19

BASICS OF ORGANIC CHEMISTRY

Student Learning Outcomes

[C-12-D-01 to C-12-D-20]

- Define catenation and explain its importance in organic chemistry.
- Recognize that hydrocarbons are compounds made up of C and H atoms only.
- Describe the shape of benzene and other aromatic molecules, including sp^2 hybridization, in terms of σ bonds and a delocalized π system.
- Recognize that compounds contain a functional group which dictates their physical and chemical properties.
- Recognize that alkanes are simple hydrocarbons with no functional group.
- Describe the use of systematic nomenclature of simple aliphatic organic molecules with functional groups.
- Interpret the general, structural, displayed and skeletal formulae of the classes of compounds.
- Deduce the molecular and / or empirical formula of a compound, given its structural, displayed or skeletal formula.
- Apply the term 'planar' when describing the arrangement of atoms in organic molecules.
- Describe terminology associated with the types of organic compounds and reactions (some examples include: Homologous series, saturated and unsaturated, homolytic and heterolytic fission, free radical, initiation, propagation, termination, nucleophile, electrophile, nucleophilic, electrophilic addition, substitution, elimination, hydrolysis, condensation, oxidation and reduction).
- Describe terminology associated with types of organic mechanisms (Some examples include: Free-radical substitution, electrophilic addition, nucleophilic substitution, nucleophilic addition).
- Draw the mechanism of a chemical reaction using curly arrows to represent the movement of a pair of electrons in at least three different types of reactions, including nucleophilic substitution, electrophilic addition, and elimination reactions.
- Describe structural isomerism (in the context of organic molecules) in its division into chain, positional, functional group isomerism, metamerism and tautomerism.
- Explain stereoisomerism and its division into cis-trans (cis/trans) and optical isomerism.
- Describe the effect of two optical isomers of a single substance on a plane polarised light.
- Explain what is meant by a chiral center and that such a center gives rise to two optical isomers (enantiomers).
- Describe that enantiomers have identical physical and chemical properties except for their ability to rotate plane-polarised light and potential biological activity.
- Apply the terms optically active, racemic mixture and mesocompounds on given structure.
- Describe cis-trans (cis/trans) isomerism in alkenes, and explain its origin in terms of restricted rotation due to the presence of π bonds.
- Explain the significance of chirality in the synthetic preparation of drug molecules, including the potential different biological activity of enantiomers, the need to separate racemic mixtures, and the use of chiral catalysts to produce a single pure optical isomer using thalidomide as an example.

Today, we are familiar with more than 20 million carbon containing compounds. Most of these are studied in organic chemistry, which is defined by IUPAC as, "the study of compounds containing carbon, where carbon is bonded to itself, hydrogen, or other elements excluding some inorganic compounds."

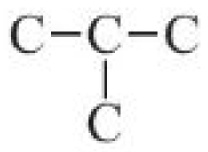
The examples of traditional inorganic compounds, which are excluded from organic chemistry are carbonates, cyanides (e.g KCl), CO_2, CO, etc. Organic compounds can be easily distinguished from inorganic compounds by their unique properties, such as low m.p's, b.p's, low densities and low solubility in water.

19.1 CATENATION

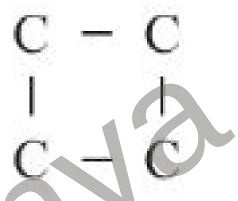
The ability of self-linkage between the atoms of the same element is known as catenation (from the Latin: Catena-Chain). Carbon forms long chains and rings through the stable C – C covalent bonds. The self-linking property of carbon atoms has unique importance in organic chemistry.

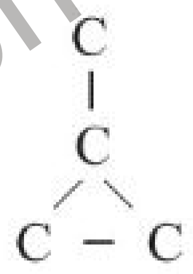
Tetravalent nature of carbon enables it to have much more different ways of arrangements to give a variety of compounds. For example, with four carbon atoms, there are four different arrangements.

$C-C-C-C$



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





Catenation explains why organic compounds are complex, having large structures and vast diversity.

Quick Check 19.1

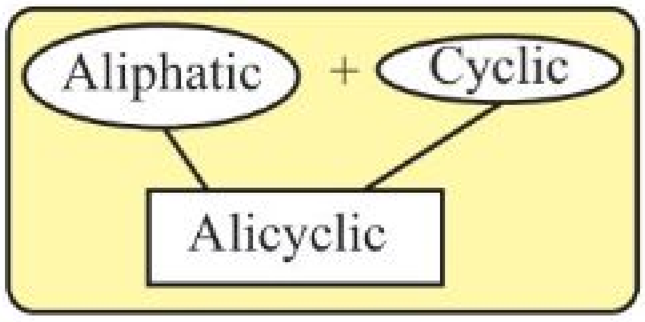
a) Draw the different possible structures containing five carbon atoms.

b) Give different open chain structures containing six carbon atoms.

19.2 HYDROCARBONS (COMPOUNDS OF CARBON AND HYDROGEN ONLY)

Compounds containing carbon and hydrogen only in their molecules are called hydrocarbons. On the basis of carbon skeleton, hydrocarbons are broadly classified into two types:

a) Hydrocarbons possessing open chain of carbon atoms are called open chain or acyclic hydrocarbons, or more commonly aliphatic hydrocarbons (aleiphatos is a Greek word meaning fat; fats have open chain structure). These can be further subdivided into saturated hydrocarbons (alkanes) or unsaturated hydrocarbons (alkenes and alkynes).



a) Hydrocarbons possessing rings of carbon atoms are called closed chain or cyclic hydrocarbons. These can be further divided into two types;

(i) Some cyclic hydrocarbons both saturated and unsaturated which behave like aliphatic hydrocarbons, are called alicyclic hydrocarbons e.g, cycloalkanes, cycloalkenes etc.

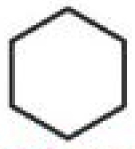
(ii) Some cyclic hydrocarbons having benzene ring or resembling structures are called aromatic hydrocarbons, e.g., benzene, naphthalene, diphenyl methane etc.

Aliphatic hydrocarbons

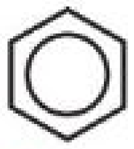
$CH_3–CH_3$,
ethane

$H_2C=CH_2$,
ethene

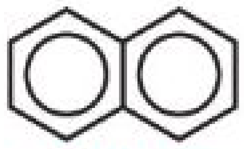
$HC≡CH$
ethyne

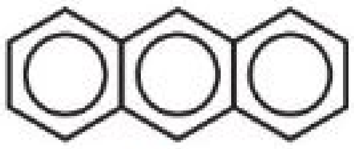

cyclohexane

Aromatic hydrocarbons


benzene

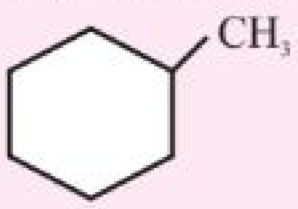

methyl benzene

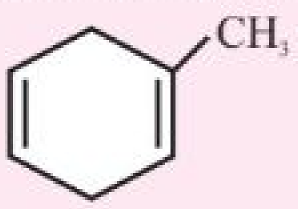

naphthalene


anthracene

Quick Check 19.2

a) Classify the following compounds as an aliphatic, alicyclic or aromatic.

i)


ii)


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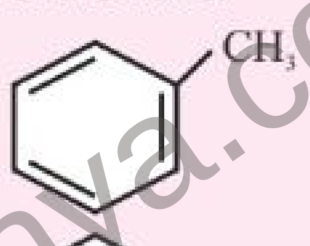

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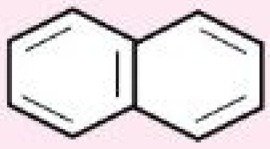


v)

vi)

vii)


19.3 FUNCTIONAL GROUPS

An atom or group of atoms or presence of double or triple bond which determines the characteristic properties of an organic compound is called functional group. Both physical and chemical properties of organic compounds are highly affected by the nature of functional groups they possess.

Methanol and ethanol are liquids while methane and ethane are gases. Likewise, m.p and b.p of alcohols are higher than their corresponding alkenes. These properties are due to the presence of the hydroxyl functional group (-OH) in alcohols. The alcohol functional group has the ability to form the hydrogen bonding. Alkanes lack this ability as they have no such functional group in their molecules. Similarly, lower alcohols and carboxylic acids, glucose and sucrose etc., are soluble in polar solvents like water due to their polar functional groups.

The types of organic compounds are dictated by the following factors in their functional groups:

i) Polarity of the bond

ii) Bond order i.e. number of bonds in the functional group

Alkanes and cycloalkanes have no functional group in them as they do not possess any charges or polarity, or double and triple bonds in their structures.

19.4 NOMENCLATURE OF ALIPHATIC ORGANIC COMPOUNDS

Since, millions of organic compounds are found in nature and hundreds and thousands of new compounds are being synthesized every year, so a need was felt to name these compounds according to their structures. A set of rules was thus formulated by IUPAC (International Union of Pure and Applied Chemistry) for systematic nomenclature of organic compounds. The systematic or IUPAC name of an organic compound is based on the parent hydrocarbon. Each name consists of the components listed below.

i) Stem or Root

It gives the longest continuous carbon chain including the carbon bearing the functional group. Lowest possible number is given to the carbon bearing the functional group. If the carbon atoms are joined in a ring, the name is started by "cyclo".

ii) Suffix

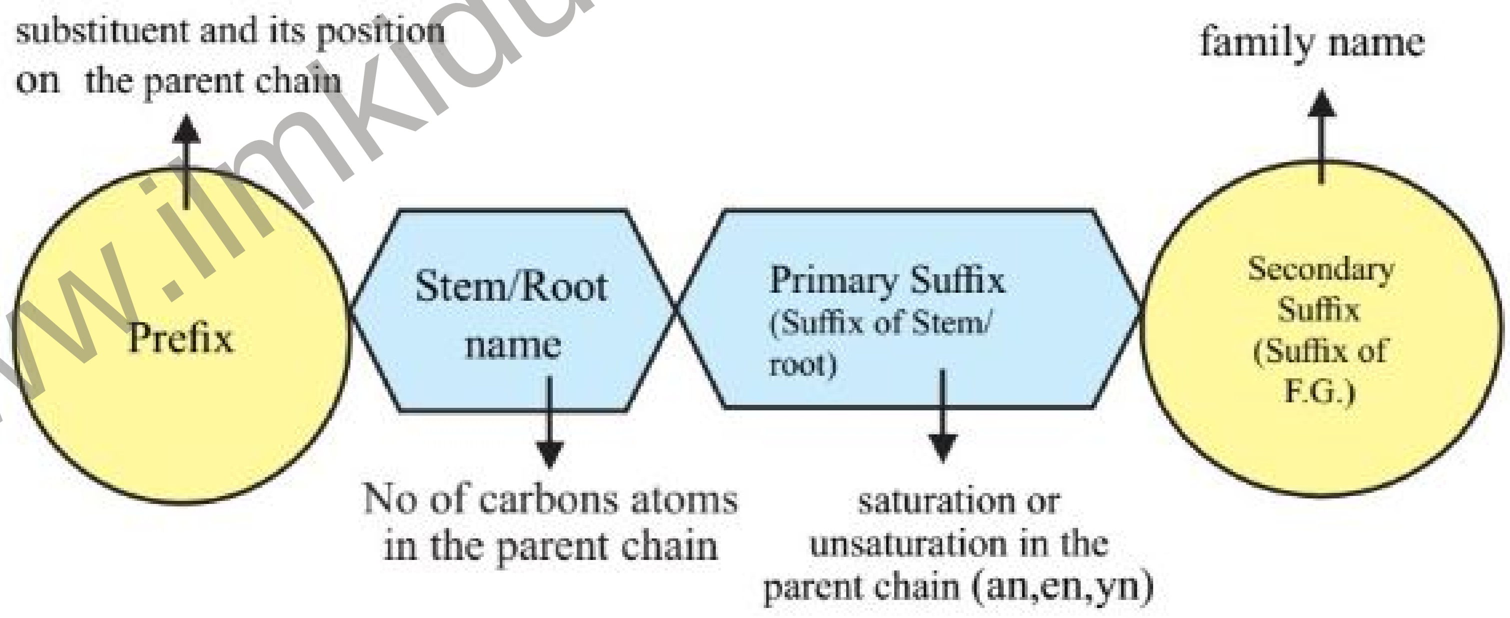
There are two types of suffixes:

a) **Primary suffix,** also called suffix of stem or root. It indicates whether the parent chain is saturated or unsaturated.

b) **Secondary suffix,** also called suffix of the key functional group. It gives family name of the compound.

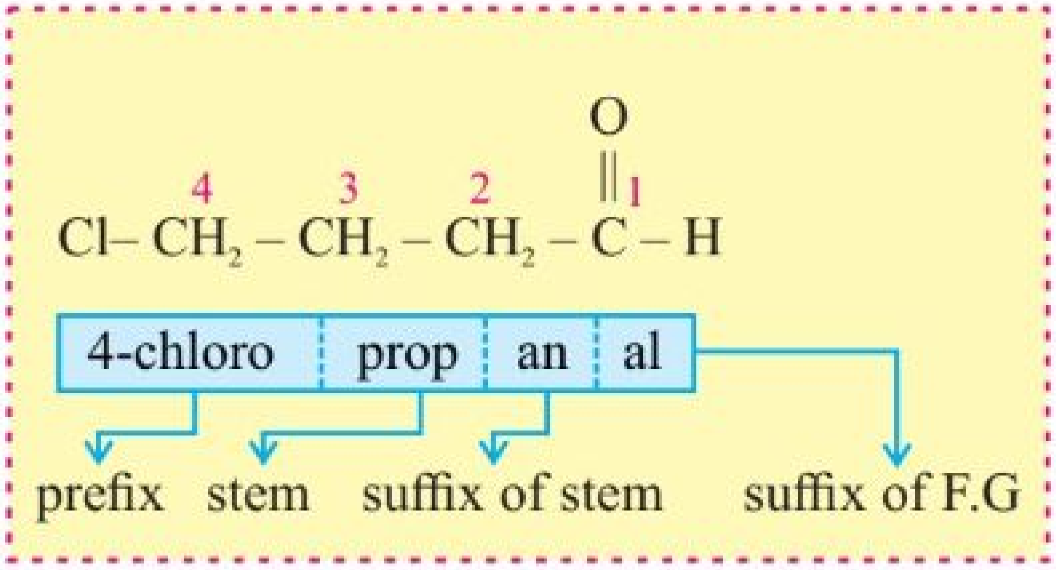
iii) Prefix

It gives the name of the side chain (alkyl group) or any substituent (e.g some functional group like halo, nitro, etc.) along with number of carbon atom to which it is attached.

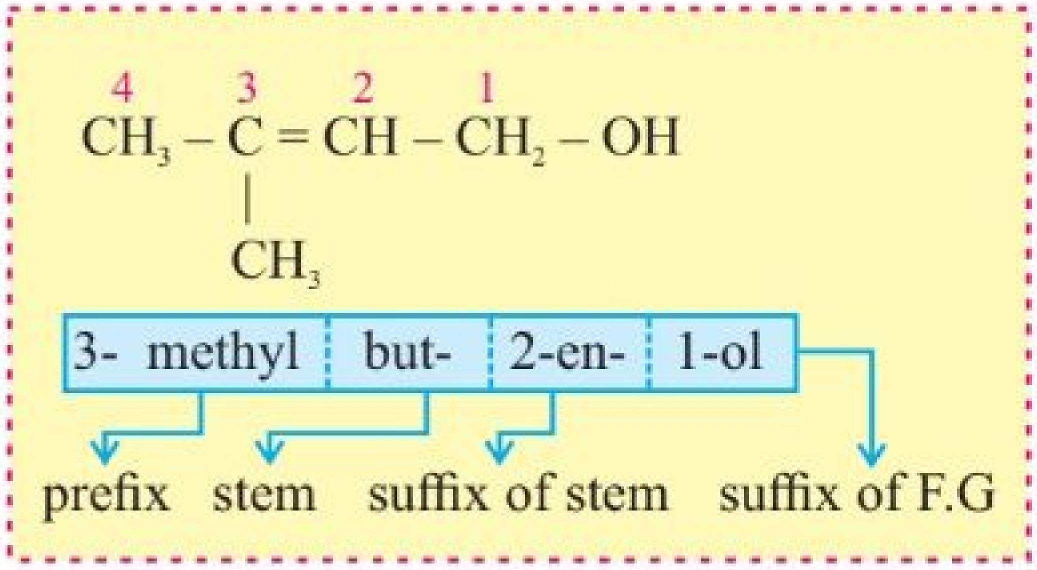


If prefix is absent, then systematic name will consist of root and suffix.

Examples:



$$Cl-\overset{4}{CH_2}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{O}{\overset{\|}{\overset{1}{C}}}-H$$



$$\overset{4}{CH_3}-\underset{CH_3}{\underset{|}{\overset{3}{C}}}=\overset{2}{CH}-\overset{1}{CH_2}-OH$$

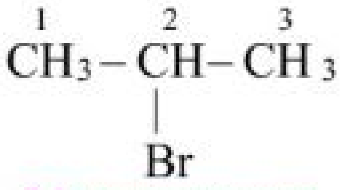
Keeping in view, the above procedure for giving systematic or IUPAC names to various organic compounds, following different classes will be discussed one by one:

1. Alkyl halides ($C_nH_{2n+1}X$) $(-C-X)$

The IUPAC name is halogenoalkane (more precisely monohaloalkane)

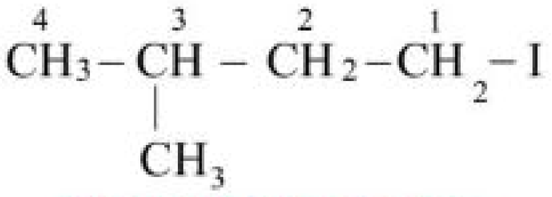
CH_3-Cl

chloromethane



$\overset{1}{C}H_3-\underset{\displaystyle Br}{\overset{2}{C}H}-\overset{3}{C}H_3$

2-bromopropane



$\overset{4}{C}H_3-\underset{\displaystyle CH_3}{\overset{3}{C}H}-\overset{2}{C}H_2-\overset{1}{C}H_2-I$

3-methyl–1-iodobutane

2. Alcohols ($C_nH_{2n+2}O$) $(-C-OH)$

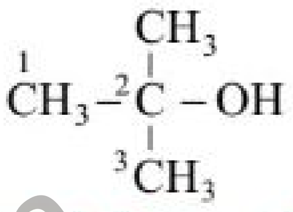
The IUPAC name is alkanol.

CH_3-OH

methanol

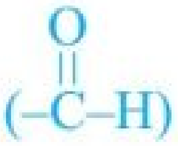
$\overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H_2-OH$

propan–1– ol



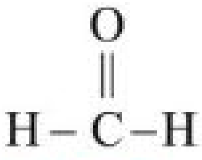
$\overset{1}{C}H_3-{}^2\underset{\displaystyle {}^3CH_3}{\overset{\displaystyle CH_3}{C}}-OH$

2-methylpropan– 2 – ol



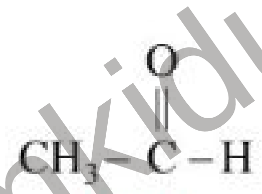
3. Aldehydes ($C_nH_{2n}O$) $(-\overset{O}{\overset{\|}{C}}-H)$

The IUPAC name is alkanal.



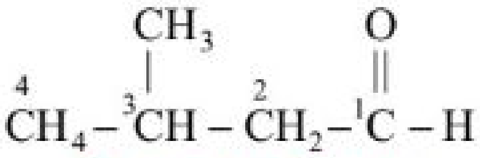
$H-\overset{O}{\overset{\|}{C}}-H$

methanal



$CH_3-\overset{O}{\overset{\|}{C}}-H$

ethanal

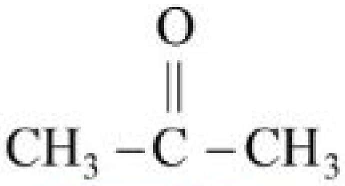


$\overset{4}{C}H_4-{}^3\overset{\displaystyle CH_3}{\overset{|}{C}H}-\overset{2}{C}H_2-{}^1\overset{O}{\overset{\|}{C}}-H$

3 – methylbutanal

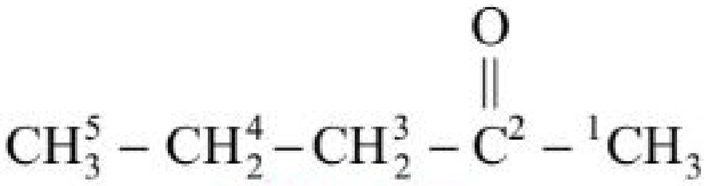
4. Ketones ($C_nH_{2n}O$) $(-C-\overset{O}{\overset{\|}{C}}-C-)$

The IUPAC name is alkanone



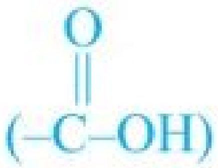
$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

propanone



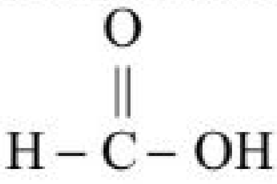
$CH_3^5-CH_2^4-CH_2^3-\overset{O}{\overset{\|}{C^2}}-{}^1CH_3$

pentan–2–one



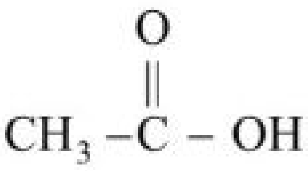
5. Carboxylic acid ($C_nH_{2n}O_2$) $(-\overset{O}{\overset{\|}{C}}-OH)$

The IUPAC name is alkanoic acid



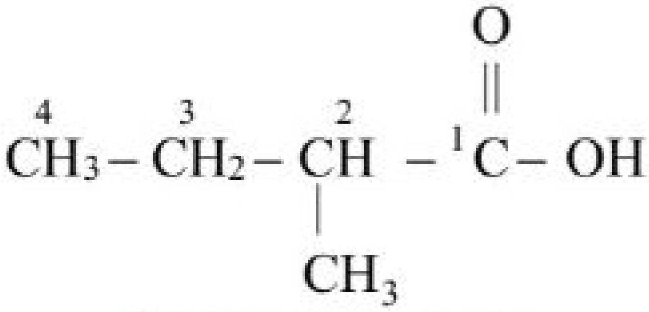
$H-\overset{O}{\overset{\|}{C}}-OH$

methanoic acid



$CH_3-\overset{O}{\overset{\|}{C}}-OH$

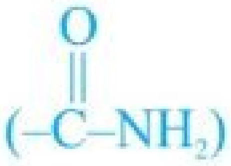
ethanoic acid



$\overset{4}{C}H_3-\overset{3}{C}H_2-\underset{\displaystyle CH_3}{\overset{2}{C}H}-{}^1\overset{O}{\overset{\|}{C}}-OH$

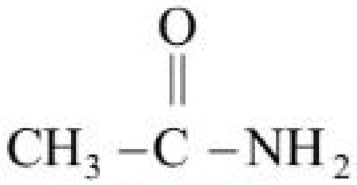
2-methylbutanoic acid

6. **Acid amides** $(C_nH_{2n-1}ONH_2)$



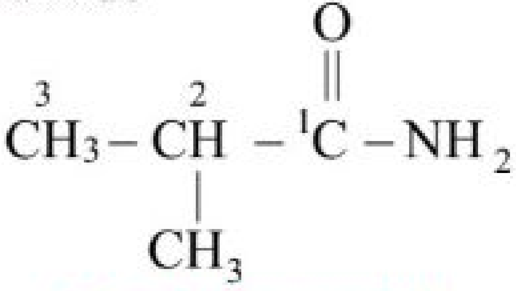
$(-\overset{O}{\overset{\|}{C}}-NH_2)$

The IUPAC name is alkanamide



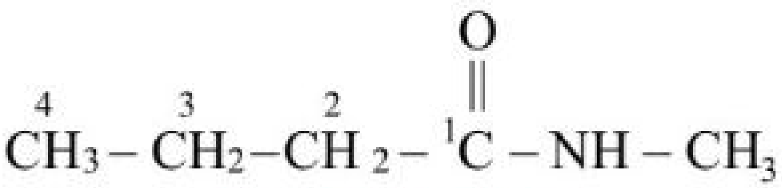
$CH_3-\overset{O}{\overset{\|}{C}}-NH_2$

ethanamide



$\overset{3}{C}H_3-\underset{CH_3}{\underset{|}{\overset{2}{C}H}}-{}^{1}\overset{O}{\overset{\|}{C}}-NH_2$

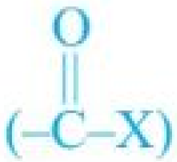
2-methylpropanamide



$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H_2-{}^{1}\overset{O}{\overset{\|}{C}}-NH-CH_3$

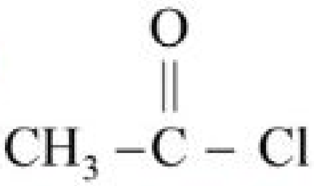
N-methylbutanamide

7. **Acid halides** $(C_nH_{2n-1}OX)$



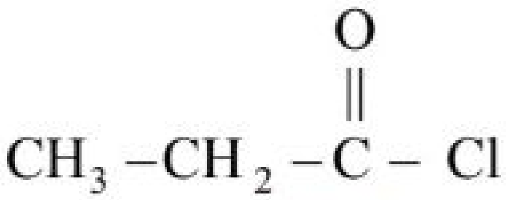
$(-\overset{O}{\overset{\|}{C}}-X)$

The IUPAC name is alkanoyl halides



$CH_3-\overset{O}{\overset{\|}{C}}-Cl$

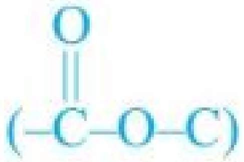
ethanoyl chloride



$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-Cl$

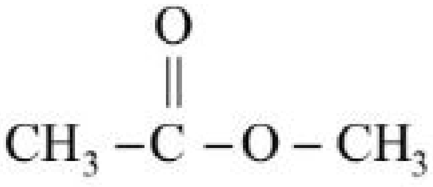
propanoyl chloride

8. **Esters** $(C_nH_{2n}O_2)$



$(-\overset{O}{\overset{\|}{C}}-O-C)$

The IUPAC name is alkyl alkanoate

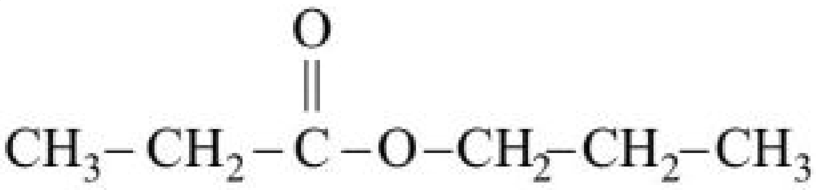


$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3$

methyl ethanoate

$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3$

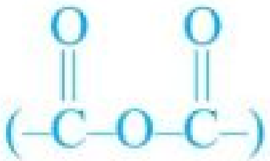
ethyl ethanoate



$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-CH_3$

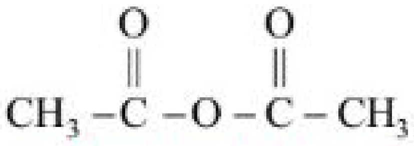
propyl propanoate

9. **Acid anhydrides**



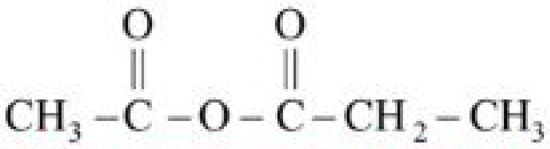
$(-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-)$

The IUPAC name is alkanoic anhydride



$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$

ethanoic anhydride



$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

ethanoic propanoic anhydride

10. **Ethers** $(C_nH_{2n+2}O)$ $(-C-O-C-)$

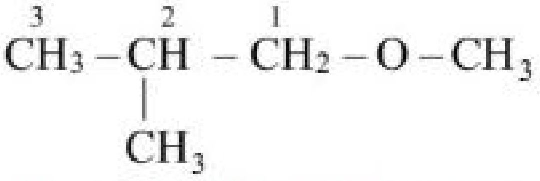
The IUPAC name is alkoxyalkane.

CH_3-O-CH_3

methoxymethane

$CH_3-CH_2-O-CH_2-CH_3$

ethoxyethane



$\overset{3}{C}H_3-\underset{CH_3}{\underset{|}{\overset{2}{C}H}}-\overset{1}{C}H_2-O-CH_3$

1-methoxy -2 methylpropane

$CH_3-CH_2-O-CH_3$

methoxyethane

11. Amines ($C_nH_{2n+1}NH_2$)

There are three types of amines

a) **Primary Amines** $(-C-NH_2)$

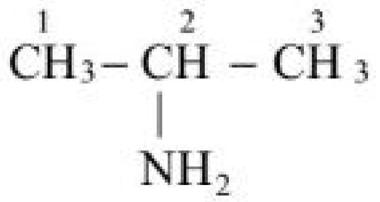
The IUPAC name is **Alkanamine**

$CH_3-CH_2-NH_2$

ethanamine

$\overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H_2-NH_2$

propan-1-amine



$\overset{1}{C}H_3-\underset{\substack{|\\ NH_2}}{\overset{2}{C}H}-\overset{3}{C}H_3$

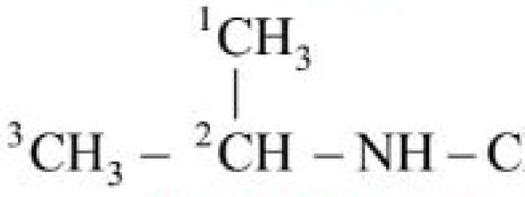
propan-2-amine

b) **Secondary Amines** $(-C-NH-R)$

The IUPAC name is **N-Alkylalkanamine**

$\overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H_2-NH-CH_3$

N-methylpropan - 1 – amine



$^{3}CH_3-\overset{\substack{^{1}CH_3\\ |}}{^{2}CH}-NH-CH_3$

N-methylpropan - 2 – amine

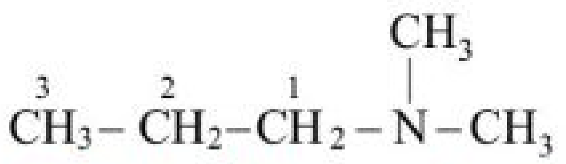
c) **Tertiary amines**

$(-C-\underset{\substack{|\\ R}}{N}-R)$

The IUPAC name may be (R=R)

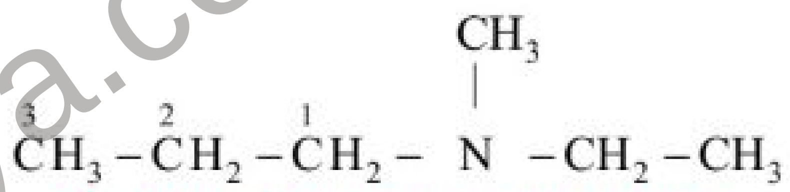
N,N – Dialkylakanamine or

(R≠R) N – alkyl – N – alkyalkanamine



$\overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H_2-\overset{\substack{CH_3\\ |}}{N}-CH_3$

N,N – dimethylpropan -1- amine



$\overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H_2-\overset{\substack{CH_3\\ |}}{N}-CH_2-CH_3$

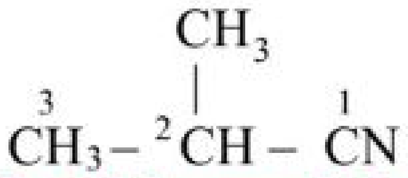
N – ethyl – N-methylpropan–1–amine

12. Alkyl cyanides ($C_nH_{2n-1}N$) $(-C\equiv N)$

The IUPAC name is **alkanenitrile**

CH_3-CN

ethanenitrile



$\overset{3}{C}H_3-\overset{\substack{CH_3\\ |}}{^{2}CH}-\overset{1}{C}N$

2- methylpropaneritrile

13. Nitroalkanes ($C_nH_{2n+1}NO_2$) $(-C-NO_2)$

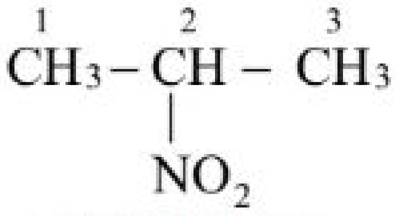
The IUPAC name is **nitroalkane**

CH_3-NO_2

nitromethane

$\overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H_2-NO_2$

nitropropane



$\overset{1}{C}H_3-\underset{\substack{|\\ NO_2}}{\overset{2}{C}H}-\overset{3}{C}H_3$

2-nitropropane

Quick Check 19.3

a) What are the systematic names of the following?

i) $(CH_3)_3COH$

ii) CH_3CCl_3

iii) $CH_2=CH-CH_2-OH$

iv) $CH_3COC_6H_5$

v) $CH_2=C(CH_3)COOCH_3$

b) Draw the structures of the following.

i) 2 - methylbutanal

ii) prop -2- ylmethanoate

iii) phenylethanoic acid

iv) cyclohexanone

v) 3 - methylpentanal

19.5 REPRESENTING ORGANIC MOLECULES

There are different types of formulae which are used to represent organic compounds.

1. Molecular Formula

"The formula which represents the actual number of atoms of each element present in a molecule of a compound is called molecular formula."

For example, molecular formula of butane is C_4H_{10}, for acetic acid $C_2H_4O_2$ and that of ethanol is C_2H_6O. However, molecular formula gives no information about the sequence in which atoms are linked together as well as the nature of a functional group. That is why two different compounds may have the same molecular formula e.g. ethanol and methoxymethane are represented by same molecular formula i.e; C_2H_6O.

2. Empirical Formula

The formula which represents the smallest whole number ratio of atoms of each element present in a molecule of a compound is called empirical formula. For example, empirical formula of butane (C_4H_{10}) is C_2H_5, and for ethanoic acid (acetic acid, $C_2H_4O_2$) is CH_2O.

3. Structural Formula

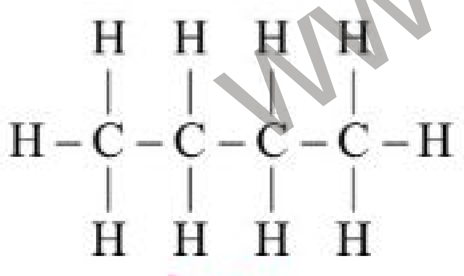
The structural formula not only shows the number of each kind of atom in the molecule but also the sequence in which atoms are joined together.

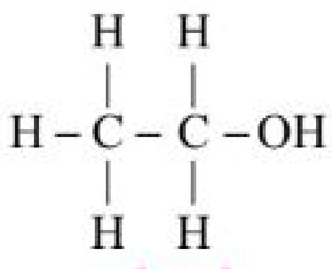
There are different types of structural formulae.

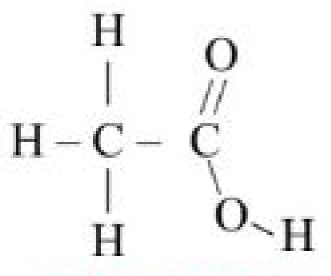
(a) Displayed formula (Graphical formula)

This formula is more complete and self-explanatory form of the structural formula.

"The formula which shows all the bonds between different atoms including the type of bonds as well as positions of functional groups in a molecule is called the displayed formula."


butane


ethanol


ethanoic acid

a) Condensed formula (Linear Formula)

Displayed formula uses a lot of space, it is very often condensed in to a one – line structure called condensed or linear formula. In this kind of formula, single covalent bonds are omitted, however, branches, functional groups, double or triple bonds and separating methylene groups in the middle of the molecule are shown in brackets e.g.

$CH_3(CH_2)_2CH_3$	CH_3CH_2OH	CH_3COOH
butane	ethanol	ethanoic acid

b) Skeletal Formula (Bond-line Formula)

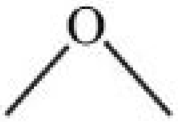
Skeletal formula is the simplified version of displayed formula which can be used to represent more complex organic molecules.

In skeletal formula, all the symbols of carbon and hydrogen atoms as well as the carbon to hydrogen bonds are removed. Bonds between carbon atoms are shown by single lines which meet at an angle. Each carbon is assumed to form enough C – H bonds to make a total of four bonds. Double and triple bonds as well as functional groups are shown in the skeletal formula. For example:

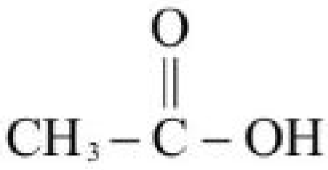
i) butane $CH_3 - CH_2 - CH_2 - CH_3$

ii) ethanol $CH_3 - CH_2 - OH$

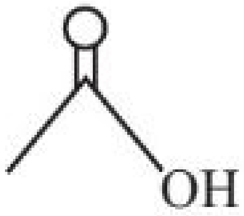
iii) Methoxymethane $CH_3 - O - CH_3$



iv) Ethanoic acid



$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - OH$



Quick Check 19.4

a) Draw the displayed and skeletal formulae of the following
   i. 3,5- diethylheptane ii. 2-bromo-3,3-dichlorohexane iii. 2 – methylbutanal

b) Draw the displayed and condensed structures of ethanol and methoxy methane, and explain whether they are isomers of the same molecule or not.

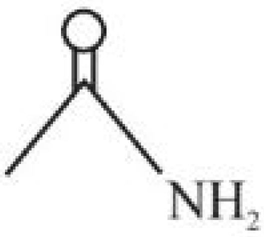
c) Draw the skeletal formula of ethanoic acid (CH_3COOH).

19.6 DETERMINATION OF THE MOLECULAR FORMULA

Let us write the molecular and empirical formulae for the following compounds.

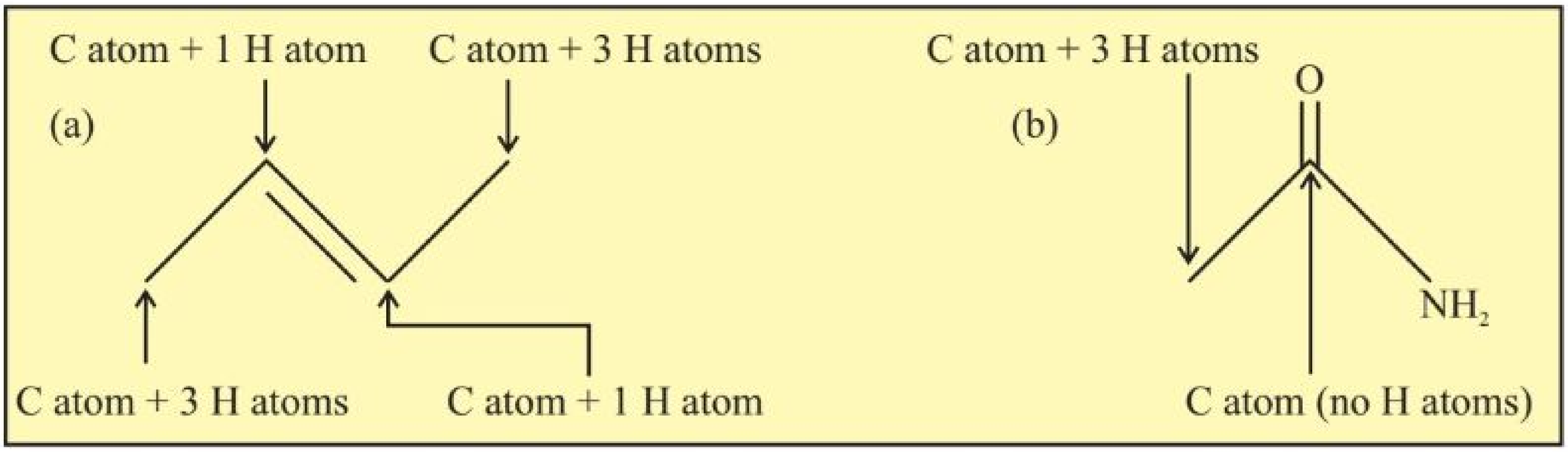
a)

b)



Steps to find molecular formula

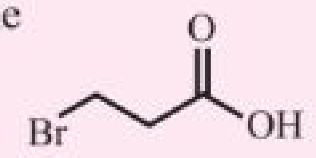
- Count the C atoms represented and the heteroatoms shown in the skeleton.
- Each line represents a bond and each joint shows a carbon atom. (Double lines represent double bonds). Count one C atom at the end of each line unless another atom is shown there.
- Count the number of H atoms necessary to complete the octet of each C atom:



Solution : a) Molecular formula: C_4H_8: Empirical formula: CH_2.
b)Molecular formula: C_2H_5NO: Empirical formula: CH_3CONH_2.

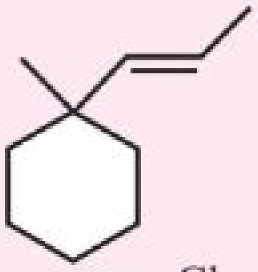
Quick Check 19.5

a) Write molecular formula for the compound represented by the following bond-line structure:

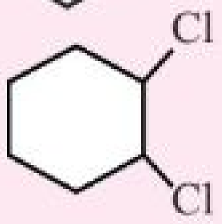


b) Draw the skeletal formula for $(CH_3)_2C{=}CHNH_2$

c) Write molecular formula for the compound represented by the following bond-line structure:



d) Give the molecular formulae of the following.

i) 

ii) 

19.7 UNDERSTANDING ORGANIC REACTIONS

Since chemical reactions of organic compounds are complex in nature, therefore, in order to have a deep insight into their chemistry, we proceed further by keeping in view the following basic statements:

A. There are two ways in which a covalent bond can break, i.e homolytic and heterolytic

B. There are basically three types of reagents, i.e free radicals electrophiles, and nucleophiles.

C. There are four generally types of organic reactions.

A. Breaking of Covalent Bonds

There are two ways in which covalent bonds can break:

I. Homolytic Fission (Homolysis)

Homolytic fission occurs when the breaking bond is nonpolar. In this type of fission, the two shared electrons in the bond are distributed equally between the two atoms.

The dot (.) beside each atom indicates the unpaired electron that the atom has gained from the shared pair in the bond.

"These atoms or groups of atoms with unpaired electrons are called free radicals."

Free radicals are formed when a nonpolar bond is broken. These free radicals are the reaction intermediates and are highly reactive because of the tendency of their unpaired electrons to be paired.

ii. Heterolytic Fission (Heterolysis)

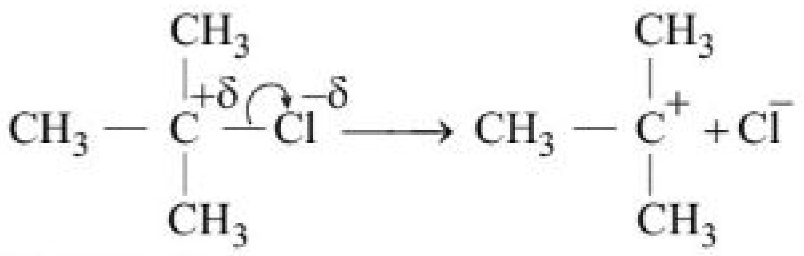
In this type of fission, the two shared electrons in the bond are distributed unequally between the two atoms. One of the atoms keeps both electrons, and it acquires a negative charge. The other atom is deficient in one electron and, thus, acquires a positive charge.

Heterolytic fission occurs when the breaking bond is polar.

iii. Carbocation Formation

A species which contains a carbon atom with a positive charge is known as carbocation:

Carbocation is formed when carbon is bonded to a heteroatom whose electronegativity is more than carbon e.g; O, N, S, P etc.


$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\overset{+\delta}{}-\overset{-\delta}{Cl} \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C^+}}+Cl^-$$

Carbanion is formed when carbon is bonded to a heteroatom (metal) whose electronegativity is lesser than carbon e.g. Li, Mg, Cd etc.

B) Types of Reagents

A chemical reaction between two reactants may be regarded as the attack of one species on the other. In this case, the attacking species is called reagent and the species which is undergoing attack is called the substrate.

i. Free Radical

An atom or group of atoms having unpaired electrons are called free radicals e.g.

$\dot{Cl}$, $H^{\bullet}$, $\dot{C}H_3$, $CH_3CO\dot{O}$ etc.

ii. Electrophile

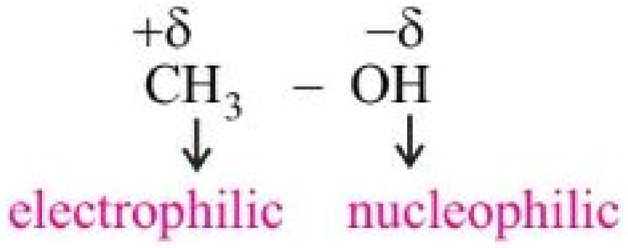
An atom or group of atoms that is able to accept a pair of electrons to form a new bond is called an electrophile. Electrophiles (electron lovers) are either positive ions (including carbocations) or neutral molecules e.g. $\overset{+}{C}H_3$, $\overset{+}{H}$, $\overset{+}{Br}$, $\overset{+}{N}O_2$, SO_3, BF_3, etc.

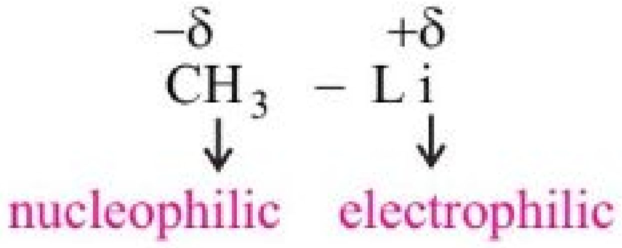
iii. Nucleophile

An atom or group of atoms that is able to donate a pair of electrons to form a new bond is called nucleophile. Nucleophiles (nucleus lovers) are either negative ions (including carbanions) or neutral molecules e.g.

$\bar{C}H_3$, Br^-, OH^-, CN^-, $\ddot{N}H_3$, $H_2\ddot{\underset{\cdot\cdot}{O}}$, $R\ddot{O}H$ etc.

The terms electrophilic and nucleophilic do not apply only to ions. Many organic compounds are polar; they carry partial charges, which can also make them electrophilic or nucleophilic.





C. Types of Organic Reactions

The reactions of organic compounds can be classified into four main types:

i. Substitution Reactions

In substitution reactions, two reactants react in such a way that an atom or group of atoms in one molecule is replaced by another atom or group of atoms. Two products may be formed. For example:

$$\underset{\text{bromoethane}}{CH_3-\overset{+\delta}{CH_2}-\overset{-\delta}{Br}}+KOH_{(aq)}\xrightarrow{H_2O}\underset{\text{ethanol}}{CH_3-CH_2-OH}+KBr$$

ii. Addition Reactions

In addition reactions, two reactants react to produce a single product. For example:

$$\underset{\text{ethene}}{CH_2=CH_2}+H_2\xrightarrow[200-300i]{Ni}\underset{\text{ethane}}{CH_3-CH_3}$$

$$\underset{\text{propene}}{CH_2-CH=CH_2}+\overset{+\delta}{H}-\overset{-\delta}{Br}\longrightarrow\underset{\text{bromopropane}}{CH_3-CH_2-CH_2-Br}$$

iii. Elimination Reactions

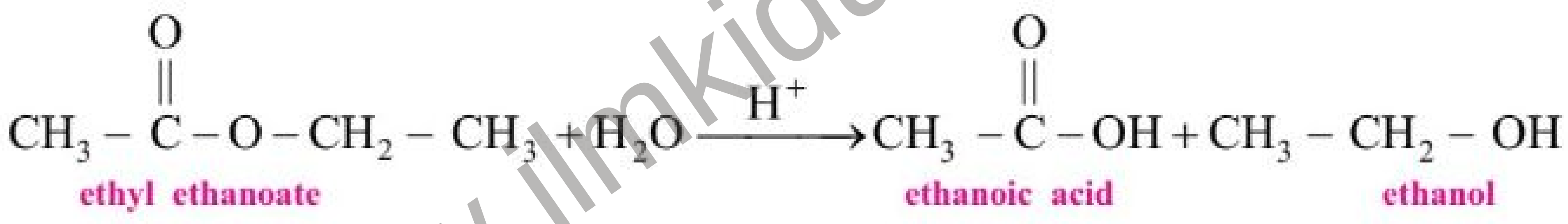
In elimination reactions, removal of atoms or groups of atoms from two adjacent atoms in the substrate molecule occurs to form a multiple bond. For example:

$$\underset{\text{bromoethane}}{CH_3-\overset{+\delta}{CH_2}-\overset{-\delta}{Br}}+KOH\xrightarrow{\text{alcohol}}\underset{\text{ethane}}{CH_2=CH_2}+KBr+H_2O$$

Elimination reactions are regarded as reverse of addition reactions.

iv. Hydrolysis

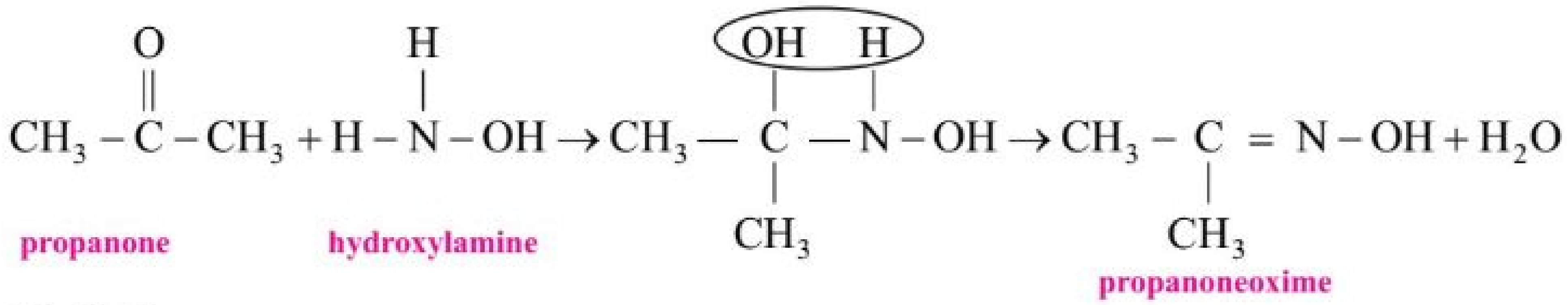
In hydrolysis, a compound breaks into two on reaction with water often helped by H^+ or OH^- as catalyst. For example,



$$\underset{\text{ethyl ethanoate}}{CH_3-\overset{\overset{O}{||}}{C}-O-CH_2-CH_3}+H_2O\xrightarrow{H^+}\underset{\text{ethanoic acid}}{CH_3-\overset{\overset{O}{||}}{C}-OH}+\underset{\text{ethanol}}{CH_3-CH_2-OH}$$

v. Condensation Reactions

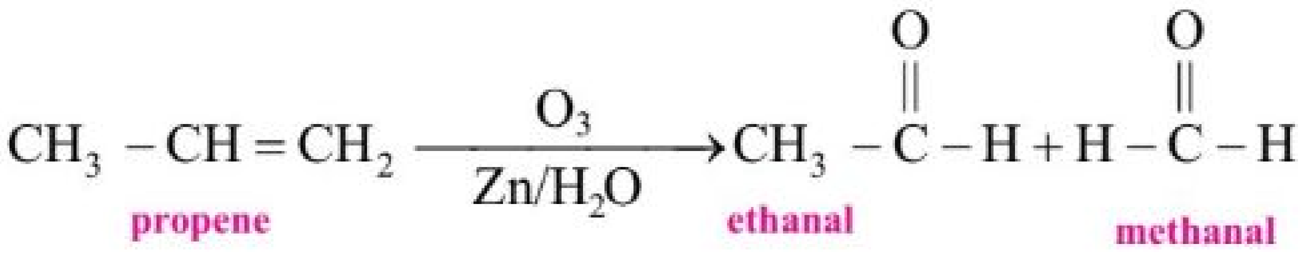
In condensation reactions two molecules combine to form a bigger molecule with or without loss of a smaller molecule like H_2O, NH_3, HCl etc. For example,



$$\underset{\text{propanone}}{CH_3-\overset{\overset{O}{||}}{C}-CH_3}+\underset{\text{hydroxylamine}}{H-\overset{\overset{H}{|}}{N}-OH}\rightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-\overset{\overset{H}{|}}{N}-OH\rightarrow\underset{\text{propanoneoxime}}{CH_3-\underset{\underset{CH_3}{|}}{C}=N-OH}+H_2O$$

vi. Oxidation

Loss of electron is called oxidation. Moreover, if a molecule gains oxygen or loses hydrogen or there is increase in number of bonds of carbon with oxygen or increase in oxidation state of carbon, it is oxidized.



$$\underset{\text{propene}}{CH_3-CH=CH_2}\xrightarrow[Zn/H_2O]{O_3}\underset{\text{ethanal}}{CH_3-\overset{\overset{O}{||}}{C}-H}+\underset{\text{methanal}}{H-\overset{\overset{O}{||}}{C}-H}$$

vii. Reduction

Reduction is a reaction where gain of electron, loss of oxygen or gain of hydrogen, or a decrease in the number of bonds of carbon with oxygen or decrease in oxidation state of carbon occurs.

$$\underset{\text{ethene}}{CH_2 = CH_2} + H_2 \xrightarrow{Ni} \underset{\text{ethane}}{CH_3 - CH_3}$$

19.8 MECHANISMS OF CHEMICAL REACTIONS

A mechanism is the pathway adapted by a reaction showing the breaking and making of bonds in the substrate leading to the formation of the product. Depending upon the nature of reagents, reaction mechanisms are divided into two main types.

1) Free radical mechanism
2) Ionic or polar mechanism

1) Free Radical Mechanism

It involves homolysis during which free radicals are produced which attach the substrate molecule e.g.

$$CH_4 + 4Cl_2 \xrightarrow{\text{Diffused sunlight}} CCl_4 + 4HCl$$

This reaction proceeds through the free radical mechanim, which was already discussed in Chemistry 11. The reaction involves initiation where initial free radicals are produced. These radicals generate more radicals in the propagation step. Finally, the reaction terminates by combining the free radicals of the same or different types.

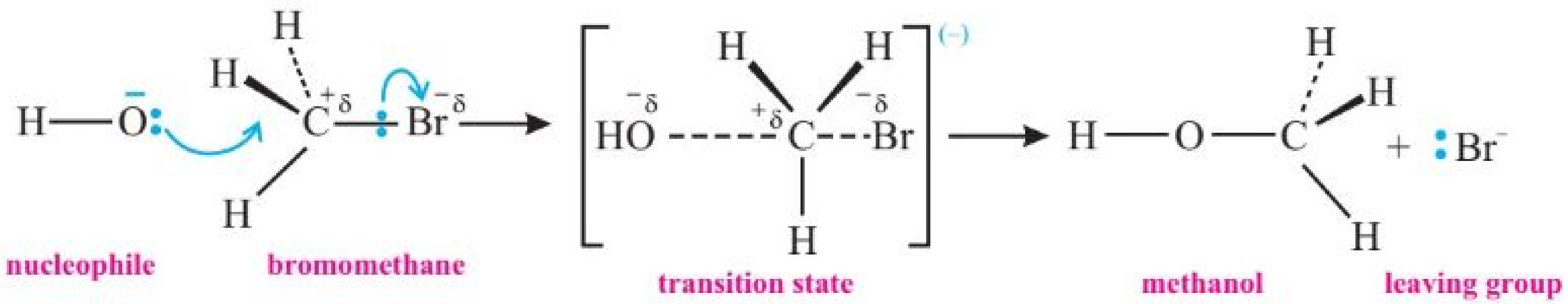
Initiation ⟶ **Propagation** ⟶ **Termination**

1) Ionic or polar mechanism

It involves heterolysis, during which electrophiles and nucleophiles are produced, which may attack polar substrate molecules. The polar mechanism is further divided into the following types.

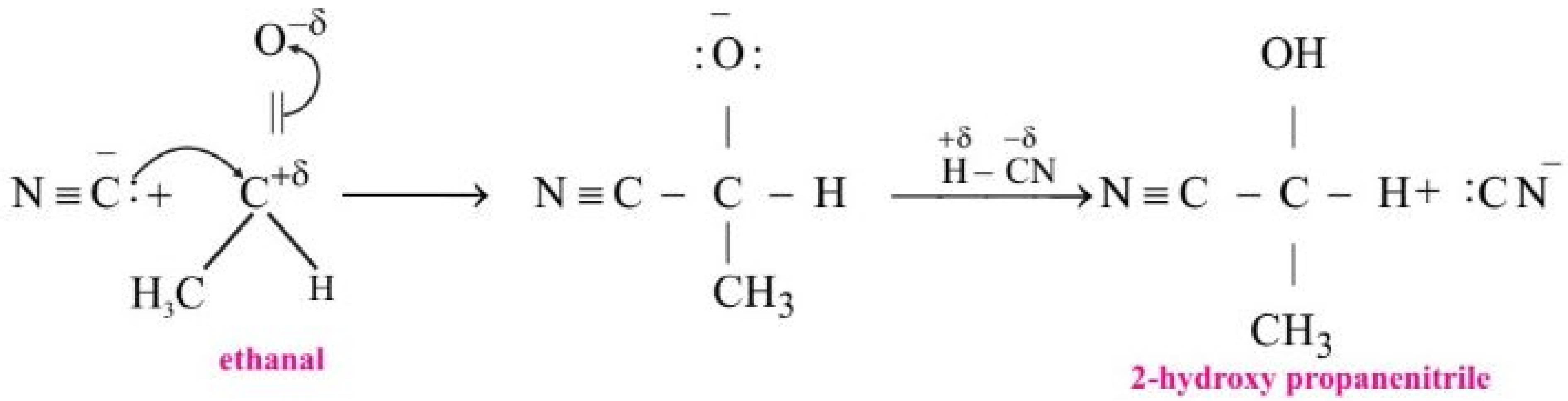
i) Nucleophilic Substitution Reactions

In this type of reaction, a nucleophile attacks on a saturated electrophilic carbon and substitutes another nucleophile called leaving group e.g.



ii) Nucleophilic Addition Reactions

In this type of reactions, a nucleophile attacks on electrophilic carbon of a carbonyl compound to give addition product e.g.



$$N\equiv \overset{-}{C}: + \overset{+\delta}{C}(=O^{-\delta})(H_3C)(H) \longrightarrow N\equiv C-C(\overset{-}{O}:)(CH_3)-H \xrightarrow{\overset{+\delta}{H}-\overset{-\delta}{CN}} N\equiv C-C(OH)(CH_3)-H + :\overset{-}{C}N$$

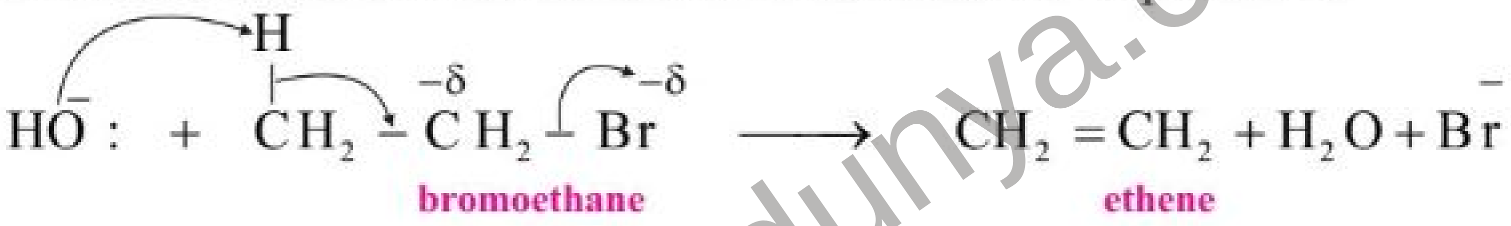
iii) Electrophilic Addition Reactions

In this type of reaction, an electrophile attacks on an electron rich position (nucleophilic) like carbon-carbon double or triple bond e.g.

$$H_2C=CH_2 + \overset{+\delta}{H}-\overset{-\delta}{Br} \longrightarrow CH_3-CH_2-Br$$

iv) Elimination Reactions

In this type of reaction, two atoms or groups are removed from two adjacent carbon atoms in molecule. The removal results in the formation of a double or triple bond.



$$H\overset{-}{O}: + \overset{H}{C}H_2-\overset{-\delta}{C}H_2-\overset{-\delta}{Br} \longrightarrow CH_2=CH_2 + H_2O + B\overset{-}{r}$$

Quick Check 19.6

a) Describe each of the following as electrophile, nucleophile or free radical.

i) NH_3 ii) Br iii) H_2O iv) $NO_2^{\oplus}$ v) $Cl^{\delta\oplus}$

b) Classify each of these reactions as addition, substitution, elimination or rearrangement.

(I) $CH_3CH=CH_2 + HBr \longrightarrow CH_3CHBrCH_3$

(ii) $CH_4 + Br_2 \longrightarrow CH_3Br + HBr$

(iii) $CH_3CH_2CHClCH_3 \longrightarrow CH_3CH_2CH=CH_2 + HCl$

c) Classify the following reactions into one (or more) of the following six categories:

Substitution, addition, hydrolysis, reduction, condensation, oxidation.

(i) $(CH_3)_2C=O + H_2N-NH_2 \longrightarrow (CH_3)_2C=N-NH_2 + H_2O$

(ii) $CH_3CHO + 2[H] \longrightarrow CH_3CH_2OH$

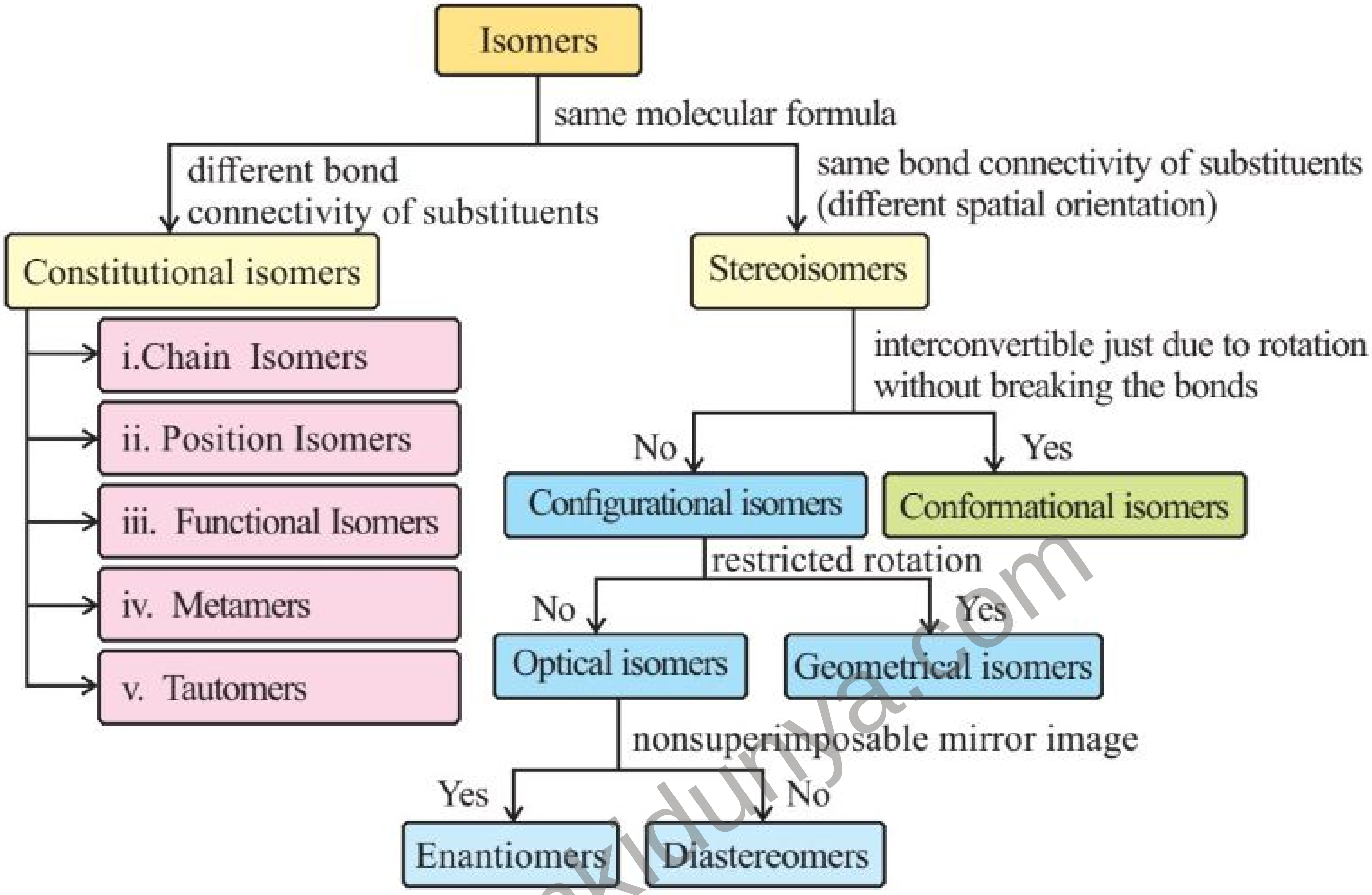
19.9 ISOMERISM

Two or more than two compounds which have same molecular formulae but different arrangement of atoms and different properties are called isomers and the phenomenon is called isomerism.

The isomerism of organic compounds stems from the two distinct features.

1. When same groups or atoms are connected at different places in two or more molecules, it results in structural or constitutional isomerism. This type of isomerism has been discussed earlier in Chemistry 11.

2. When the substituents or groups have different spatial arrangement in isomers, they are said to have different configuration. This type of isomerism is called stereoisomerism.



19.9.1 Stereoisomerism

Stereoisomers are further divided into two types.

a) Optical isomers

b) cis-trans isomers

Optical Isomers are the stereoisomers which have identical physical and chemical properties except their ability to rotate the plane polarised light. Such isomers are said to be optically active and this property of these isomers of rotating the plane of polarization is called optical activity. Optical activity of a compound is identified by using plane polarised light (PPL). If the compound rotates the plane of polarised light to right (clockwise), it is called dextrorotatory indicated by symbol (+) and if it rotates the plane to left (anticlockwise), it is called levorotatory indicated by the symbol (-).

Keep in Mind

A polarimeter is used to identify and measure quantitively the optical activity of a compound by using PPL. PPL is a monochromatic light having single wavelength which moves only in one plane. A solution of the compound under investigation is placed before PPL. If the compound rotates the PPL, it is optically active and if not, it is optically inactive.

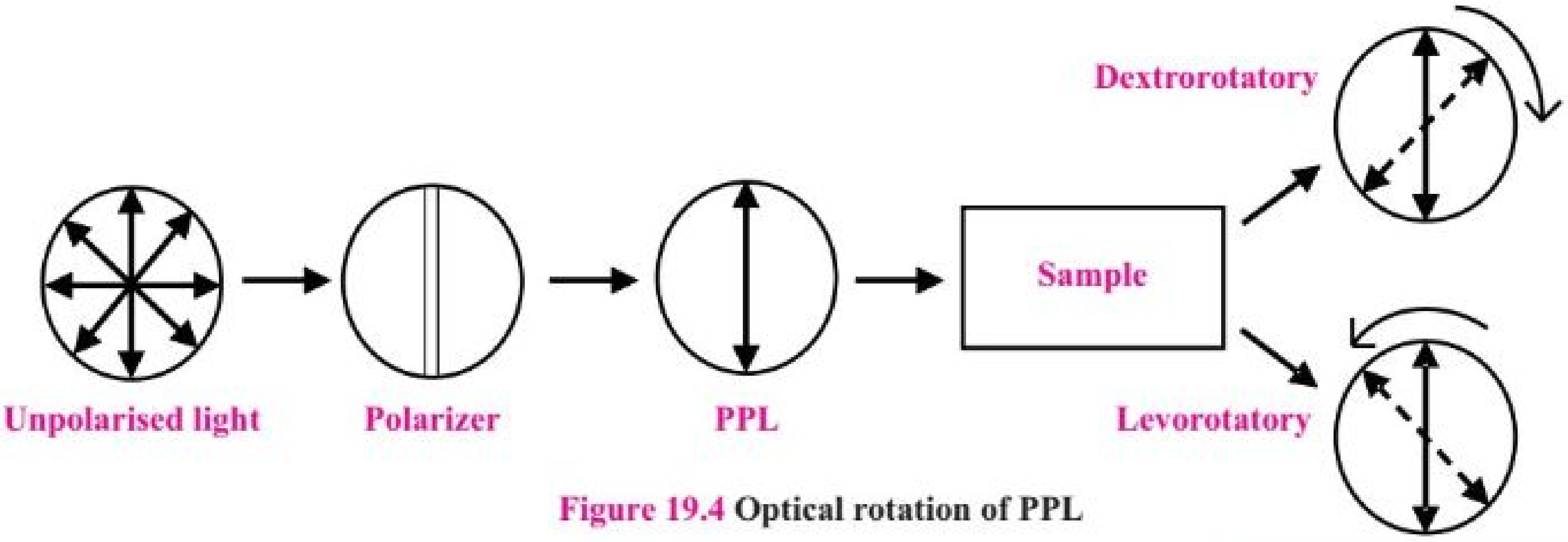


Figure 19.4 Optical rotation of PPL

Optical activity and the structure of a compound

The basic requirement for a compound to be optically active is that it is non-superimposable on its mirror image. This condition is fulfilled by asymmetric/chiral molecules. It can be understood by considering an analogy of our right and left hands, which are non-superimposable as in **Figure 19.5**. the word 'chiral' is from a Greek word 'Cheir' which means hand. Hence, chirality is also called handedness.

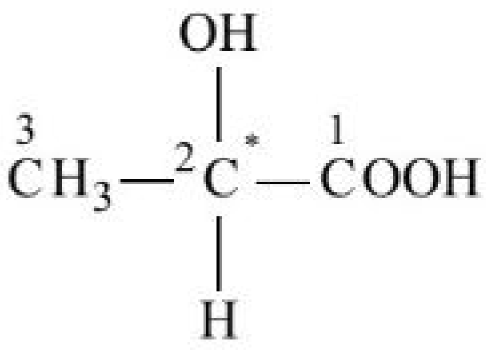
Molecules which are superimposable on their mirror images are achiral and they are optically inactive.

Figure 19.5 Our hands are non-superimposable on their mirror images.

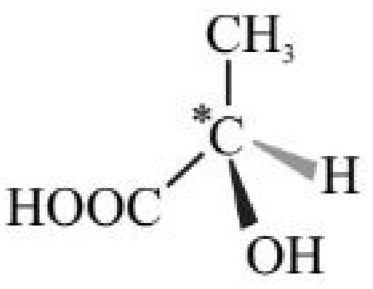
A carbon atom bearing four different atoms or group of atoms is called chiral carbon. Any organic molecule which is not symmetric and it rotates the plane polarised light is a chiral or asymmetric molecule. If a molecule has only one chiral carbon atom, it is always asymmetric and hence optically active. However, if there are more than one chiral atoms, a molecule may or not be asymmetric and optically active.

Enantiomers

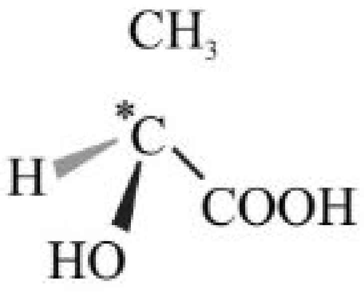
If a molecule has only one chiral carbon atom, it is always chiral and hence optically active. For example consider the structure of lactic acid. It has a chiral carbon (indicated by an asterisk) bonded to four different groups, i.e, CH_3, H, OH and COOH.



$$\overset{3}{C}H_3-\underset{H}{\overset{OH}{{}^{2}C^{*}}}-\overset{1}{C}OOH$$



(–) lactic acid

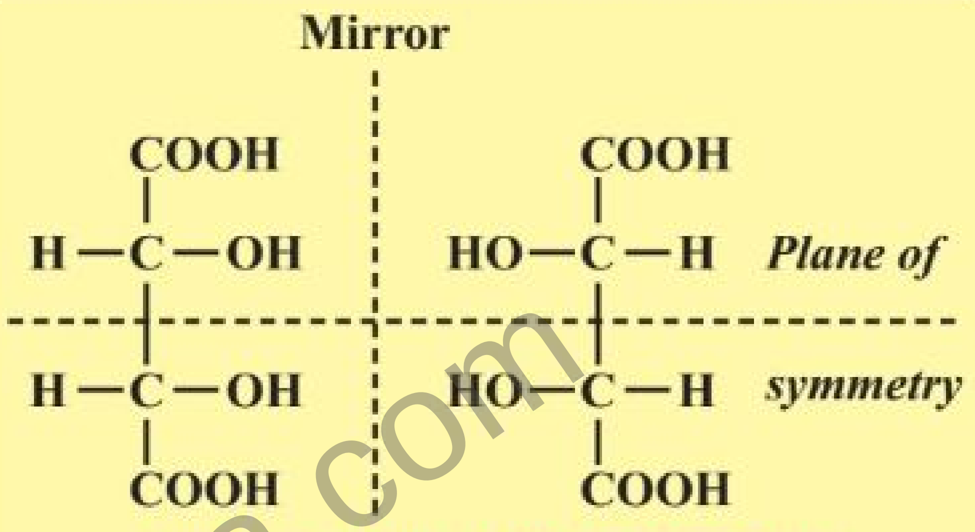


(+) lactic acid

Its three dimensional structure shows that it has two stereoisomers which are non-superimposable mirror image of each other and are called enantiomers ('enantio' means opposite). The **enantiomers** have identical physical and chemical properties but they rotate the plane of polarised light in opposite directions, with the same extent. One enantiomer is, therefore, dextrorotatory (+) and the other is levorotatory (-). When 50% dextrorotatory and 50% levorotatory enantiomers are present, they form an optically inactive mixture. Such a mixture is called a racemic mixtur. A racemic mixture is symbolized by placing symbol (±)in front of the name of the compound. Thus, lactic acid exists in two different optically active forms i.e, (+) lactic acid, (-) lactic acid and an inactive racemic mixture (±).

Meso Isomers

The stereoisomers which contain at least two similar chiral carbon atoms and also possess a plane of symmetry are optically inactive. The plane of symmetry divides the molecule into two equal halves, one half of the molecule being mirror image of the other half. The two halves will rotate the plane of polarised light in opposite direction. As a result, rotation of one half of molecule is internally compensated (cancelled) by the other half and the molecule will become optically inactive. Such stereo isomers are called meso forms. Tartaric acid is the classic example of this phenomenon.



1 and 2 are Identical and represent meso form of tartaric acid

Maximum number of optical isomers of an optically active compound is given by the formula 2^n, where 'n' is the number of chiral carbon atoms. This number is reduced, however, if there are two or more similar chiral carbon atoms.

Quick Check 19.7

Q1: Classify the following objects as chiral or achiral.

(a) Pencil (b) Book (c) Shoe (d) Cup
(e) Ear (f) Foot (g) Egg (h) Spoon

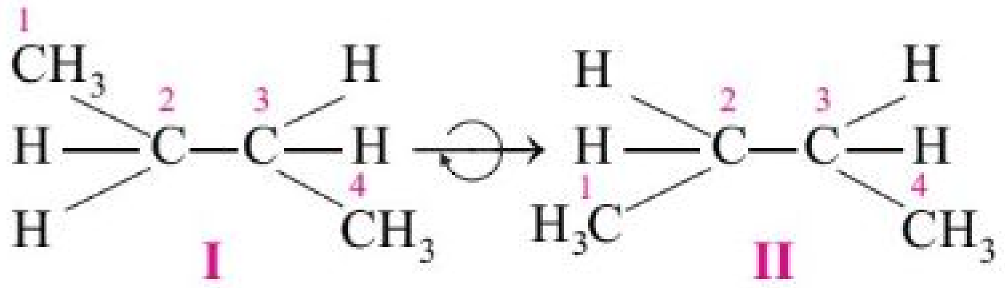
Q2: Glucose and fructose are two monosaccharides.

i. How many chiral carbon atoms are there in glucose and fructose?
ii. Calculate the possible number of optical isomers of glucose and fructose.
iii. Is there any meso form in glucose or fructose? Give reason.

19.9.1 Cis-trans Isomerism

The stereoisomers having different spatial arrangement of atoms due to restricted rotation about a double bond in open chain compounds are called cis-trans isomers.

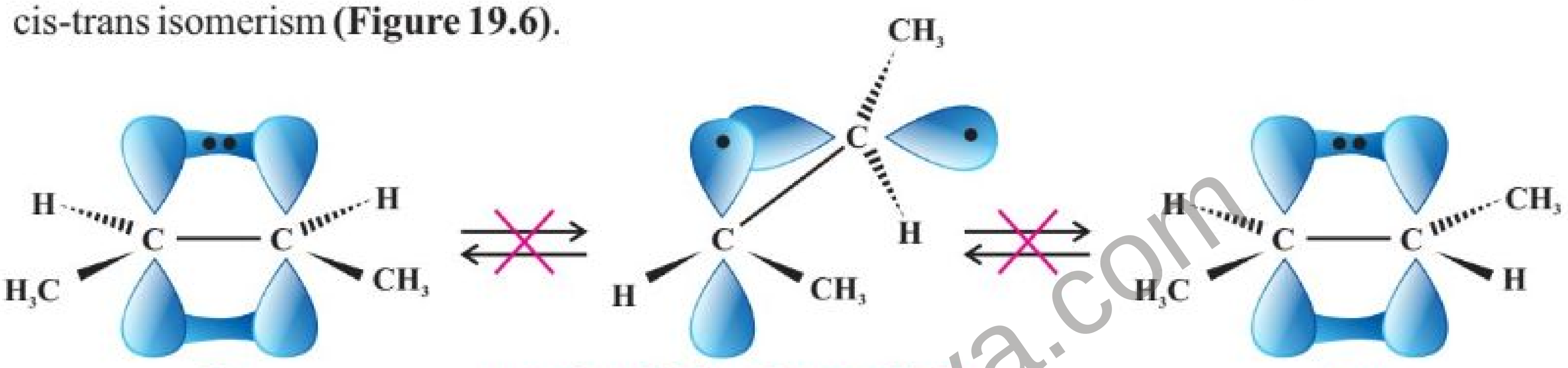
First of all we consider free rotation about C-C single bond in butane.



In butane, forms I or II are called conformational isomers because they are interconvertable into each other due to free rotation of the C-C single bond. They cannot be separated at room temperature.

When the C-C single bond between C-2 and C-3 atoms rotates, the methyl groups also rotate and structure I changes in II and II back into I due to this free rotation.

Now, consider but-2-ene $\overset{1}{C}H_3-\overset{2}{C}H=\overset{3}{C}H-\overset{4}{C}H_3$ in which both carbon atoms 2 and 3 are sp^2 hybridized. The C-C double bond consists of a σ bond formed by the linear overlap of sp^2 hybrid orbitals and a π bond formed by the parallel overlap of ρ orbitals. The presence of π bond locks the molecule in one position. The two carbon atoms C-2 and C-3 of the double bond and all the groups attached to them lie in the same plane and their position in space is fixed. For free rotation around the C-C double bond, π bond should be broken first. It requires energy equal to 263 kJ/mol, which is not possible at room temperature. The rotation about C-C double bond is therefore restricted. This restriction of rotation about the C-C double bond is responsible for the cis-trans isomerism **(Figure 19.6)**.



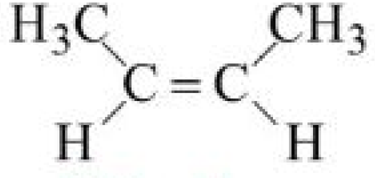
Cis

no overlap with the ends perpendicular

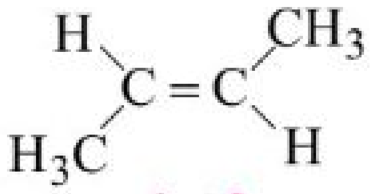
trans

Figure 19.6 The two isomers of but-2-ene cannot interconvert by rotation about the C-C double bond without breaking the π bond

Now the above sturctures can be considered as cis-trans isomers and named as follows.

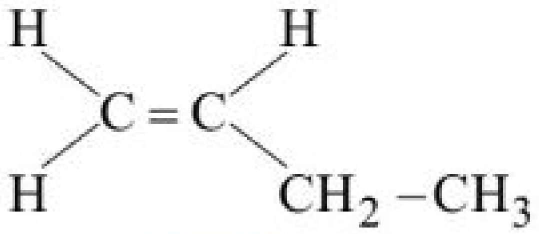


Cis-but-2-ene

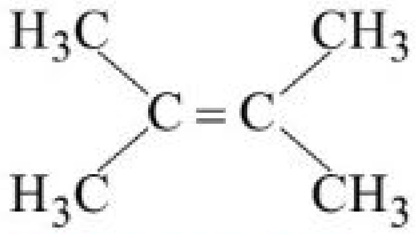


trans-but-2-ene

The cis isomer is one in which two similar groups are on the same side of the double bond. The trans isomer is that in which two similar groups are on the opposite side of the double bond. It is important to note that cis-trans isomerism will not be possible, if one of the unsaturated carbon atom is bonded to two identical groups. For example:



but-1-ene



2,3-dimethylbut-2-ene

Each of the above two compounds does not show cis-trans isomerism.

KEEP IN MIND

The cis-trans isomers have different physical and chemical properties. The trans isomers are more stable than the corresponding cis isomers and hence differ in chemical reactivity. Similarly, both types of isomers have different physical properties like melting point, boiling point, dipole moment, density, heat of vapourisation etc.

"Thus for an open chain compound the necessary and sufficient condition to show cis-trans isomerism is that, it should have double bond in its molecule and that two different groups must be attacked to each of the doubly bonded carbon atoms."

19.10 STEREOCHEMISTRY IN DRUG DEVELOPMENT

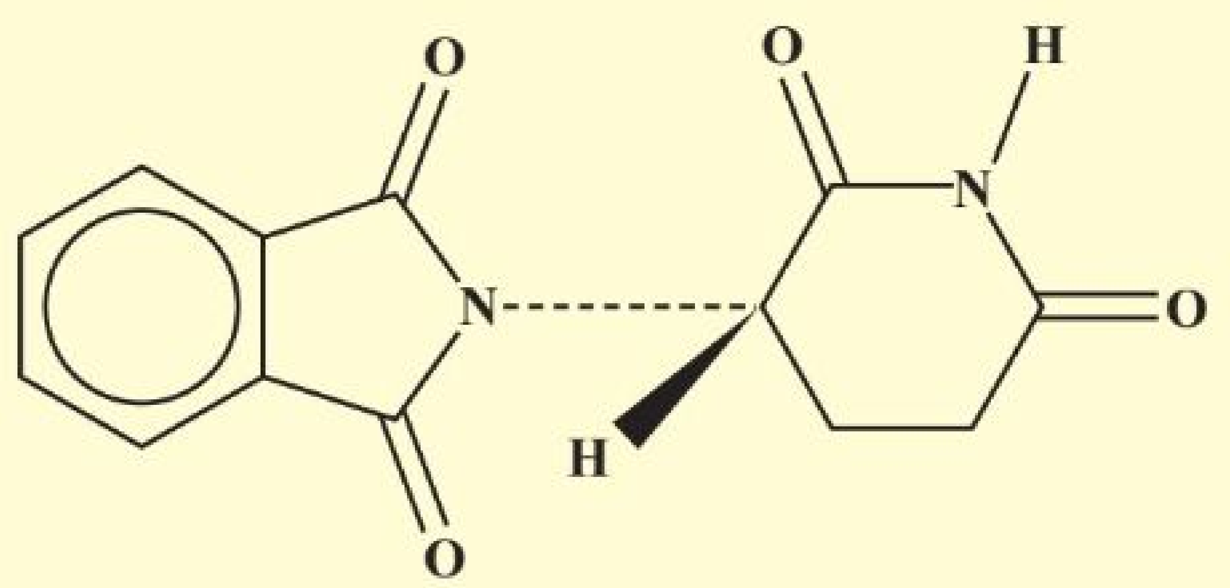


Figure 19.7: Thalidomide

In the synthesis of pharmaceutical products chirality is a critical feature to determine safety and efficacy. Because biological system are composed of chiral building block drug receptors which function as highly specific "chiral locks". Consequently, the two enantiomers of a chiral drug often exhibit vastly different potentials and profiles. Thalidomide, a tranquilliser was originally distributed as racemic mixture **Figure 19.7**. It seemed to be a very successful, non-toxic sedative with no known side-effects. In the early 1960s, however, it was discovered that women who had been prescribed the sedative to treat the nausea ('morning sickness') in early pregnancy had produced badly deformed babies. The drug was immediately withdrawn.

Research showed that whilst the (+) isomer was an effective and safe tranquilliser, the (-) isomer was the culprit in damaging the fetus. Originally it was thought that the problem had been due to contamination by the (-) isomer in some production batches, but subsequent research has shown that racemisation of the pure (+) isomer occurs rapidly as soon as it enters the blood stream. Within 10 minutes racemisation is over 50% complete. Thalidomide will never be marketed again, although analogues, that are chirality stable are being, investigated as possible anti-inflammatory drugs.

Exercise

Q1. Multiple Choice Questions (MCQs):

I) Which of the following is organic in nature?

a) CO_2 b) CS_2

c) HCN d) CCl_4

II) The empirical formula of $CH_3CH_2CH{=}CH_2$ matches with:

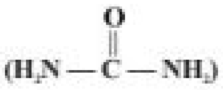
a) CH_3CH_3 b) $CH_2{=}CHCH_3$

c) $CH_3CH_2CH_2CH_3$ d) $CH{\equiv}CH$

III) Compounds having single bonds usually undergo reactions:

a) addition b) elimination

c) substitution d) both elimination and substation

IV) The functional group present in urea  $(H_2N-\overset{\overset{O}{\|}}{C}-NH_2)$ **is:**

a) carbonyl b) amino

c) amide d) all of these

V) Which molecule is chiral and can rotate the plane polarised light?

a) Pentan-1-ol b) Pentan-2-ol
c) 2,2-dimethylpropan-1-ol d) 2-methylbutan-2-ol

VI) Which carbon in $CH_3CH(CH_3)CH_2CH(OH)CH_3$ is chiral?

a) C–1 b) C–2
c) C–3 d) C–4

VII) In what ways could two compounds of molecular formula $C_2H_2Br_2$ be related to each other?

a) optical isomers b) cis-trans isomers
c) constitutional isomers d) both b and c

VIII) Which of following shows cis-trans isomerism?

a) 1-butene b) propene
c) 2-butene d) 1,1-dichloro ethene

IX) Which one of the following pairs do the isomers have identical boiling points?

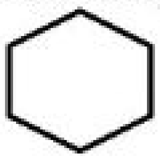
a) cis and trans isomers b) (+) and (-) enantiomers
c) cis-trans and optical isomers d) structural isomers

Q2. SHORT ANSWER QUESTIONS

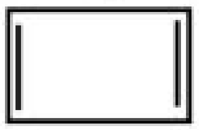
a) Define enantioers. Give enantiomers of 2-methylbutan-2-ol.

b) Alkanes have no functional group. Justify.

c) Deduce the empirical and molecular formulae of the following compounds.

a) 

b) 

c) 

d) Give systematic names of the following compounds.

i) CH_3-CH_2-CN ii) $CH_3COCH_2CH_2$-CH_3 iii) $CH_3CH_2COOCH_3$

e) Define electrophile and nucleophile with two examples each.

f) Pent-2-ene shows cis-trans isomerism but pent-1-ene does not. Give reason.

g) Define:

i) Constitutional isomerism ii) Stereoisomerism

h) Define:

i) racemic mixture ii) Optical activity

i Explain why meso tartaric acid is optically inactive although it has two chiral carbon atoms.

Q3. CONSTRUCTED RESPONSE QUESTION

a) A compound $C_6H_5CH_3$ reacts with Cl_2 in the presence of sunlight to form the product $C_6H_5CCl_3$. Name the mechanism of the reaction. Give its different steps.

b) Draw the mirror image of each of the following compounds. Label each molecule as chiral or achiral.

i) 2-bromo-2-chloropropane ii) 1-bromo-1-chloroethane iii) ethoxyethane

iv) 2-aminopropanoic acid

c) What is the alkane of lowest relative molecular mass that contains a chiral centre? Give its systematic name and molecular formula. Also draw mirror image of this compound.

d) 3-chlorobutan-2-ol is an optically active compound. Draw all its possible optical isomers. Is there any meso form of this compound? Give reason.

DESCRIPTIVE QUESTIONS

Q4. Explain the difference between homolytic and heterolytic fissions of a covalent bond.

Q5. Discuss cis-trans isomerism. Explain with two examples.

Q6. Describe the phenomenon of optical activity. Explain with an example.

Q7. What is the difference between racemic mixture and meso compound? Draw the structures of enantiomers and meso form of lactic acid.