	−182·5		
Ethane	CH_3CH_3	−88·6	−183 3		Gases (C_1—C_4)
Propane	$CH_3CH_2CH_3$	−42·1	−187·7	0·501	
n-Butane	$CH_3(CH_2)_2CH_3$	−0·5	−138·4	0·579	
n-Pentane	$CH_3(CH_2)_3CH_3$	36·1	−129·7	0·626	
n-Hexane	$CH_3(CH_2)_4CH_3$	68·7	−95·3	0·659	
n-Heptane	$CH_3(CH_2)_5CH_3$	98·4	−90·6	0·684	
n-Octane	$CH_3(CH_2)_6CH_3$	125·7	−56·8	0·703	Liquids (C_5—C_{17})
n-Nonane	$CH_3(CH_2)_7CH_3$	150·8	−53·5	0·718	
n-Decane	$CH_3(CH_2)_8CH_3$	174·1	−29·7	0·730	
n-Pentadecane	$CH_3(CH_2)_{13}CH_3$	270·6	9·9	0·768	
n-Eicosane	$CH_3(CH_2)_{18}CH_3$	343·8	36·4	0·789	Solids (C_{18}⟶)

CHEMICAL PROPERTIES

Alkanes are relatively stable to most of the common reagents at room temperature. They do not react with *acids* like hydrochloric acid and sulphuric acid, *bases* like sodium hydroxide and potassium hydroxide, *oxidising agents* like potassium permanganate or sodium dichromate, *reducing agents* like stannous chloride and lithium-aluminium hydride, and *active metals* like sodium or potassium.

The relative stability or inactivity of alkanes may be explained by considering the nature of C—C and C—H bonds present in their molecules.

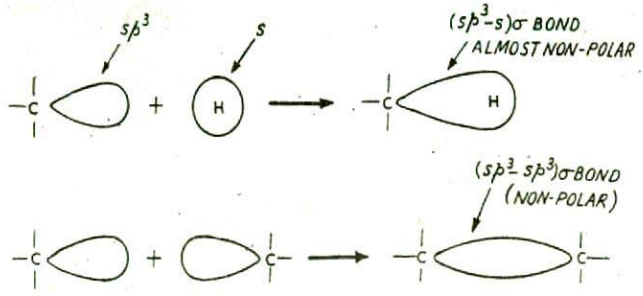
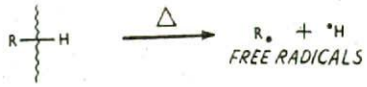


Fig. 9·5. C—H and C—C bonds are nonpolar and strong.

Since the electronegativities of carbon (2·60) and of hydrogen (2·1) do not differ appreciably, the bond electrons in C—H are equally shared between them. Thus C—H bonds encountered in alkanes are almost nonpolar and the same is true of C—C bonds. Thus polar and

ionic reagents (acids, alkalies, etc.) find no reaction sites on alkane molecules to which they could be attracted. Moreover, C—C and C—H bonds are short and strong. The random collisions between the molecules of potential reactants (alkanes and reagents) occur but the energies of these collisions are not sufficient to bring about a chemical reaction. At high temperatures, however, the energies of collisions are much frequently powerful enough to 'break and make' bonds. Thus alkanes undergo most of their reactions through the formation of the highly reactive 'free radicals' as a result of 'energetic collisions' between their molecules at high temperature.



Alkanes give only two types of reactions.

(*A*) *Substitution Reactions*; *and*

(*B*) *Thermal and Catalytic Reactions.*

A. SUBSTITUTION REACTIONS

In these reactions, one or more of the H-atoms of alkane are substituted by either atoms like chlorine and bromine or by certain groups like nitro ($-NO_2$), sulphuric ($-SO_3H$), etc. Some of the most common reactions shown by alkanes are given below.

(1) **Halogenation.** It involves the substitution of H-atoms of alkanes by as many halogen atoms *i.e.*, by chlorine (*chlorination*); by bromine (*bromination*); by iodine (*iodination*); or by fluorine (*fluorination*). The order of reactivity of halogens in this regard is

$$F_2 > Cl_2 > Br_2 > I_2.$$

(a) **Chlorination.** The chlorination of alkanes can be brought about by the reaction of chlorine on them in the presence of diffused sunlight or ultraviolet light, or when heated to high temperature (300—400°).

Methane reacts with chlorine in the presence of ultraviolet light or at high temperature (300°C) to yield methyl chloride or chloromethane and hydrogen chloride.

$$\underset{\text{methane}}{CH_4} + Cl_2 \xrightarrow[\text{or } \Delta]{\text{UV light}} \underset{\substack{\text{methyl chloride,}\\ \text{chloromethane}}}{CH_3Cl} + HCl$$

The reaction does not stop at this stage and the remaining three H-atoms of methyl-chloride can be successively replaced by chlorine atoms.

$$CH_3Cl + Cl_2 \xrightarrow[\text{or } \Delta]{\text{UV light}} \underset{\substack{\text{methylene chloride,}\\ \text{dichloromethane}}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \longrightarrow \underset{\substack{\text{chloroform,}\\ \text{trichloromethane}}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \longrightarrow \underset{\substack{\text{carbon tetrachloride,}\\ \text{tetrachloromethane}}}{CCl_4} + HCl$$

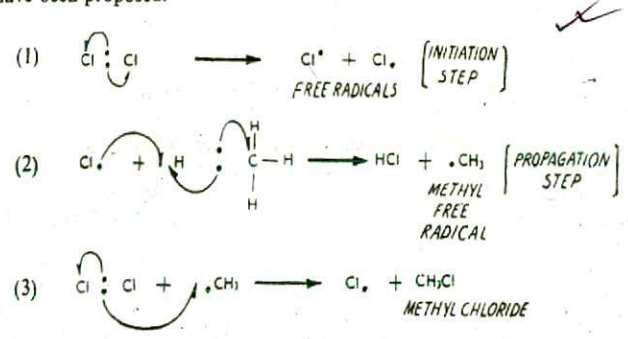
In actual practice all the four (CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4) substitution products are obtained. The extent to which each product is formed depends on the initial chlorine to methane ratio. The resulting mixture may be separated by fractional distillation.

Ethane and higher alkanes react with chlorine in a similar way and all possible substitution products are obtained. Thus, in the first instance, the chlorination of propane yields both 1-chloro and 2-chloropropanes.

$$CH_3CH_2CH_3 \begin{cases} \nearrow CH_3CH_2CH_2Cl & \text{1-chloroparone} \\ \searrow CH_3CHClCH_3 & \text{2-chloropropane} \end{cases}$$

Generally speaking, a tertiary hydrogen is more readily replaced than a secondary one, and a secondary more readily than a primary hydrogen.

Mechanism of Chlorination. The chlorination of alkanes takes place through the formation of free radicals as intermediates. Thus, for the *chlorination of methane* the following steps have been proposed.



Then steps 2, 3 ; 2, 3 ; 2, 3 ; etc.

$$\text{(4)} \quad Cl\cdot + Cl\cdot \longrightarrow Cl{-}Cl$$
$$\text{(5)} \quad Cl\cdot + \cdot CH_3 \longrightarrow CH_3{-}Cl$$
$$\text{(6)} \quad CH_3\cdot + \cdot CH_3 \longrightarrow \underset{\text{ethane}}{CH_3{-}CH_3}$$

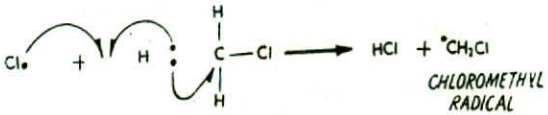
Termination steps

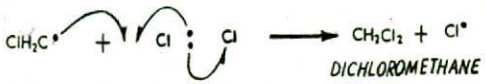
The reaction is initiated in step 1 by the homolytic fission of the chlorine molecule due to the action of heat or light resulting in the production of chlorine free radicals. This homolytic fission is an endothermic process and here requires 58 kcal/mole of energy. Hence the free radicals thus produced are 'energy rich chemical species' and can readily enter into bond formation by releasing energy.

In step (2), the chlorine free radical attacks a molecule of methane to form a stable molecule of HCl and a methyl free radical. In step (3) the methyl free radical reacts with chlorine molecule to yield methyl chloride and a chlorine free radical. The chlorine free radical can again attack another molecule of methane as in step (2). The sequence of reactions in steps (2) and (3) is repeated over and over again, and thus the chain reaction is propagated.

The chain reaction taking place by steps (2) and (3) comes to a halt if a chlorine free radical meets another chlorine free radical to from a chlorine molecule in step (4); or if a chlorine free radical meets a methyl radical to produce a molecule of methyl chloride as in step (5) : or if two methyl radicals combine to give ethane as shown in step (6). The steps 4, 5 and 6 which form stable terminal products are referred to as the '*Termination steps*'. On the other hand, since steps (2) and (3) produce a molecule of the product and also a free radical to continue the chain, these are called '*Chain propagation steps*'. The first step which generates the free radicals is called 'Chain initiation step' because without these free radicals the reaction would not start. Thus truly speaking, as illustrated above a free radical mechanism, in general has three major steps namely *initiaton*, *propagation* and *termination*.

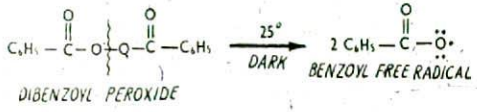
When the concentation of methyl chloride produced as a result of chain propagation steps increases sufficiently, then it can combine with a chlorine free radical to produce chloromethyl radical and HCl. This radical participates further in chain reaction to form dichloromethane (methylene chloride) and chlorine free radical which can continue the chain by reacting with another molecule of CH_3Cl.





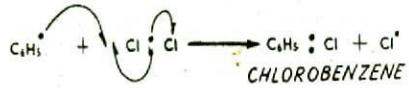
Similarly trichloromethane (chloroform) and tetrachloromethane (carbon tetrachloride) are obtained by further chain reactions.

Evidence for the Free Radical mechanism. If the reaction actually follows the above mechanism, then the addition of substances that are sources of free radicals should initiate the reaction even in the dark at room temperature. This is actually so. Methane reacts with chlorine in the dark at room temperature in the presence of catalytic amounts of dibenzoyl peroxide.





Phenyl free radical then reacts with a chlorine molecule to produce a chlorine free radical.



Once the chlorine free radicals are produced, the reaction can proceed in the manner described above.

What is Inhibition ?. The free radical mechanism also explains why the presence of a small amount of oxygen slows down the reaction. This is due to the fact that methyl free radial $CH_3\cdot$ reacts with an oxygen molecule to give a much less reactive $CH_3—O—O\cdot$ free radical. This contributes very little towards the propagation of the chain reaction and its lesser activity slows down the reaction considerably.



Such a substance that slows down or stops a reaction even though present in small amounts is called an **Inhibitor** *and the process is called* **Inhibition**. The time for which the inhibition lasts depends upon the amount of oxygen. After all tne oxygen has reacted with methyl free radicals, the reaction proceeds normally. This period during which inhibition lasts and after which the reaction proceeds normally, is called the **inhibition period**.

(*b*) **Bromination.** Bromine reacts upon alkanes in a manner similar to chlorine but less vigorously. The substitution products obtained are exactly similar. Thus methane gives

CH_3Br	CH_2Br_2	$CHBr_3$	CBr_4
bromomethane, methyl bromide	dibromomethane, methylene bromide	tribromomethane, bromoform	tetrabromomethane, carbon tetrabromide

(*c*) **Iodination.** Iodine reacts with alkanes reversibly. The hydrogen iodide formed as the by-product is a powerful reducing agent and is capable of reducing the iodoalkane to the alkane.

$$CH_4 + I_2 \rightleftharpoons \underset{\text{methyl iodide}}{CH_3I} + HI$$

However, alkanes can be iodinated in the presence of an oxidising agent such as iodic acid (HIO_3) or nitric acid which destroys the hydriodic acid (HI) as it is formed.

$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

(*d*) **Fluorination.** Fluorine is the most reactive of the halogens towards alkanes. Pure fluorine reacts with alkanes explosively under most conditions. Fluoroalkanes can, however, be obtained from alkanes by the action of fluorine diluted with nitrogen.

In the halogenation of propane and higher alkanes, all the possible halogenated products are formed. It has been observed that the order of reactivity of different hydrogens in alkanes is as follows :

Tertiary > Secondary > Primary

Thus the chlorination of n-butane yields both the isomers *i.e.*, 1-chlorobutane and 2-chlorobutane but the latter is obtained in greater mount.

$$\underset{\text{n-butane}}{CH_3CH_2CH_2CH_3} \xrightarrow[300—400°]{Cl_2} \underset{\substack{\text{1-chlorobutane}\\(32\%)}}{CH_3CH_2CH_2CH_2Cl} + \underset{\substack{\text{2-chlorobutane}\\(68\%)}}{CH_3\overset{\overset{Cl}{|}}{C}HCH_2CH_3}$$

This shows that a secondary H-atom is substituted more readily than a primary H-atom.

(2) **Nitration** (*Substitution of —NO_2 group for H*). At ordinary temperatures alkanes do not react with nitric acid. However, when a mixture of an alkane and nitric acid vapours is heated at 400° to 500°C, one hydrogen atom on the alkane is substituted by a nitro group (—NO_2). The process is called **vapour phase nitration**, and yields a class of compounds called *nitroalkanes*.

$$\underset{\text{alkane}}{R—H} + \underset{\text{nitric acid}}{HO—NO_2} \xrightarrow{400—500°} \underset{\text{nitroalkane}}{R—NO_2} + H_2O$$

$$\underset{\text{methane}}{CH_3—H} + HO—NO_2 \xrightarrow{450°} \underset{\text{nitromethane}}{CH_3—NO_2} + H_2O$$

The reaction is more complicated than suggested above. Since the reaction is carried out at high temperatures, the rupture of carbon-carbon bonds occurs during the process. Thus ethane actually gives a mixture of nitroethane and nitromethane.

MECHANISM. Nitration, like halogenation, also proceeds by a free radical mechanism. Thus nitration of ethane can be explained as follows.

(*i*) $2HNO_3 \xrightarrow{-H_2O} N_2O_5 \longrightarrow \underset{\text{(free radicals)}}{\cdot NO_2 + .NO_2}$

(*ii*) $CH_3—CH_3 + \cdot NO_2\ (\cdot NO_2) \longrightarrow \underset{\text{ethyl free radical}}{CH_3—CH_2\cdot} + HNO_2(HNO_3)$

(*iii*) Since $\cdot NO_2$ exists as

$$\underset{\text{(nitro group)}}{O=N\rightarrow O} \text{ or } \underset{\text{(nitrite radical)}}{\dot{O}—N=O}$$

$$CH_3—CH_2\cdot + \cdot NO_2 \longrightarrow \underset{\text{nitroethane}}{CH_3CH_2NO_2} + \underset{\text{ethyl nitrite}}{CH_3CH_2—O—N=O}$$

(*iv*) $CH_3CH_2—O—N=O \longrightarrow CH_3—CH_2—O + \cdot N=O$

(v) $CH_3-CH_2-O \longrightarrow {}^{\bullet}CH_3 + CH_2=O$ (FORMALDEHYDE)

(vi) $CH_3^{\bullet} + {}^{\bullet}NO_2 \longrightarrow CH_3NO_2$ (from step 1) — nitromethane

Thus as shown in steps (*iii*) and (*vi*) a mixture of nitroethane and nitromethane is produced.

The nitration of propane yields a mixture of four nitroalkanes.

$$\underset{\text{propane}}{CH_3CH_2CH_3} \xrightarrow{+HNO_3} \underset{\text{1-nitropropane}}{CH_3CH_2CH_2NO_2} + \underset{\text{2-nitropropane}}{CH_3CH(NO_2)CH_3} + \underset{\text{nitroethane}}{CH_3CH_2NO_2} + \underset{\text{nitromethane}}{CH_3NO_2}$$

Fractional distillation of this mixture gives commercial quantities of the individual components.

Again as in the case of halogenation, tertiary hydrogen atoms are the ones most easily replaced.

$$\underset{\text{isobutane, 2-methylpropane}}{(CH_3)_3CH} + HNO_3 \xrightarrow{150^\circ} \underset{\text{tert-nitrobutane, 2-nitro-2-methylpropane}}{(CH_3)_2C(NO_2)CH_3}$$

Nitroalkanes are used as solvents, fuels and starting materials for the synthesis of other types of aliphatic compounds.

(3) **Sulphonation** (*Substitution of-SO_3H for H*). At ordinary temperatures neither concentrated nor fuming sulphuric acid reacts with alkanes. However, when alkanes are subjected to a prolonged reaction with fuming sulphuric acid, one hydrogen atom on the alkane is replaced by a sulphonic acid group (—SO_3H). This process is called *sulphonation* and the products are *alkylsulphonic acids.*

$$R-H + HO\,SO_3H \xrightarrow{\Delta} \underset{\text{alkylsulphonic acid}}{R-SO_3H} + H_2O$$

where R is C_6H_{13}— or larger alkyl group.

$$\underset{\text{n-hexane}}{C_6H_{13}-H} + HO\,SO_3H \xrightarrow{\Delta} \underset{\text{hexylsulphoic acid}}{C_6H_{13}-SO_3H} + H_2O$$

The lower alkanes do not react unless they have a tertiary H-atom because the ease of replacement of hydrogen atoms is : tertiary > secondary > primary.

MECHANISM. Sulphonation like halogenation and nitration also proceeds by the following possible mechanism.

$$HO-SO_3H \xrightarrow{400^\circ} HO^{\bullet} + {}^{\bullet}SO_3H$$

$$C_6H_{13}-H + HO^{\bullet} \longrightarrow C_6H_{13}^{\bullet} + H_2O$$

$$C_6H_{13}^{\bullet} + {}^{\bullet}SO_3H \longrightarrow \underset{\text{hexylsulphonic acid}}{C_6H_{13}SO_3H}$$

(4) **Chlorosulphonation** (*Substitution of —SO_2Cl for H*). When alkanes are treated with a mixture of sulphur dioxide and chlorine in the presence of ultraviolet light, a hydrogen atom of the alkane is replaced by a chlorosulphonyl group ($-SO_2Cl$).

$$\underset{\text{propane}}{CH_3CH_2CH_3} + 2SO_2 + 2Cl_2 \xrightarrow[50^\circ]{\text{UV light}} \underset{\text{1-propane sulphonyl chloride}}{CH_3CH_2CH_2SO_2Cl} + \underset{\text{2-propanesulphonyl chloride}}{CH_3\underset{\displaystyle SO_2Cl}{\underset{|}{C}}HCH_3} + 2HCl$$

MECHANISM. Chlorosulphonation of alkanes proceeds by free radical mechanism as follows.

$$Cl_2 \longrightarrow 2Cl\cdot$$
$$RH + Cl\cdot \longrightarrow R\cdot + HCl$$
$$R\cdot + SO_2 \longrightarrow RSO_2\cdot$$
$$RSO_2\cdot + Cl_2 \longrightarrow RSO_2Cl + Cl\cdot$$

Chlorosulphonation is used commercially in the preparation of sodium alkyl sulphonate detergents from alkanes. This involves the chlorosulphonation of C_{14}—C_{16} petroleum fractions, followed by sodium hydroxide hydrolysis.

B. THERMAL AND CATALYTIC REACTIONS

(5) **Oxidation**. When ignited in the presence of sufficient excess of oxygen, alkanes burn to form carbon dioxide and water. The combustion of these hydrocarbons is accompanied by the evolution of large quantities of heat.

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

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + 213 \text{ kcal}$$

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3 + \frac{25}{2}O_2 \longrightarrow 8CO_2 + 9H_2O + 1223 \text{ kcal}$$

The heat of combustion increases with molecular weight. The widespread use of these hydrocarbons as fuels is due to their high heat of combustion.

When burnt in insufficient supply of oxygen, they form carbon monoxide and carbon (*carbon black*). Thus,

$$2CH_4 + 3O_2 \longrightarrow 2CO + 4H_2O$$
$$CH_4 + O_2 \longrightarrow C + 2H_2O$$

The oxidation of alkanes does not have to proceed to completion. For example, the partial oxidation of methane at 1500° produces acetylene.

$$6CH_4 + 2O_2 \xrightarrow{1500^\circ} \underset{\text{acetylene}}{2HC{\equiv}CH} + 2CO_2 + 10H_2$$

This reaction has become an important method for large scale production of acetylene.

The oxidation of alkanes is a free radical chain process which is much more complex than halogenation.

(6) **Pyrolysis (Cracking)**. The decomposition of a compound by heat is called *pyrolysis* (Greek, pyro-fire ; *lysis*-loosening). This process when applied to alkanes is known as *cracking*.

When alkanes are heated to a high temperature in the absence of air, pyrolysis or a 'thermal decomposition' occurs. Large alkane molecules are broken down or 'cracked' to give a mixture of smaller, lower molecular weight *alkanes*, *alkenes* and *hydrogen*. Pyrolysis generally requires temperatures in the range 500–800°. However, in the presence of a catalyst (finely divided silica-alumina) reactions can be carried at less high temperatures and this is called **catalytic cracking**.

Ethane when heated to 500° in the absence of air gives a mixture of methane, ethylene and hydrogen.

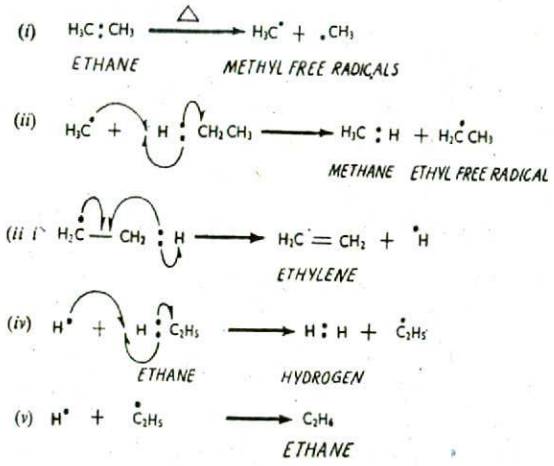
$$\underset{\text{ethane}}{3CH_3CH_3} \xrightarrow{500^\circ} \underset{\text{ethylene}}{2H_2C{=}CH_2} + H_2 + \underset{\text{methane}}{2CH_4}$$

Propane when pyrolysed at 600° gives a mixture of propylene, ethylene, methane and hydrogen.

$$\underset{\text{propane}}{2CH_3CH_2CH_3} \xrightarrow{600^\circ} \underset{\text{propylene}}{CH_3{-}CH{=}CH_2} + H_2 + \underset{\text{ethylene}}{CH_2{=}CH_2} + \underset{\text{methane}}{CH_4}$$

Larger molecules yield even more complex mixtures because the initial products can also undergo further pyrolysis.

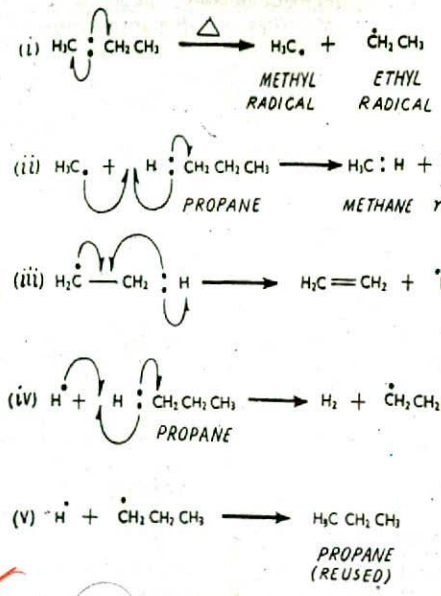
MECHANISM. The pyrolysis or cracking of alkanes occurs by free radical mechanism. The following mechanism has been proposed for the cracking of ethane.



Step (*i*) involves the decomposition of ethane due to the action of heat. The carbon-carbon bond in ethane dissociates (Homolytic fission) to give two methyl free radicals. In step (*ii*), a methyl free radical attacks ethane to produce methane and ethyl free radical. In step (*iii*) ethyl free radical gives ethylene and a hydrogen free radical. Step (*iv*) involves the attack of hydrogen free radical on ethane to produce molecular hydrogen and ethyl free radical. Steps (*iii*) and (*iv*) are repeated over and over again. They lead to the formation of ethylene and hydrogen. Methane is formed (step *ii*) only in very small quantity. Experimentally, ethylene and hydrogen are found to be the major products.

Unreacted ethyl free radicals and hydrogen free radicals undergo combination to regenerate ethane (step *v*) which can further take part in the reaction.

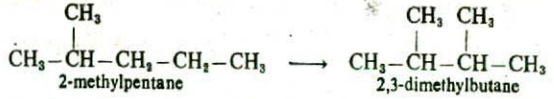
The free radical mechanism of the cracking of propane to give methane, propylene, ethylene and hydrogen may be depicted as follows.



(7) **Isomerisation.** *The molecular rearrangement of one isomer into one or more other isomers is called isomerisation.* Normal alkanes are converted to their branched-chain isomers in the presence of aluminium chloride and hydrogen chloride at 25°.



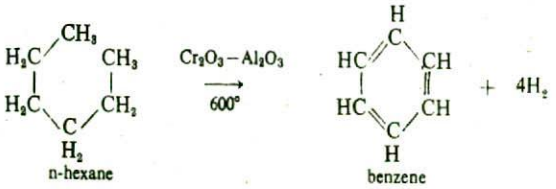
Similarly other less branched alkanes isomerise to the more branched ones. Thus,



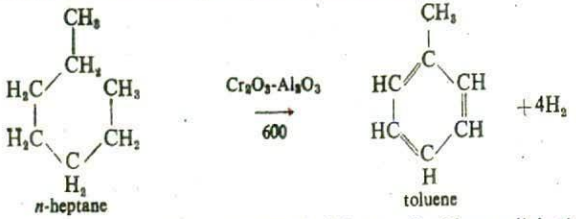
Isomerisation is used to increase the branched chain content of lower alkanes produced by cracking, as branched chain alkanes are more valuable than *n*-alkanes in motor spirit.

(8) **Aromatisation.** Alkanes containing six to ten carbon atoms are converted into benzene and its homologues at high temperature and in the presence of a catalyst. The process called *aromatisation* takes place by simultaneous dehydrogenation and *cyclization* of an alkane to give the aromatic hydrocarbon containing the same number of carbon atoms.

Thus when n-hexane is passed over Cr_2O_3 supported over alumina at 600°, benzene is produced.



Under similar conditions, n-heptane yields toluene.



n-heptane toluene

Aromatisation provides a good method for passing from aliphatic to aromatic series. This has been used for the preparation of aromatic hydrocarbons from alkanes derived from petroleum.

INDIVIDUAL MEMBERS

METHANE, CH_4

It is the first member of the alkane series. It is also called *marsh gas* because it is found bubbling from marshy places where it is produced as a result of bacterial decomposition of dead vegetable matter. It also occurs under pressure in many coal seams. The coal miners call it *fire damp* because it forms explosive mixtures with air. The biggest source of methane is *natural gas* issuing from the petroleum wells and it contains 85 per cent methane. It also occurs in coal gas up to the extent of 35 per cent.

Preparation. Methane can be prepared by the general methods of preparation 2, 3, 6.

LABORATORY METHODS. Methane is obtained in the laboratory by the following methods.

(1) By the decarboxylation of sodium acetate with sodalime,

$$\underset{\text{Sod. aceate}}{CH_3COONa} + NaOH \xrightarrow{\Delta} \underset{\text{methane}}{CH_4} + Na_2CO_3$$

(2) By the reduction of methyl iodide with zinc-copper couple and methyl alcohol.

$$\underset{\text{methyl iodide}}{CH_3I} + 2[H] \longrightarrow \underset{\text{methane}}{CH_4} + HI$$

This method is particularly useful when a pure sample of methane is needed.

OTHER METHODS. (.) Methane can also be prepared by the action of water on aluminium carbide.

$$\underset{\text{aluminium carbide}}{Al_4C_3} + 12H_2O \longrightarrow 4Al(OH)_3 + \underset{\text{methane}}{3CH_4}$$

(2) By the bacterial fermentation of wet cellulose material.

$$\underset{\text{cellulose}}{(C_6H_{10}O_5)_n} + n\,H_2O \longrightarrow 3n\,CO_2 + \underset{\text{methane}}{3n\,CH_4}$$

This is also an industrial method used in great Britain where large volumes of the gas are produced from sewrage stuff.

(3) By the direct combination of carbon and hydrogen in the electric arc.

$$C + 2H_2 \xrightarrow{1200^\circ} \underset{\text{methane}}{CH_4}$$

This provides a method for the 'total synthesis' (synthesis from elements) of many organic compounds which can be produced from methane.

(4) By passing a mixture of carbon monoxide and hydrogen over nickel at 200-500° C.

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$

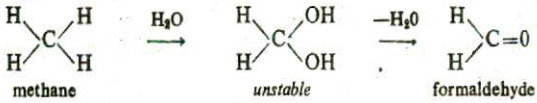
(5) Large quantities of methane are obtained by the cracking of petroleum as also from natural gas.

Properties. Methane is a colourless gas, insoluble in water but soluble in organic solvents like acetone, ether and alcohol It has all the properties of alkanes discussed earlier. Some of its characteristic reactions are :

(1) Methane reacts violently with chlorine in presence of sunlight to produce carbon and hydrogen chloride.

$$CH_4 + 2Cl_2 \xrightarrow{\text{sunlight}} C + 4HCl$$

(2) On incomplete oxidation in air at 350°-500°C or by oxidation with ozone, methane is converted to formaldelyde.



(3) It reacts with steam in the presence of nickel catalyst yielding carbon monoxide.

$$CH_4 + H_2O \xrightarrow[Ni]{1000^\circ} CO + 3H_2$$

This reaction is used for the industrial production of hydrogen.

(4) On pyrolysis at 1000°, methane gives carbon and hydrogen.

$$CH_4 \xrightarrow{1000^\circ} C + 2H_2$$

This free carbon is known as 'carbon black' and finds use in paints, black printing ink and in the production of automobile tyres.

(5) According to a most recent cracking process, methane (from natural gas) is converted to acetylene by subjecting it to high temperature produced by partial combustion.

$$2CH_4 \longrightarrow HC{\equiv}CH + \text{other products}$$

Acetylene in turn is a source of numerous aliphatic and aromatic compounds.

(6) Methane is converted to hydrogen cyanide (HCN) by reaction with nitrogen or ammonia as follows (*Industrial*).

$$2CH_4 + N_2 \xrightarrow[arc]{\text{electric}} 2HCN + 3H_2$$

$$CH_4 + NH_3 \xrightarrow[Al_2O_3]{1000^\circ} HCN + 3H_2$$

Uses. Methane is used : (1) as *illuminant* and *domestic fuel* ; (2) for making 'carbon black' needed for paints, printing inks and automobile tyres ; (3) for the preparation of CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 ; (4) for the technical production of methyl alcohol, *formaldehyde*, acetylene and hydrogen cyanide.

ETHANE, C_2H_6

It is the second member of the homologous series of alkanes. Ethane occurs to the extent of 10—21 per cent alongwith methane in natural gas. In small amounts it is present in coal gas and in 'cracked petroleum' products.

Preparation. Ethane can be prepared by all the general methods of preparation of alkanes discussed before.

LABORATORY METHODS. It is prepared in the laboratory by the following methods.

(1) By electrolysis of a concentrated solution of sodium or potassium acetate (*Kolbe's method*).

$$\underset{\text{sod. acetate}}{2CH_3COONa} + 2H_2O \longrightarrow \underset{\text{ethane}}{CH_3CH_3} + 2CO_2 + 2KOH + H_2$$

(2) A pure sample of ethane is prepared by the reduction of ethyl iodide with Zn—Cu couple and ethyl alcohol mixed with 5 per cent water.

$$\underset{\text{ethyl iodide}}{C_2H_5I} + 2H \xrightarrow[C_2H_5OH]{Zn/Cu} \underset{\text{ethane}}{C_2H_6} + HI$$

COMMERCIAL METHODS. (1) Ethane is prepared commercially by the fractional distillation of 'wet' natural gas.

(2) Ethane is also obtained on a large scale by cracking of long-chain alkanes during the refining of petroleum.

Properties (*Physical*). Ethane is a colourless gas, b.p. $-89°$. It is sparingly soluble in water and readily soluble in ethyl alcohol.

(*Chemical*). It gives all the general reactions of alkanes.

(1) It burns in air or oxygen to form carbon dioxide and water.

$$2C_2H_6 + 7O_2 \longrightarrow 4CO_2 + 6H_2O + 736{\cdot}8 \text{ cals}$$

(2) It reacts with halogens in a similar manner to methane to form substitution products. The number of substitution products with ethane is quite large when compared to methane. Firstly because it contains six H-atoms (instead of four in methane) and secondly because of the fact that isomerism is possible in its substitution products. Thus two dichloroethanes are possible *viz. gem* and *vicinal*.

$CH_3—CHCl_2$	$CH_2Cl—CH_2Cl$
gem .dichloroethane or 1,1-dichloroethane	vic. dichloroethane or 1, 2-dichloroethane

(3) Ethane when heated in the absence of oxygen and in the presence of a catalyst at 450°C, dehydrogenates to produce ethylene.

$$\underset{\text{ethane}}{CH_3—CH_3} \xrightarrow[\text{cat.}]{450°C} \underset{\text{ethylene}}{CH_2=CH_2} + H_2$$

This provides an important method for the preparation of ethylene on a large scale from natural gas.

Uses. Ethane is used for making chloroethanes. It is produced on a large scale in United States of America and used to make ethene by catalytic dehydrogenation. Ethene is again a starting material for a wide variety of important products.

CONFORMATIONS OF ALKANES

Free rotation is possible around C—C single bonds. The different arrangements of a molecule that can be obtained by rotation around C—C single bonds are called **Conformations** or **Conformational Isomers.**

Conformations of Ethane

Let us consider ethane ($H_3C—CH_3$). The carbon atoms in ethane are not frozen in space. The two methyl groups can rotate about the C—C bond. As a result, an infinite number of spatial arrangements (called

conformations) of ethane are possible. There are two extreme forms : the **Staggered Conformation** and the **Eclipsed Conformation.** They can be represented by sawhorse or Newman projections, as shown in Figures 9.6 and 9.7.

In *sawhorse projection,* the carbon atom at the left of the structure is considered to be closer to the observer than is carbon at the right. In *Newman Projection,* one is viewing the C—C bond end-on along the axis of connection. The front carbon atom is represented by the intersection of bonds from it, while the rear carbon appears as a circle. Notice that the bonds of the rear carbon in the eclipsed form are shown slightly displaced simply to make them visible.

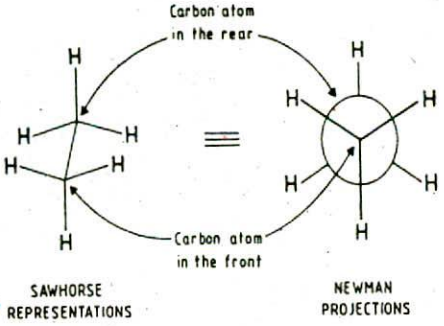


Fig. 9.6. Staggered conformation of ethane.

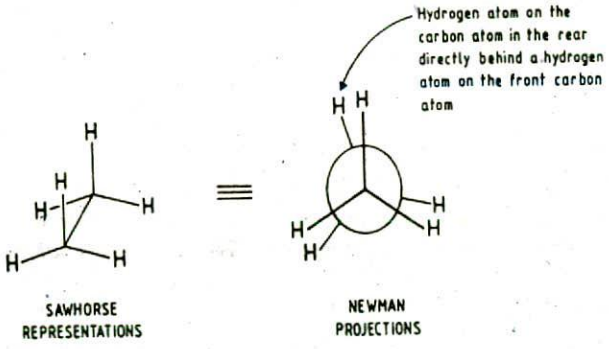
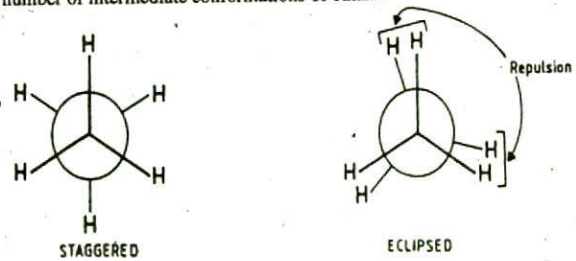


Fig. 9.7 Eclipsed conformation of ethane.

The staggered and eclipsed conformations of ethane can be regarded as **Rotational Isomers** (or **Rotamers),** because they can be converted into one another by rotation about the C—C bond. A rotation of 60° converts a staggered conformation into an eclipsed conformation, *vice versa.* Between these two extremes there is an infinite number of intermediate conformations of ethane.



The rotation around C—C bonds is often called **Free Rotation,** but it is not entirely free. The eclipsed conformation is about 3 kcal/mole *less* stable (of higher energy) than the staggered conformation because of repulsions between the hydrogen atoms. To undergo rotation from a staggered to an eclipsed conformation, a mole of ethane molecules would require 3 kcal. Since this amount of energy is readily available to molecules at room temperature, the rotation can occur easily. However, even though the conformations of ethane are interconvertible at room temperature, at any given time we would expect a greater percentage of ethane molecules to be in staggered conformation because of its lower energy. Figure 9.8 shows the energy difference between the staggered and eclipsed conformations of ethane. Staggered conformations are more stable than the eclipsed conformations.

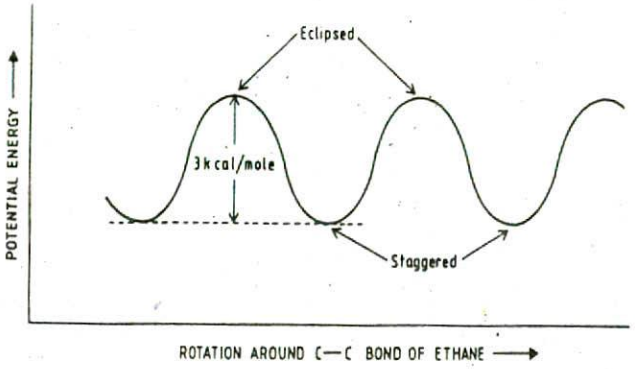


Fig. 9.8. Energy diagram showing energy difference between the staggered and eclipsed conformations of ethane.

The most important thing to remember about conformational isomers is that they are just different forms of a single molecule that can be interconverted by rotation about single (σ) bonds. Sufficient thermal energy for this rotation is available at room temperature. Consequently, at room temperature it is usually not possible to separate them from one another.

Conformations of Propane

The conformations of propane ($CH_3CH_2CH_3$) are similar to those of ethane except that one of the hydrogen atoms is replaced by a methyl group. The two extreme conformations (eclipsed and staggered) of propane are shown in Figure 9.9.

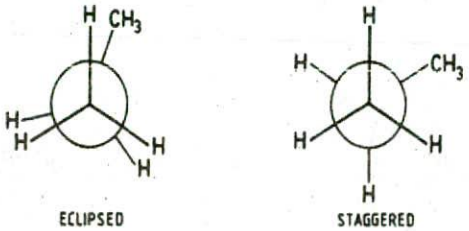


Fig. 9.9. Conformations of propane.

Conformations of Butane

Butane (CH_3CH_2—CH_2CH_3), like ethane, can exist in eclipsed and staggered conformations. In butane, there are two relatively large methyl groups attached to the centre two carbons. Viewing butane from the centre two carbons, the presence of these methyl groups gives rise to two types of staggered conformation that differ in the positions of the methyl groups in relation to each other. The staggered conformations in which the methyl groups are the maximum distance apart are called the **Anti conformation.** The staggered conformations in which the methyl groups are closer are called **Gauche conformations.** Newman projections for one-half rotation are shown in Figure 9.10.

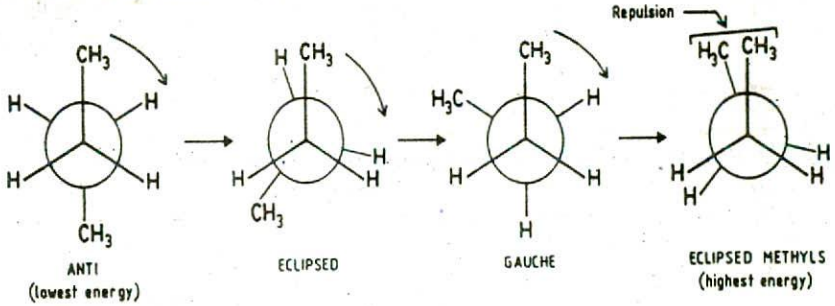


Fig. 9.10. Partial rotation around C2—C3 bond of butane (rear carbon rotating).

The larger the groups attached to two carbons, the greater is the energy difference between the molecule's conformations, It takes more energy to push two bulky groups together than two small groups. While it takes only 3 kcal/mole for ethane to rotate from staggered to eclipsed conformation, it takes 4—6 kcal, mole for butane to rotate from *anti* to the conformation in which the methyls are eclipsed. Fig. 9.11 shows energy relationship of the complete rotation around the C2—C3 bond of butane.

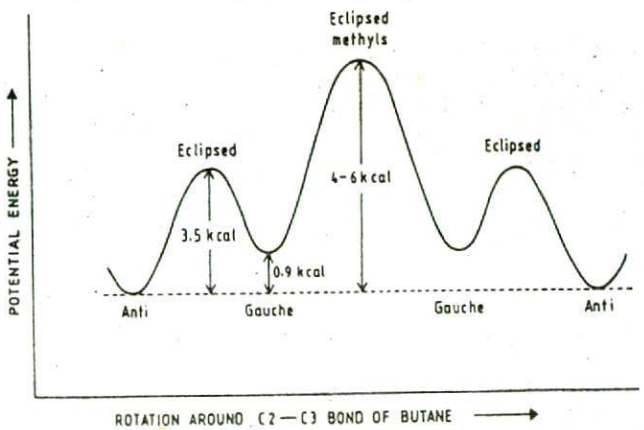


Fig. 9.11. Energy diagram showing energy differences between various conformations of butane.

In larger alkanes too, the most stable conformations are generally staggered, with the largest groups *anti* to each other. The *gauche* conformations are only slightly less stable than the *anti* ones, and are also present. Thus, while the structural formulas of alkanes are usually written in a straight line for convenience, it is important to keep in mind the zig-zag nature of hydrocarbon chains.

IDENTIFICATION OF ALKANES

Because alkanes have no functional groups, they are usually identified on the basis of their non-reactivity rather than their transformations to other molecules. Alkanes are often identified by means of their physical properties such as boiling points, melting points, densities, and refractive indices. They are insoluble in water, dil NaOH, dil HCl and conc H_2SO_4.

Infrared Spectra of Alkanes. The alkanes show characteristic infrared spectra which are helpful in determining their structure. For example, the infrared spectrum of normal hexane indicates that there is maximum absorption (or minimum transmittance) at the wave number 2882—2940 and 1370—1452 which correspond to the presence of —C—H and C—C bonds.

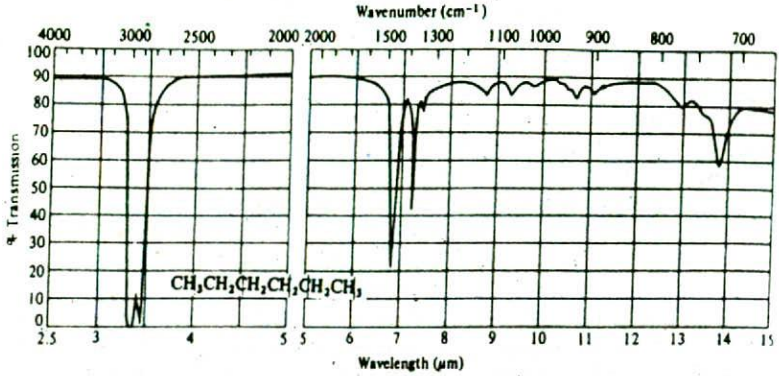


Fig 9·12. **Infrared spectrum of n-Hexane**

QUESTIONS

1. What are alkanes ? Why are they called saturated hydrocarbons ?

2. Draw neatly the molecular orbital structure of methane and ethane. Label the hybridization of each orbital. On a separate diagram containing only the atomic symbols and bonds show the theoretical bond angles.

3. Give IUPAC names for the following alkanes.

(*a*) $CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

(*b*) $CH_3-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

(*c*) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

(*d*) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

4. Draw all hydrocarbon structures possible for the molecular formula C_5H_{12}. Identify the primary, secondary and tertiary hydrogen atoms in these structures. Name each according to the IUPAC system.

5. Give the general methods of preparation of alkanes, taking example of propane.

6. How would you synthesise the following :—
   (*a*) n-butane from ethane.
   (*b*) benzene from n-hexane.
   (*c*) benzene from propane.
   (*d*) 2, 3-dimethylbutane from isopropyl bromide.

7. How do the physical properties of the members of the methane series of hydrocarbons vary with the increase of the number of carbon atoms ?

8. Complete the following equations:

(a) $CH_3CH_2OH + HI \xrightarrow[150^\circ]{P}$

(b) $CH_3CH_2Br + Mg \xrightarrow{ether}$ (?)

(?) $+ H_2O \longrightarrow$

(c) $CH_3CH_2CH_3 \xrightarrow[\text{(absence of air)}]{500^\circ}$

(d) $CH_3CH_2CH_2CH_3 \xrightarrow[25^\circ]{AlCl_3-HCl}$

(e) $CH_3(CH_2)_4CH_3 \xrightarrow[600^\circ]{Cr_2O_3-Al_2O_3}$

(f) $CH_4 + Cl_2 \xrightarrow{UV\ light}$

(g) $CH_3CH_2CH_3 + SO_2 + Cl_2 \xrightarrow[50^\circ]{UV\ light}$

9. (a) How can ethane be prepared ?

(b) How does ethane react with the following reagents ?

(i) Br_2 ; in the presence of UV light at room temperature.

(ii) Cl_2 ; in the dark at room temperature.

(iii) HNO_3 ; at 400-500°C.

(iv) $SO_2 + Cl_2$; in the presence of UV light at 50°C.

(v) Upon heating to 500° in the absence of air.

10. Discuss the free radical mechanism for the chlorination of methane.

If 2-methylpropane were heated with chlorine in the presence of ultraviolet light, which hydrogen atom would likely be the first to be replaced by chlorine ?

11. How is that while chlorination and bromination of alkanes proceeds fairly readily, their direct iodination is not possible ? Describe the conditions under which iodo derivatives of alkanes can be obtained.

12. Discuss the mechanism of chlorination of methane. *(Madurai BSc, 1993 ; Devi Ahilya BSc, 1994)*

13. Discuss the mechanism of cracking of ethane. *(Punjab BSc, 1993)*

14. An alkane with molecular weight 72 formed only one monochloro substitution product. Suggest the structure of the alkane. *(Kerala BSc, 1994)*

Answer. $(CH_3)_4C$; 2,2-Dimethylpropane.

15. The compound with highest boiling point among the followings is :

(a) *n*-Hexane (b Neopentane

(c) *n*-Pentane (d) 2-Methylbutane

Answer. (a)

16. How will you synthesis :

(a) Ethane from Acetic acid

(b) *n*-Butane from Ethyl bromide *(Sri Venkateswara BSc, 1993)*

17. Write notes on :

(a) Wurtz reaction

(b) Conformations of ethane

(c) Conformations of butane *(Poona BSc, 1994)*

Cycloalkanes

Cycloalkanes or cycloparaffins are saturated hydrocarbons in which the carbon atoms are joined by single covalent bonds to form a ring. They are also known as **Alicyclic Compounds** (*aliphatic + cyclic*) because their properties are very similar to those of aliphatic hydrocarbons, the alkanes.

The unsubstituted cycloalkanes form a homologous series with the general formula C_nH_{2n}, where n is the number of carbon atoms in the molecule. The first member of he series has the molecular formula C_3H_6 and is known as cyclopropane. Cycloalkanes containitng up to fifty carbon atoms are known.

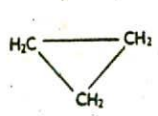
Cycloalkanes contain two hydrogen atoms less than the corresponding alkanes. Their general formula is the same as the one for alkenes. They are thus structural isomers of alkenes.

NOMENCLATURE

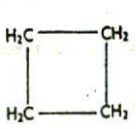
The naming of the cycloalkanes by the IUPAC rules is very similar to the naming of the alkanes.

1. The name of an unsubstituted cycloalkane is obtained by attaching the prefix *cyclo-* to the name of the corresponding normal alkane having the same number of carbon atoms as in the ring.
2. Substituents on the ring are named, and their positions are indicated by numbers. The ring is numbered so that the carbons bearing the substituents will have lowest possible numbers.

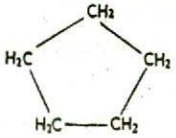
The following examples illustrate the application of these rules :



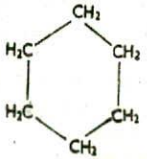
CYCLOPROPANE



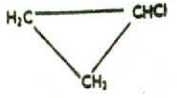
CYCLOBUTANE



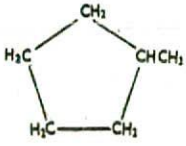
CYCLOPENTANE



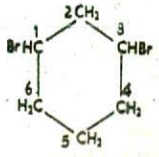
CYCLOHEXANE



CHLOROCYCLOPROPANE

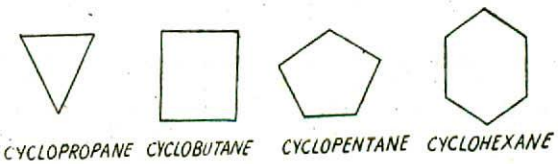


METHYLCYCLOPENTANE

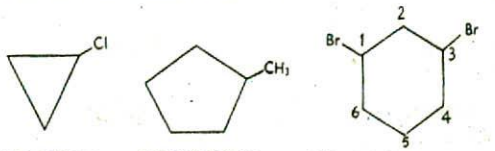


1,3-DIBROMOCYCLOHEXANE

Condensed Symbols for Cycloalkanes. For convenience and simplicity, aliphatic rings are often represented by simple geometric figures : a triangle for cyclopropane, a square for cyclobutane, a pentagon for cyclopentane, a hexagon for cyclohexane, and so on. It is understood that there is a CH_2 group at each corner unless some substituent is indicated. Thus,



CYCLOPROPANE CYCLOBUTANE CYCLOPENTANE CYCLOHEXANE



CHLOROCYCLO-PROPANE METHYLCYCLO-PENTANE 1,3-DIBROMOCYCLO-HEXANE

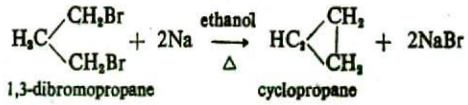
PREPARATION

Preparation of a cycloalkane from other aliphatic compounds generally involves two stages.

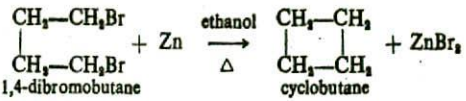
1. *Conversion of some compound that contains an open chain into a compound that contains a ring.* The process of conversion of an open-chain compound into a ring compound is called **Cyclization.**
2. *Conversion of the cyclic compound thus obtained into the kind of compound we want.*

There are many methods of forming cycloalkanes, but only a few of the most common procedures are given below.

1. **From Dihalogen Compounds.** Suitable dihalogen compounds on treatment with sodium or zinc give corresponding cycloalkanes. For example,



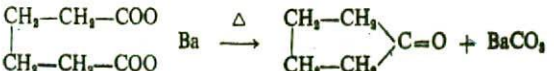
1,3-dibromopropane cyclopropane



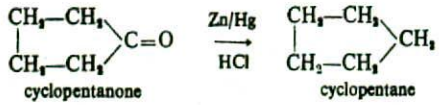
1,4-dibromobutane cyclobutane

This reaction is an extension of *Wurtz Reaction* and may be regarded as an **Internal Wurtz Reaction.** The reaction is useful for the preparation of three- to six-membered rings. With higher homologues various side reactions occur.

2. **From Calcium or Barium salts of Dicarboxylic acids.** When the calcium or barium salt of adipic, pimelic, or suberic acid is heated, a cyclic ketone is formed. Cyclic ketones may be readily converted into the corresponding cycloalkanes by means of the *Clemmensen Reduction.*

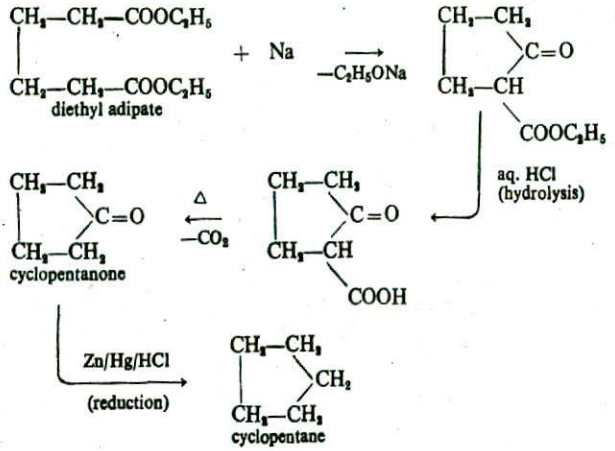


barium adipate cyclopentanone

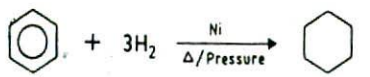


Cyclopropane cannot be prepared by this method.

3. **From Esters of Dicarboxylic acids (Dieckmann Reaction).** The diester of adipic, pimelic, or suberic acid when treated with sodium undergoes intramolecular acetoacetic ester condensation and a β-ketoester is formed. The β-ketoesters on hydrolysis give corresponding cyclic ketones. Cyclic ketones on reduction yield the corresponding cycloketones.



4. **From Aromatic Compounds.** Benzene may be catalytically hydrogenated at elevated temperature and pressure to yield cyclohexane.



PHYSICAL PROPERTIES

(1) Cyclopropane and cyclobutane are gases at ordinary temperatures; the remaining cycloalkanes are liquids. Their melting points and boiling points show a gradual rise with the increase in molecular weight.

(2) They are all lighter than water; the series has a limiting density of less than 0·9.

(3) They are insoluble in water but are soluble in organic solvents such as ethers and alcohols.

The physical constants of some selected cycloalkanes are given below

Compound	Structure	bp °C	mp °C	Density (g/ml at 20°)
Cyclopropane	$CH_2\,CH_2\,CH_2$	−32.8	−127.4	
Cyclobutane	$CH_2(CH_2)_2CH_2$	12.5	−90.7	0.694
Cyclopentane	$CH_2(CH_2)_3CH_2$	49·3	−93.9	0.745
Cyclohexane	$CH_2(CH_2)_4CH_2$	80.7	6.6	0.779
Cycloheptane	$CH_2(CH_2)_5CH_2$	118.8	−8·0	0.811
Cyclooctane	$CH_2(CH_2)_6CH_2$	151.1	−14·8	0.836
Cyclononane	$CH_2(CH_2)_7CH_2$	178.4	11	0.850
Cyclodecane	$CH_2(CH_2)_8CH_2$	202	10	0.858
Cycloundecane	$CH_2(CH_2)_9CH_2$	221	−7	0.862
Cyclododecane	$CH_2(CH_2)_{10}CH_2$	239	61	0.863
Cyclopentadecane	$CH_2\,(CH_2)_{13}\,CH_2$	286	62	0.859
Cyclohexadecane	$CH_2\,(CH_2)_{14}\,CH_2$	300	61	0.857

CHEMICAL PROPERTIES

Cycloalkanes resemble alkanes in their chemical behaviour.

(*a*) *They do not react with acids, bases, oxidizing agents and reducing agents.*

(*b*) *They undergo substitution reactions with halogens. However, cyclopropane and cyclobutane are the exceptions.* With certain reagents they undergo ring-opening and give addition products.

The more important reactions of cycloalkanes are given below.

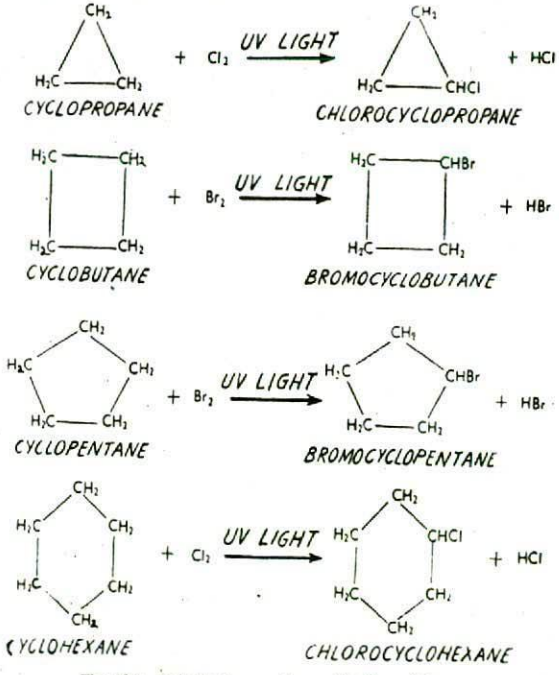


Fig. 10·1 Substitution reactions with Cl_2 and Br_2

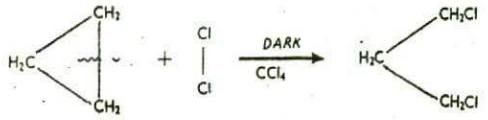
SUBSTITUTION REACTIONS WITH Cl_2 AND Br_2

1. Cycloalkanes react with Cl_2 and Br_2 in the presence of diffused sunlight or ultraviolet light to give a monochlorination and monobromination product respectively (Fig. 10·1).

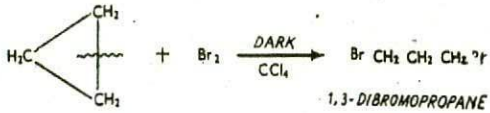
In each case only one monosubstitution product is possible because all hydrogens are chemically identical.

SPECIAL REACTIONS OF CYCLOPROPANE CYCLOBUTANE

2. **Addition of Cl_2 and Br_2.** Cyclopropane reacts with Cl_2 and Br_2 at room temperature and in the absence of diffused sunlight to produce 1,3-dichlorocyclopropane and 1,3-dibromocyclopropane respectively. One of the carbon-carbon bonds of cyclopropane is broken and the two halogen atoms appear at the ends of the propane chain.



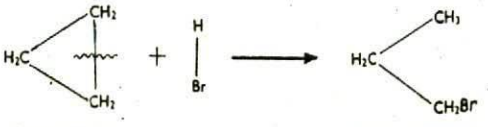
CYCLOPROPANE 1,3-DICHLOROPROPANE



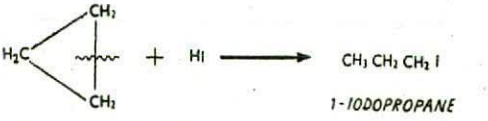
1,3-DIBROMOPROPANE

Cyclobutane and higher members of the family do not give this reaction.

3. **Addition of HBr and HI.** Cyclopropane reacts with conc HBr and HI to give 1-bromopropane and 1-iodopropane respectively.



CYCLOPROPANE 1-BROMOPROPANE

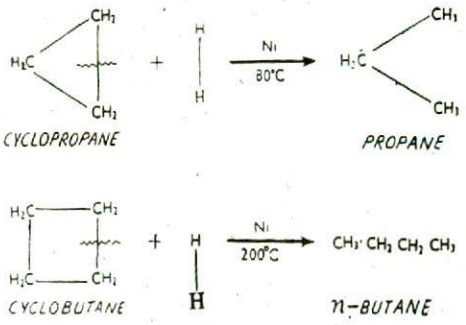


CYCLOPROPANE 1-IODOPROPANE

Cyclobutane and the higher members of the family do not give this reaction.

4. **Addition of Hydrogen; Calalytic Reduction.** Cyclopropane and cyclobutane react with hydrogen in the presence of a nickel catalyst to produce propane and n-butane respectively.

Hydrogenation of cyclobutane takes place at a higher temperature (200°C) than that required for cyclopropane (80°C).



Cyclopentane and higher members of the family do not give this reaction.

STABILITY OF CYCLOHEXANES — BAEYER STRAIN THEORY

In 1885 Adolf von Baeyer proposed a theory to explain the relative stability of the first few cycloalkanes. This theory named after him, accounted for the ease of opening of cyclopropane and cyclobutane rings as also the stability of the cyclopentane ring. He based his theory on the classical Le Bel and van't Hoff hypothesis that the four valencies of a carbon atom are directed towards the corners of a regular tetrahedron. Therefore, the normal angle between any pair of bonds of a carbon atom is 109°28′. Baeyer postulated that *any deviation of bond angles from the normal tetrahedral value would impose a condition of internal strain on the ring. He also assumed that all cyclic rings were planar* and thus calculated the angles through which each of the valency bonds was deflected from the normal direction in the formation of the various rings. This he called the **Angle strain** which determined the stability of the ring.

In cyclopropane, the three carbon atoms occupy the corners of an equilateral triangle. Thus cyclopropane has C—C—C bond angles of 60° (the internal angle of an equilateral triangle). This implies that the normal tetrahedral angle of 109°28′ between any two bonds is compressed to 60°, and that each of the two bonds involved is pulled in by $\frac{1}{2}(109°28′ - 60°) = 24°44′$ (Fig. 10·2). The value 24°44′ then represents the *angle strain* or the deviation through which each bond bends from the normal tetrahedral direction.

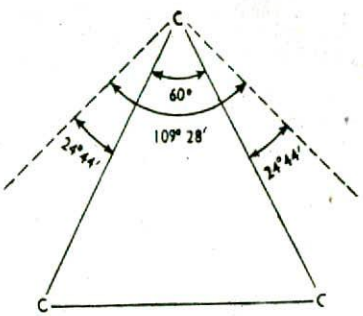


Fig. 10·2. Deviation of bond angles in cyclopropane molecule from normal tetrahedral angles.

In cyclobutane the four carbon atoms occupy the corners of a square. Thus cyclobutane has C—C—C bond angles of 90°. The deviation from the normal tetrahedral angle which each bond shows is, therefore,

$$\frac{1}{2}(109°28′ - 90°) = 9°44′.$$

In cyclopentane the five carbon atoms lie at the corners of a regular pentagon. Thus cyclopentane has C—C—C bond angles of 108°. The deviation from the normal tetrahedral angle which each bond shows is, therefore, $\frac{1}{2}(109°28′ - 108°) = 0·44′$.

In cyclohexane the six carbon atoms occupy the corners of a regular hexagon. Thus cyclohexane has C—C—C bond angles of 120°. The deviation from the normal tetrahedral angle which each bond shows is, therefore, $\frac{1}{2}(109°28′ - 120°) = -5°16′$

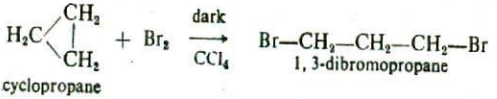
Similarly, in the case of cycloheptane the deviation from the normal tetrahedral angle is $-9°33'$. In the case of cyclooctane it comes out to be $-12°46'$.

The results from the above calculations are summarised below.

Cycloalkane	*Deviation from normal tetrahedral angle (Angle strain)*
Cyclopropane (C_3H_6)	$+25°44'$
Cyclobutane (C_4H_8)	$+9°44'$
Cyclopentane (C_5H_{10})	$+44'$
Cyclohexane (C_6H_{12})	$-5°16'$
Cycloheptane (C_7H_{14})	$-9°33'$
Cyclooctane (C_8H_{16})	$-12°46'$

The + sign indicates that the C—C bonds have to be compressed to satisfy the geometry of the ring. The − sign indicates that the C—C bonds have to be widened to satisfy the geometry of the ring. *Whether the angle strain is positive or negative, its magnitude determines the extent of strain in the ring.*

In the examples given above, the deviation from the normal tetrahedral angle is *maximum* in the case of cyclopropane. Thus according to the Baeyer Strain Theory, cyclopropane should be a highly strained molecule and consequently most unstable. The cyclopropane ring should, therefore, be expected to open up on the slightest provocation and thus releasing the strain within it. This is actually so. Cyclopropane is known to undergo ring opening reactions with Br_2, HBr, and H_2(Ni) to yield open chain addition compounds.



The deviation from the normal tetrahedral angle in the case of cyclobutane is *less* than that in case of cyclopropane. This signifies greater stability. Thus as expected, cyclobutane undergoes ring-opening reactions but only under more drastic conditions.

The deviation from the normal tetrahedral angle is *minimum* in the case of cyclopentane. This implies that cyclopentane is under least strain and should be most stable. Thus it is not surprising that cyclopentane does not undergo ring-opening reactions.

The deviation from the normal tetrahedral angle in the case of cyclohexane is *higher* than that in case of cyclopentane. The deviation increases continuously with increase in the number of carbon atoms in the ring. According to the Baeyer Strain Theory, cyclohexane and the higher cycloalkanes should become increasingly unstable and hence more reactive. Contrary to this prediction, cyclohexane and the higher homologues are found to be quite stable. They do not undergo ring-opening reactions. Instead they resemble open-chain alkanes in reactivity, that is, they react by substitution. Thus, the Baeyer Strain Theory satisfactorily accounts for the exceptional reactivity of cyclopropane, cyclobutane and cyclopentane, but it is not valid for cyclohexane and the higher cycloalkanes.

SACHSE-MOHR CONCEPT OF STRAINLESS RINGS

In order to account for the stability of cycloalkanes beyond cyclopentane, Sachse and Mohr (1918) pointed out *that such rings can become absolutely free of strain if all the ring carbons are not forced into one plane*, as was supposed by Baeyer. If the ring assumes a 'puckered' condition, the normal tetrahedral angles of $109°28'$ are retained and as a result, the strain within the ring is relieved. Thus cyclohexane can exist in two non-planar strainless forms, namely, the Boat form and the Chair form.

In the Boat form, carbons 1, 2, 4 and 5 lie in the same plane and carbons 3 and 6 above the plane. In the chair form, carbons 1, 2, 4 and 5 lie in the same plane, but carbon 6 is above the plane and carbon 3 is below it.

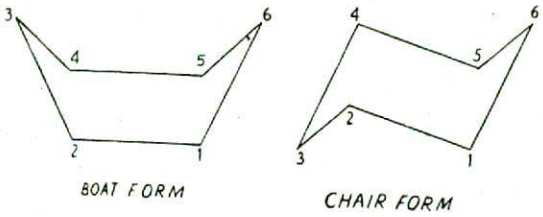


Fig. 10·3. Forms of cyclohexane.

Actually, only one form of cyclohexane is known and not two forms as shown above. The failure to isolate the two forms is ascribed to rapid interconversions between them.

Such non-planar strainless rings in which the ring carbon atoms can have normal tetrahedral angles are also possible for larger ring compounds.

Orbital Picture of Angle Strain. Let us now see what is the meaning of the Baeyer's angle strain in terms of the modern Molecular Orbital Theory.

We know that for a bond to form, two atoms must be involved so that an orbital of one atom overlaps with an orbital of the other atom. *For a given pair of atoms, the greater the overlapping of atomic orbitals, the stronger the bond.*

When carbon is bonded to four other atoms its bonding orbitals (sp^3 orbitals) are directed to the corners of a regular tetrahedron ; the angle between any pair of orbitals is thus 109°28′.

Formation of a C—C bond involves the overlapping of sp^3 orbitals of one carbon atom with a similar sp^3 orbital of the other carbon atom. The C—C bond will be strongest when an sp^3 orbital of one carbon overlaps with an sp^3 orbital of the other carbon atom to a maximum extent. This will happen only if the sp^3 orbitals overlap along their axes. As the axes of sp^3 orbitals are at angles of 109°28′ to each other, the C—C bonds will have their maximum strength if C—C—C bond angles have a value 109°28′.

Cyclopropane has C—C—C bond angles of 60°. Cyclobutane has C—C—C bond angles of 90°. The higher cycloalkanes or the n-alkanes have C—C—C bond angles of approximately 109°28′.

As shown in the following figure, the small bond angles of cyclopropane indicate that in cyclopropane the overlap of the sp^3 orbitals of carbons is *less* than the overlap of the sp^3 orbitals of carbons in n-alkanes (*e.g.*, propane).

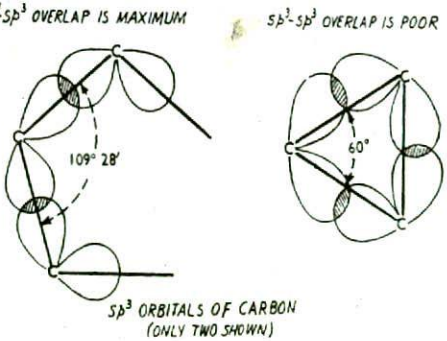
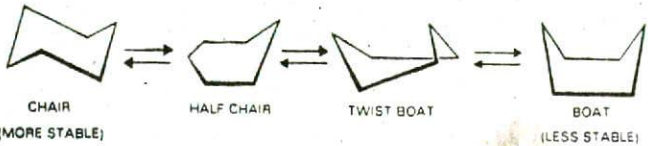


Fig. 10·4

The bond angles of cyclopropane are less than the bond angles of cyclobutane, which in turn are less than the bond angles of higher cycloalkanes or n-alkanes. Therefore, the overlap in cyclopropane is less than that in cyclobutane, which in turn is less than that in higher cycloalknes or n-alkanes. The overlap of sp^3 orbitals of carbons in cyclopentane, higher cycloalkanes or n-alkanes is maximum because in these cases it is possible for the sp^3 orbitals to overlap along their axes, the bond angles being approximately equal to 109°28′. This implies that the C—C bonds in cyclopropane are weaker than the C—C bonds of cyclobutane, which in turn are weaker than the C—C bonds in higher cycloalkanes and n-alkanes. Thus, it is not surprising that cyclopropane undergoes ring opening reactions very readily and more drastic conditions are required to bring about the cleavage of the cyclobutane ring. Cyclopentane and higher members, as expected, do not undergo ring opening reactions and behave very much like the alkanes.

CONFORMATIONS OF CYCLOHEXANE AND ITS DERIVATIVES

The cyclohexane ring can assume many shapes. A single cyclohexane molecule is in a continuous state of flexing or flipping into different shapes or conformations. Some of these shapes are shown below :



These conformations arise due to rotation around carbon-carbon bonds. The chair form and the boat form are the extreme cases.

Figure 10·5 shows the energy requirements for the interconversion of the different conformations of cyclohexane. Notice that the **chair form has the lowest energy**, while the half-chair has the highest energy. At any given time, we would expect most of the cyclohexane molecules to be in the chair form. Indeed, it has been calculated that about 99·9% of cyclohexane molecules are in the chair form at any one time.

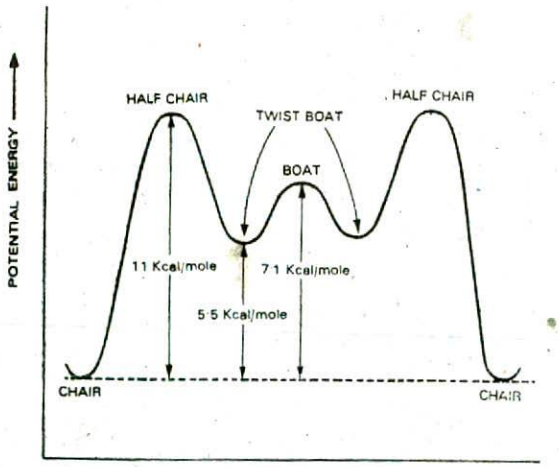


Fig. 10·5. Relative energies of the conformations of cyclohexane molecule.

Equatorial and Axial Hydrogens. The carbon atoms of the chair form of cyclohexane lie in one plane, and an axis can be drawn perpendicular to this plane (See Figure 10·6).

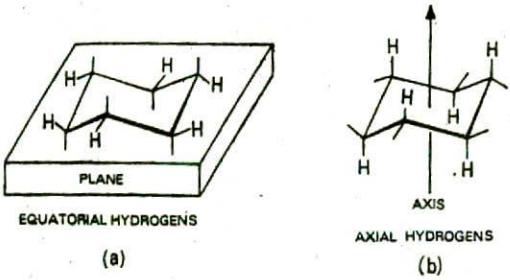
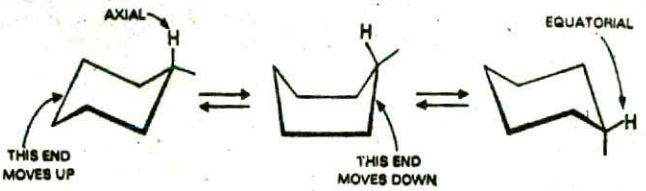


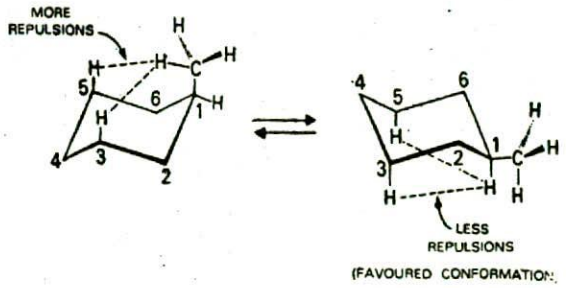
Fig. 10·6. The equatorial and axial hydrogens of cyclohexane :
(*a*) Equatorial hydrogens lie in the plane of the ring carbons ;
(*b*) Axial hydrogens lie (up or down) parallel to the perpendicular, axis.

Each carbon atom of cyclohexane is bonded to two hydrogens. The bond to one of these hydrogens lies in the plane of the ring ; this hydrogen is called **Equatorial Hydrogen.** The bond to the other hydrogen atom is parallel to the axis ; this hydrogen atom is called **Axial Hydrogen.**

Each of the six carbon atoms of cyclohexane has one equatorial and one axial hydrogen atom. *Note that there are six equatorial hydrogens, and six axial hydrogens.* In the flipping and reflipping between conformations, axial becomes equatorial, while equatorial becomes axial.



Conformations of Substituted Cyclohexanes. A methyl group is bulkier than a hydrogen atom. When the methyl group in methylcyclohexane is in the axial position, the methyl group and the axial hydrogens of the ring repel each other. These interactions are called **Axial-Axial Interactions.** When the methyl group is in the equatorial position, the repulsions are minimum. Thus, the energy of the conformation with equatorial methyl group is lower. *At room temperature, about 95% methylcyclohexane molecules are in the conformation in which the methyl group is equatorial.*

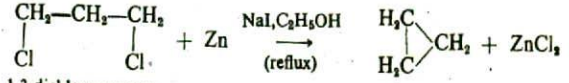


The bulkier the group, the greater is the energy difference between equatorial and axial conformations. In other words, a *cyclohexane ring with a bulky substituent (e.g., t-Butyl group) is more likely to have that group in the equatorial position.*

INDIVIDUAL MEMBERS

Cyclopropane, C_3H_6

Commercially cyclopropane is obtained by refluxing a mixture of 1,3-dichloropropane, zinc dust, sodium iodide and alcohol.



1,3-dichloropropane cyclopropane

Cyclopropane is a colourless gas (bp $-32{\cdot}8°C$). It reacts with Cl_2 and Br_2 in the presence of diffused sunlight to give chlorocyclopropane and bromocyclopropane respectively. In the absence of diffused sunlight it adds Cl_2 and Br_2 to give 1,3-dichloropropane and 1,3-dibromopropane respectively. It reacts with conc HBr and HI to give 1-bromopropane and 1-iodopropane respectively. It reacts with H_2 in the presence of a nickel catalyst at 80°C to give propane.

Cyclobutane, C_4H_8

Cyclobutane is obtained by refluxing a mixture of 1,4-dichlorobutane, zinc dust, sodium iodide and alcohol.

Cyclobutane is a colourless gas (bp 12·5°C). It reacts with Cl_2 and Br_2 in the presence of diffused sunlight to give chlorocyclobutane and bromocyclobutane respectively. In the absence of diffused sunlight, cyclobutane does not react with Cl_2 or Br_2. It reacts with H_2 in the presence of a nickel catalyst at 200°C to give n-butane.

Cyclopentane, C_5H_{10}

Cyclopentane may be obtained by the action of zinc on 1,5-dibromopentane. It may also be prepared by reduction of cyclopentanone by the Clemmensen method with amalgamated zinc and dil HCl. Cyclopentanone is obtained by heating calcium adipate.

Cyclopentane is a liquid hydrocarbon (bp 49·3°C) and is found in petroleum. It reacts with Cl_2 and Br_2 in the presence of diffused sunlight to give chlorocyclopentane and bromocyclopentane respectively.

Cyclohexane, C_6H_{12}

Cyclohexane may be obtained by catalytic reduction of benzene in the presence of a nickel catalyst at 200°C.

It is a liquid hydrocarbon (bp 80·7°C). It is found to some extent in petroleum, and the cyclohexane nucleus is found in many naturally occurring compounds (*e.g.*, terpenes). It reacts with Cl_2 and Br_2 in the presence of diffused sunlight to give chlorocyclohexane and bromocyclohexane respectively.

QUESTIONS

1. What are cycloalkanes? Write structural formulae of the first five members of the series and name them.
2. How would you synthesise the following compounds from the indicated materials :
   (*a*) Cyclopropane from 1, 3-dichloropropane.
   (*b*) Cyclobutane from 1, 4-dibromobutane.
   (*c*) Cyclopentane from barium adipate.
   (*d*) Cyclohexane from benzene.
3. (*a*) How can cyclopropane be prepared ?
   (*b*) How does cyclopropane react with the following reagents ?
   (*i*) Conc HBr.
   (*ii*) H_2 : Ni at 80°C.

(*iii*) Br_2 ; in the presence of diffused sunlight.

(*iv*) Cl_2 ; in the dark.

(*c*) The C—C bonds in cyclopropane are weaker than the C—C bonds in cyclopentane. Explain this fact on the basis of Molecular orbital theory.

4. A hydrocarbon, C_4H_8, neither decolourised bromine in CCl_4 nor reacted with HBr. When heated to 200°C with hydrogen in the presence of a nickel catalyst, a new hydrocarbon, C_4H_{10}, was formed. What was the structure of the original hydrocarbon.

Answer. Cyclobutane.

5. How will you synthesis cyclopentane from diethyl adipate.

(North Eastern Hill BSc, 1993 ; Osmania BSc, 1993 ; Delhi BSc Hons, 1994)

6. Explain why cyclopentane is more stable than cyclobutane. *(Kalyani BSc Hons, 1993)*

7. Write a note on : Baeyer strain theory.

(Dibrugarh BSc Hons, 1993 ; Gauhati BSc Hons, 1993 ; Madurai BSc, 1994)

8. Explain why :

(*a*) Chair conformation of cyclohexane is more stable than Boat conformation.

(*b*) Equatorial conformation of methylcyclohexane is more stable than the corresponding axial conformation.

(Calicut BSc III, 1994)

9. Describe the Dieckmann's method of preparing cycloalkanes. *(Indore BSc, 1993)*

10. Discuss the conformations of cyclohexane and its derivaties.

(Kerala BSc III, 1992 ; Karnataka BSc III, 1993 ; Punjab BSc, 1994)

11. (*a*) What are axial and equatorial bonds of cyclohexane ?

(*b*) Which of the following ring systems is most stable ?

(*i*) Cyclopentane (*ii*) Cyclopropane

(*iii*) Cyclobutane (*iv*) Cyclohexane *(Mangalore BSc III, 1993)*

12. Discuss the conformations of methylcyclohexane. *(Baroda BSc, 1993)*

13. Comment on relative stability of chair and boat conformations of cyclohexane and its monosubstituted derivatives.

(Jiwaji BSc III, 1994)