



Isomerism

In the study of organic chemistry we come across many cases when two or more compounds consist of equal number of like atoms. These compounds have the same molecular formula but differ from each other in physical or chemical properties, and are called **Isomers** and the phenomenon is called **Isomerism**. 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. There are two main types of isomerism :

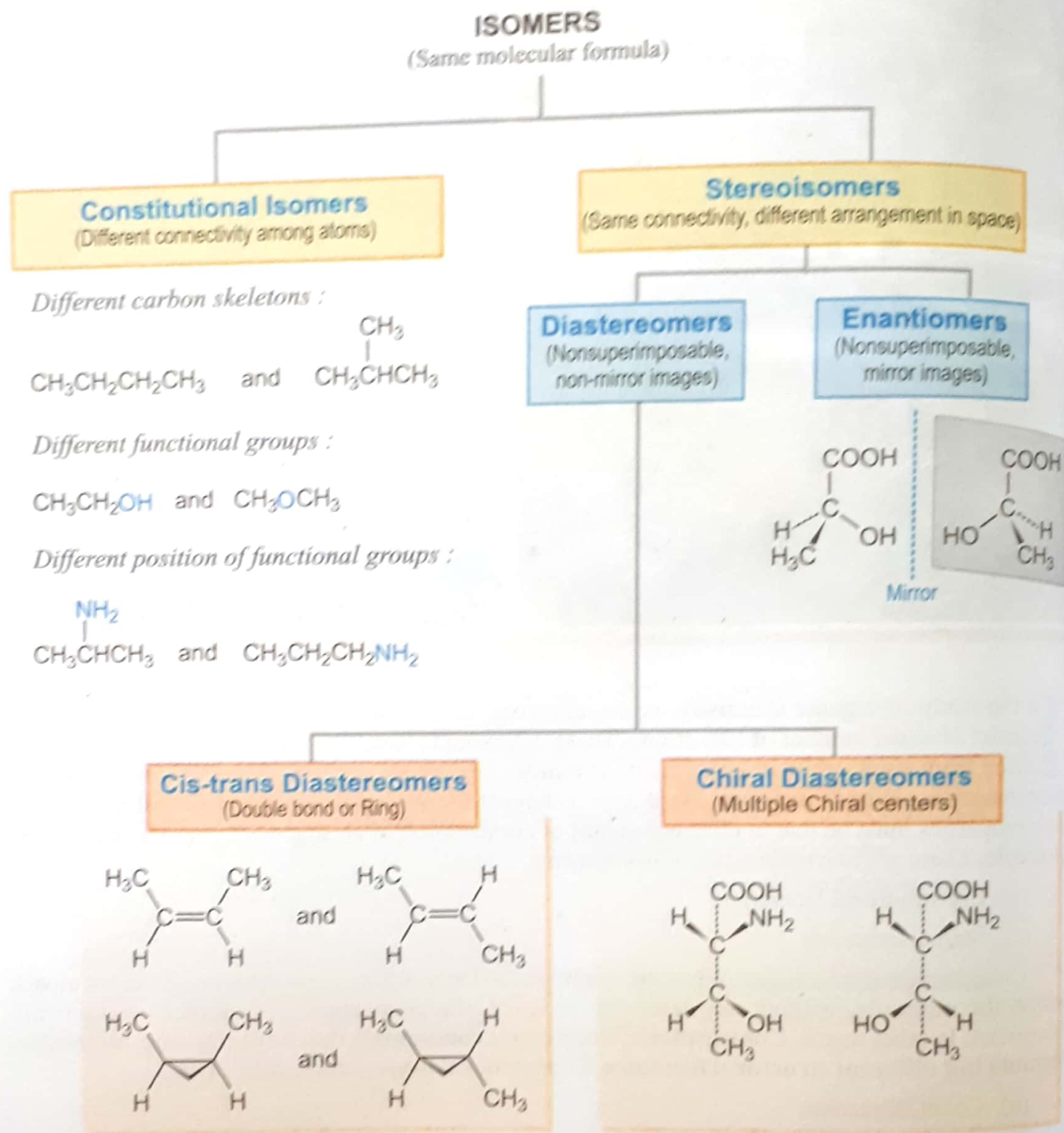
- (1) Constitutional Isomerism
- (2) Stereoisomerism

Constitutional Isomerism. When the isomerism is due to difference in the arrangement of atoms within the molecule, without any reference to space, the phenomenon is called *Constitutional Isomerism*. In other words, **Constitutional isomers are compounds that have the same molecular formula but different structural formulas**. Constitutional isomerism is of five types :

- (a) Chain Isomerism
- (b) Position Isomerism
- (c) Functional Isomerism
- (d) Metamerism
- (e) Tautomerism

Stereoisomerism. When isomerism is caused by the different arrangements of atoms or groups in space, the phenomenon is called *Stereoisomerism*. **The stereoisomers have the same structural formulas but differ in arrangement of atoms in space**. In other words, stereoisomerism is exhibited by such compounds which have the same structural formula but differ in *configuration*. (The term configuration refers to the three-dimensional arrangement of atoms that characterizes a particular compound). Stereoisomerism is of two types :

- (a) Geometrical or Cis-Trans Isomerism
- (b) Optical Isomerism



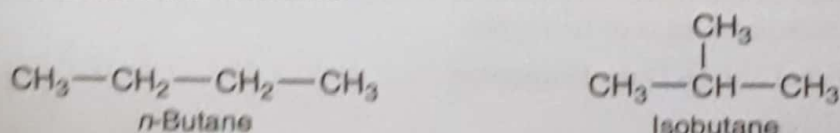
CONSTITUTIONAL ISOMERISM (STRUCTURAL ISOMERISM)

In constitutional isomerism the isomers have the same molecular formula but differ in constitutional formula, that is, in the order in which the different atoms are linked in the molecule. Constitutional isomerism is of five types :

(1) **Chain Isomerism**

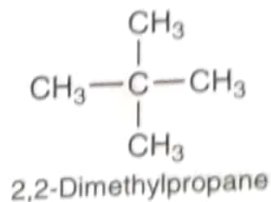
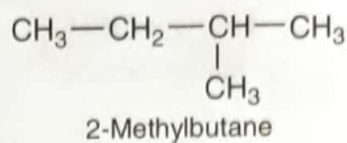
Chain isomers (also called skeletal isomers) have the same molecular formula but differ in the order in which the carbon atoms are bonded to each other.

Example 1. *n*-Butane and Isobutane





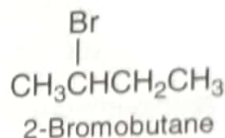
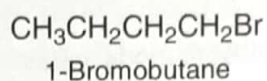
Example 2. 2-Methylbutane and 2,2-Dimethylpropane



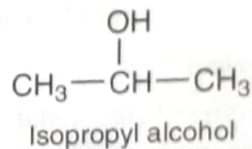
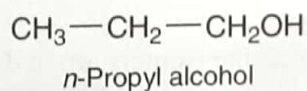
(2) Position Isomerism

Position isomers have the same molecular formula but differ in the position of a functional group on the carbon chain.

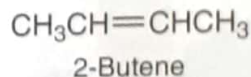
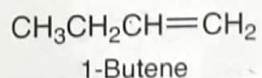
Example 1. 1-Bromobutane and 2-Bromobutane



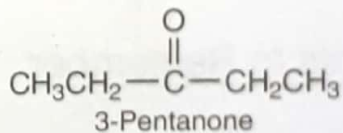
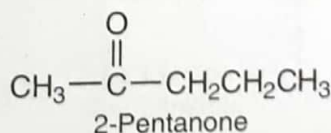
Example 2. *n*-Propyl alcohol and Isopropyl alcohol



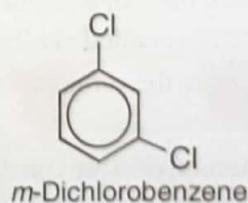
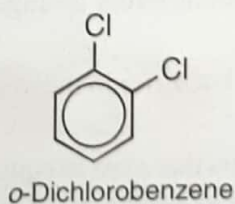
Example 3. 1-Butene and 2-Butene



Example 4. 2-Pentanone and 3-Pentanone



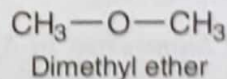
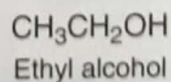
Example 5. *o*-Dichlorobenzene and *m*-Dichlorobenzene



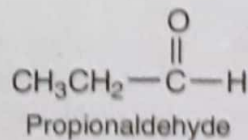
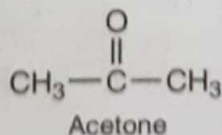
(3) Functional Isomerism

Functional isomers have the same molecular formula but different functional groups.

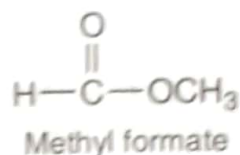
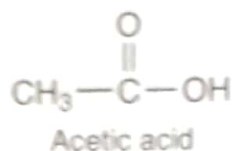
Example 1. Ethyl alcohol and Dimethyl ether



Example 2. Acetone and Propionaldehyde



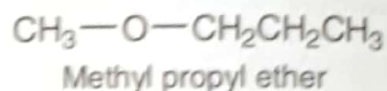
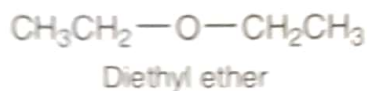
Example 3. Acetic acid and Methyl formate



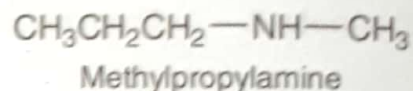
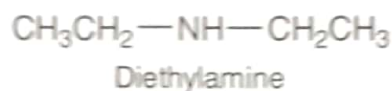
(4) Metamerism

This type of isomerism is due to the unequal distribution of carbon atoms on either side of the functional group. Members belong to the same homologous series.

Example 1. Diethyl ether and Methyl propyl ether



Example 2. Diethylamine and Methylpropylamine



(5) Tautomerism

It is a special type of functional isomerism in which the isomers are in dynamic equilibrium with each other. For example, ethyl acetoacetate is an equilibrium mixture of the following two forms. At room temperature, the mixture contains 93% of keto-form plus 6% of the enol-form.



Points to Remember

1. Constitutional isomers are also called structural isomers.
2. Chain isomers have the same molecular formula but different arrangement of carbon atoms. Chain isomers are also called skeletal isomers.
3. Position isomers have the same molecular formula but differ in the position of a substituent or functional group.
4. Tautomers are interconvertible constitutional isomers that exist in equilibrium with each other.

GEOMETRICAL ISOMERISM

Geometrical isomerism (also called *cis-trans* isomerism) results from a restriction in rotation about double bonds, or about single bonds in cyclic compounds.

(1) Geometrical Isomerism in Alkenes

The carbon atoms of the carbon-carbon double bond are sp^2 hybridized. The carbon-carbon double bond consists of a σ bond and a π bond. The σ bond is formed by the overlap of sp^2 hybrid orbitals. The π bond is formed by the overlap of p orbitals. The presence of the π bond locks the molecule in one position. The *two* carbon atoms of the $\text{C}=\text{C}$ bond and the *four* atoms that are attached to them lie in one plane and their positions in space are fixed. Rotation around the $\text{C}=\text{C}$ bond is not possible because rotation would break the π bond (Fig. 7.1).

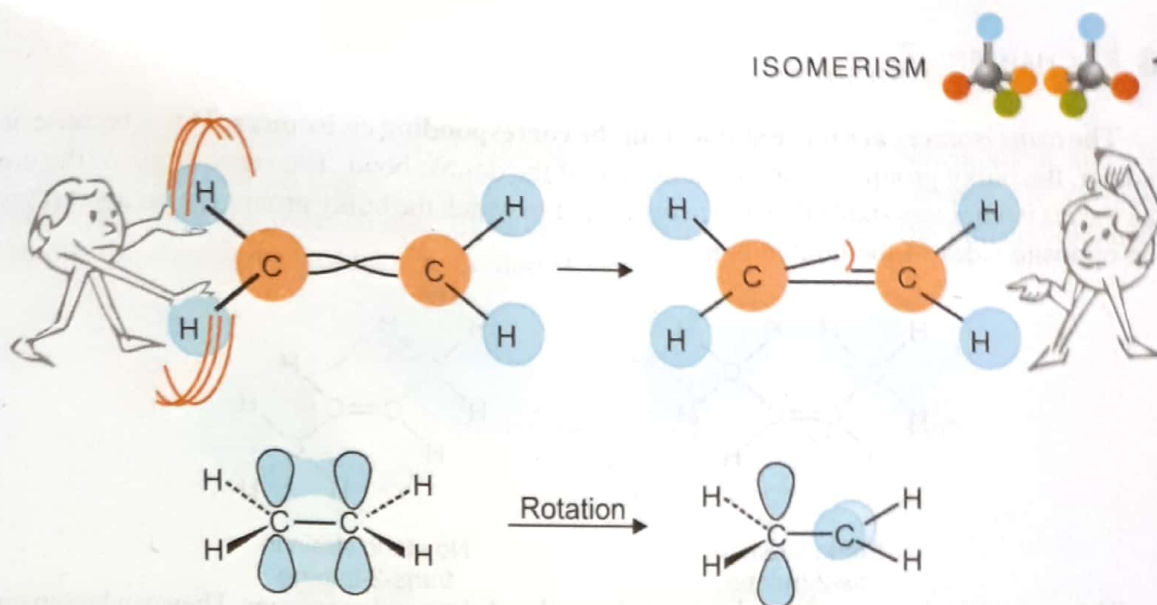
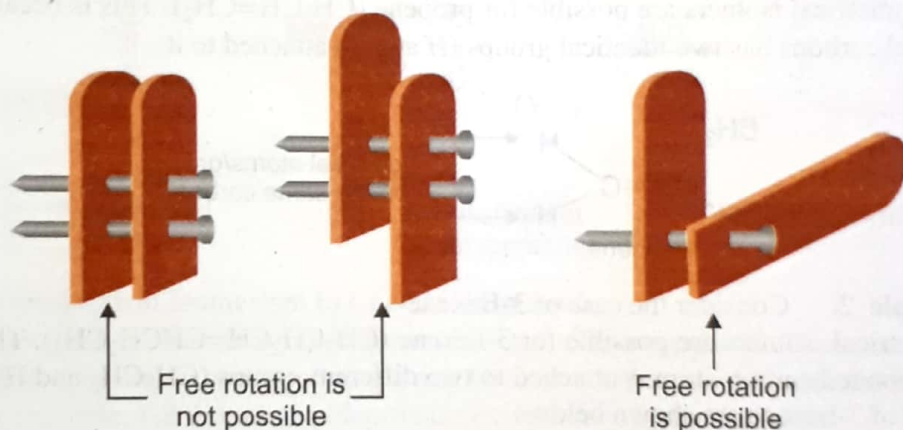
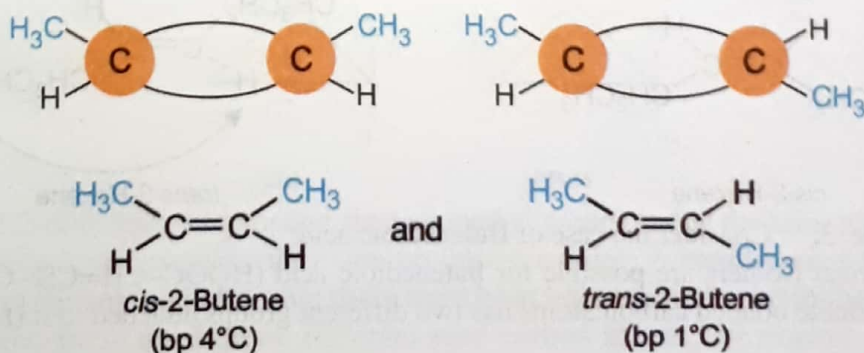


Fig.7.1 Rotation about π bond is not possible because it would break the π bond.

This restriction of rotation about the carbon-carbon double bond is responsible for the geometrical isomerism in alkenes. A popular analogy for this situation is based upon two boards and two nails. Driving one nail through two boards will not prevent free rotation of the two boards. But once a second nail is used, the boards cannot be freely rotated.

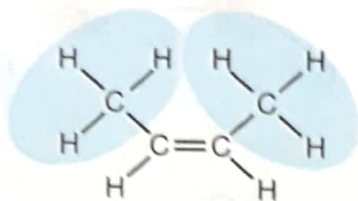


Consider the case of 2-butene. It exists in two spacial arrangements :

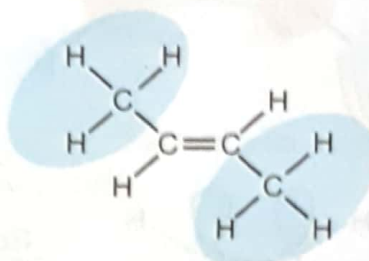


These two compounds are referred to as geometrical isomers and are distinguished from each other by the terms *cis* and *trans*. The *cis* isomer is one in which two similar groups are on the same side of the double bond. The *trans* isomer is that in which two similar groups are on the opposite sides of the double bond. Consequently, this type of isomerism is often called *cis-trans* isomerism. Geometrical isomers are stereoisomers, because they have the same structural formula but different spacial arrangement of atoms.

The *trans* isomers are more stable than the corresponding *cis* isomers. This is because, in the *cis* isomer, the bulky groups are on the same side of the double bond. The steric strain of the groups makes the *cis* isomer less stable than the *trans* isomer in which the bulky groups are far apart (they are on the opposite sides of the double bond).



Steric strain in
cis-2-butene



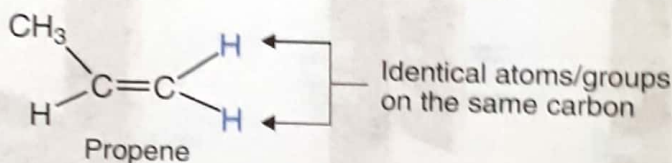
No steric strain in
trans-2-butene

The geometrical isomers have different physical and chemical properties. They can be separated by conventional techniques like fractional distillation, gas chromatography etc.

All alkenes do not show geometrical isomerism. Geometrical isomerism is possible only when each double bonded carbon atom is attached to two different atoms or groups. The following examples illustrate this condition for the existence of geometrical isomers.

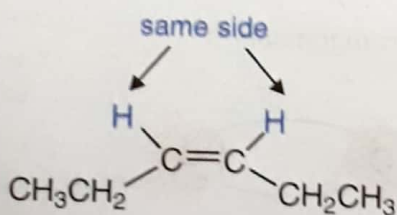
Example 1. Consider the case of Propene

No geometrical isomers are possible for propene ($\text{CH}_3\text{CH}=\text{CH}_2$). This is because one of the double bonded carbons has two identical groups (*H* atoms) attached to it.

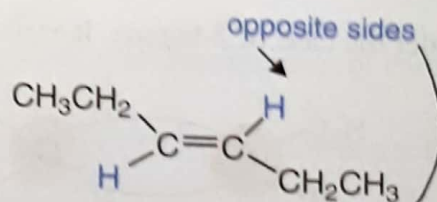


Example 2. Consider the case of 3-Hexene

Geometrical isomers are possible for 3-hexene ($\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_3$). This is because each double bonded carbon atom is attached to two different groups (CH_3CH_2 and *H*). The *cis* and *trans* isomers of 3-hexene are shown below :



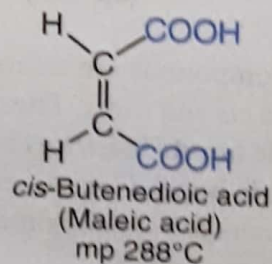
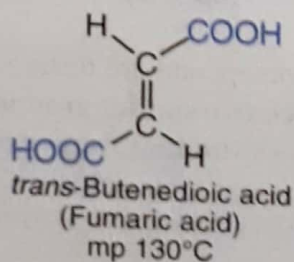
cis-3-Hexene

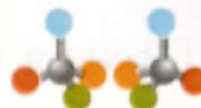


trans-3-Hexene

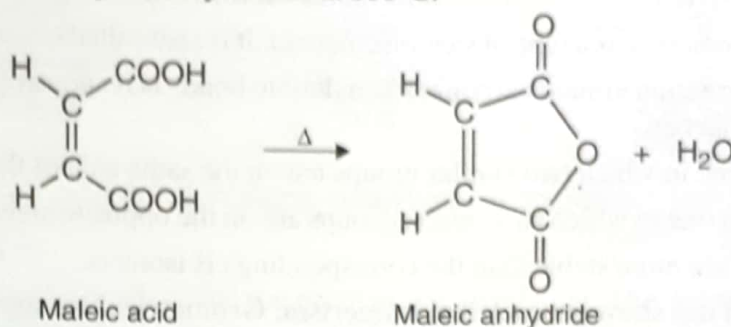
Example 3. Consider the case of Butenedioic acid

Geometrical isomers are possible for butenedioic acid ($\text{HOOC}-\text{CH}=\text{CH}-\text{COOH}$). This is because each double bonded carbon atoms has two different groups attached to it (*H* and COOH).

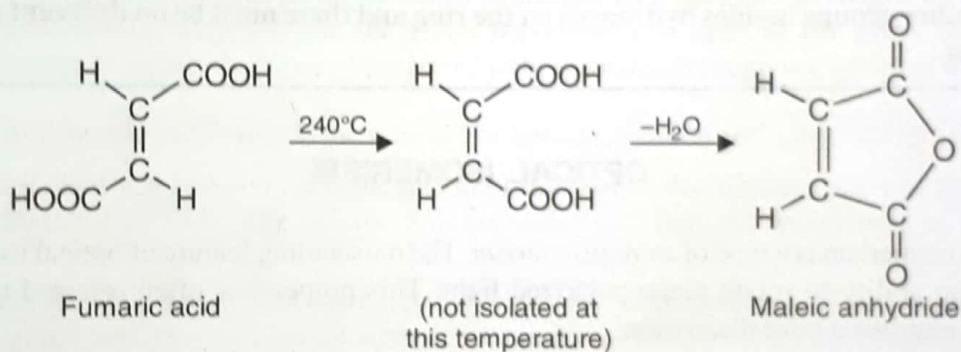




These isomers differ in physical properties such as melting point, dipole moment, and acidities. The *trans*-isomer has no dipole, since it is symmetrical, unlike the *cis*-isomer. The *cis*-isomer is stronger acid than the *trans*-isomer. Even chemical properties differ in the butenedioic acids. For example, the *cis*-acid undergoes dehydration at 100°C.

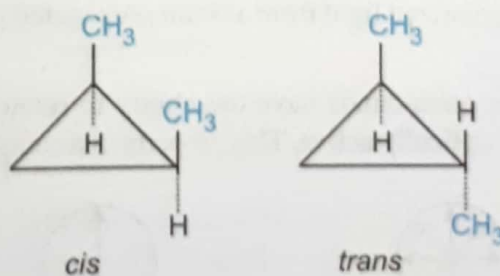


However, the *trans*-acid does not form an anhydride until heated to 240°C. At that temperature there is sufficient thermal energy to break the double bond, so that the *cis*-acid and the anhydride are formed in succession.

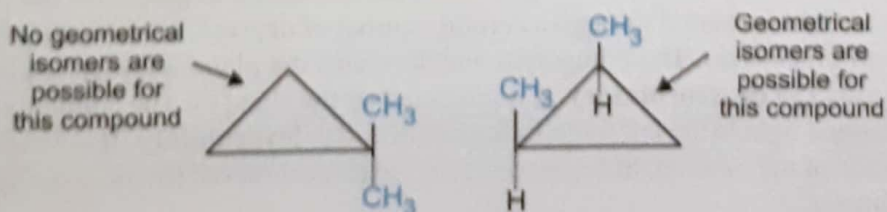


(2) Geometrical Isomerism in Cyclic Compounds

Geometrical isomerism is also possible in cyclic compounds. There can be no rotation about carbon-carbon single bonds forming a ring because rotation would break the bonds and break the ring. For example, 1,2-dimethylcyclopropane exists in two isomeric forms.



In *cis*-1,2-dimethylcyclopropane, the two methyl groups are on the same side of the ring. In *trans*-1,2-dimethylcyclopropane, they are on opposite sides. A requirement for geometrical isomerism in cyclic compounds is that there must be at least two other groups besides hydrogens on the ring and these must be on different ring carbon atoms. For example, no geometrical isomers are possible for 1,1-dimethylcyclopropane.



OPTICAL ISOMERISM

Optical isomerism is a type of *stereoisomerism*. The outstanding feature of optical isomers is that they have the ability to rotate plane-polarized light. This property is often referred to as optical activity and requires a brief discussion.

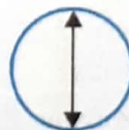
OPTICAL ACTIVITY - PLANE-POLARIZED LIGHT

Light from ordinary electric lamp is composed of waves vibrating in many different planes. When it is passed through Nicol prism (made of calcite, CaCO_3) or polaroid lense, light is found to vibrate in only one plane, and is said to be **plane-polarized** or simply polarized. The diagrams illustrate the vibrations of ordinary and polarized light from a beam propagated perpendicularly to the plane of paper.

Solutions of some organic compounds have the ability to rotate the plane of polarized light. These compounds are said to be **optically active**. This property of a compound is called **optical activity**.



Ordinary Light



Plane-Polarized Light
(Polarized Light)

Optical activity in a compound is detected and measured by means of a **polarimeter**. When a solution of a known concentration of an optically active material is placed in the polarimeter, the beam of polarized light is rotated through a certain number of degrees, either to the right (*clockwise*) or to the left (*anti-clockwise*). The compound which rotates the plane of polarized light to the right (clockwise) is said to be **dextrorotatory**. It is indicated by the sign (+). The compound which rotates the plane of polarized light to the left (anticlockwise) is said to be **levorotatory**. It is indicated by the sign (-). The magnitude of the rotation, in degrees, is referred to as observed rotation, α . Fig. 7.2 shows the parts of a polarimeter.

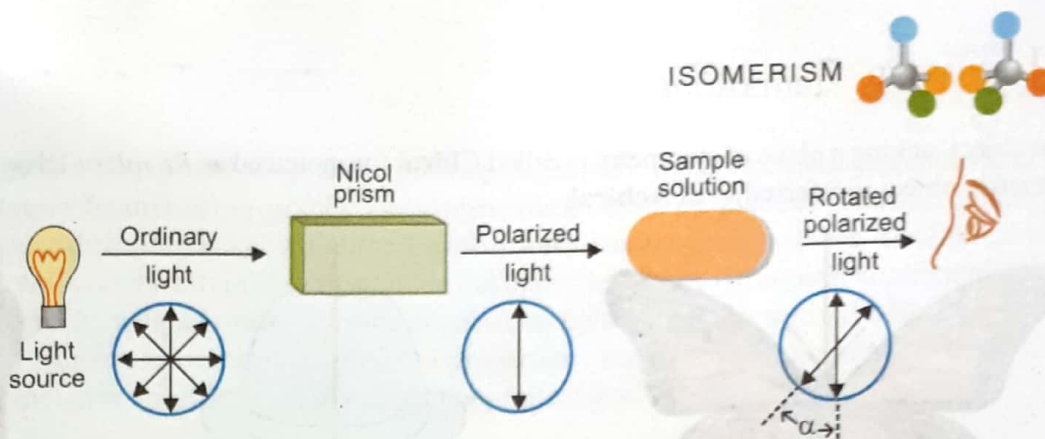


Fig.7.2. A simple polarimeter in operation.

SPECIFIC ROTATION

Optically active compounds rotate the plane of polarized light. The degree of rotation depends upon the number of molecules of the compound encountered by light along its path. It is, therefore, necessary to introduce some standard by which the rotating powers of different compounds may be compared.

Specific rotation is defined as the rotation produced by a solution of length 10 centimeters and unit concentration (1 g/ml) for the given wavelength of light at the given temperature. Consider a system in which the plane of polarized light is rotated through α degrees at a temperature

of $t^\circ\text{C}$ and using the sodium D-line as the source. The specific rotation $[\alpha]_D^t$ is given by $[\alpha]_D^t = \frac{100\alpha}{lc}$ where α is the observed rotation ; l is the length of the tube in decimeters ; and c is the number of grams per 100 ml of solution. The specific rotation varies with both the wavelength of light and the temperature.

Problem. A 1.20 g sample of cocaine, $[\alpha]_D = -16^\circ$, was dissolved in 7.50 ml of chloroform and placed in a sample tube having a path length of 5.0 cm. What was the observed rotation ? Is cocaine dextrorotatory or levorotatory ?

Solution. Use the following relationship :

$$[\alpha]_D^t = \frac{\alpha}{l \times c}$$

Where, α = observed rotation in degrees

l = length of tube (dm) = path length

c = concentration of sample (g/ml)

The given values are :

$$[\alpha]_D^t = -16^\circ$$

$$\alpha = ?$$

$$l = 5.0 \text{ cm} = 0.50 \text{ dm} \quad (1 \text{ dm} = 10 \text{ cm})$$

$$c = 1.20 \text{ g}/7.50 \text{ ml} = 0.160 \text{ g/ml}$$

$$\text{Thus, } -16^\circ = \frac{\alpha}{0.50 \times 0.160}$$

$$\alpha = -16^\circ \times 0.50 \times 0.160$$

$$= -1.3^\circ$$

The observed rotation is -1.3° .

Cocaine is levorotatory.

PLANE OF SYMMETRY

A plane which divides an object into two symmetrical halves, is said to be *plane of symmetry*. For example, a person or a hat has a plane of symmetry (Fig. 7.3). A person's hand or gloves lack a plane of symmetry.

An object lacking a plane of symmetry is called **Chiral** (pronounced as *Ki-ral*) or **Dissymmetric**. A symmetric object is referred to as **Achiral**.



Plane of symmetry

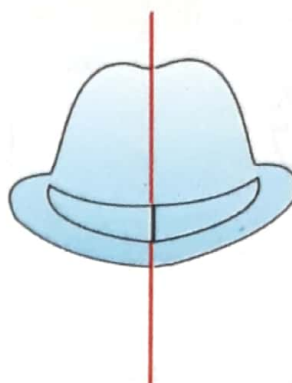


Fig. 7.3. Planes of symmetry.

A chiral object cannot be superimposed on its mirror image. A left hand, for example, does not possess a plane of symmetry, and its mirror image is not another left hand but a right hand (Fig. 7.4). The two are not identical, because they cannot be superimposed. If we were to lay one hand on top of the other, the fingers and the thumbs would clash.

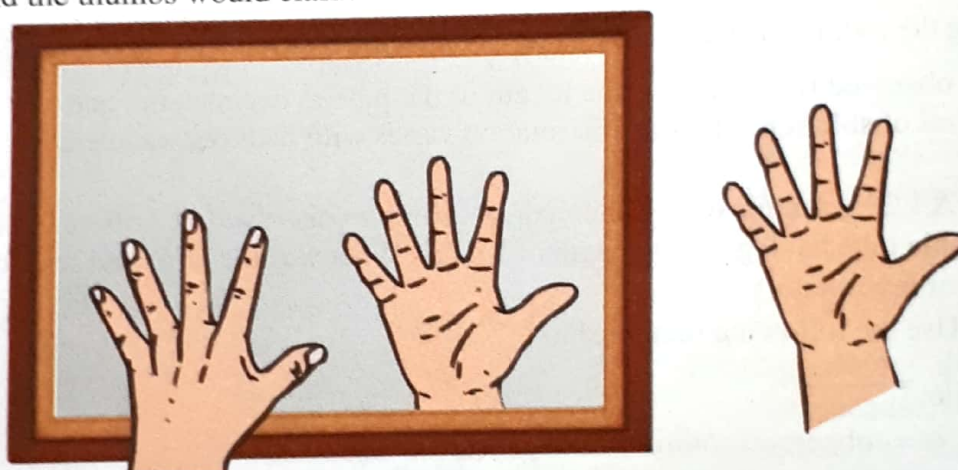
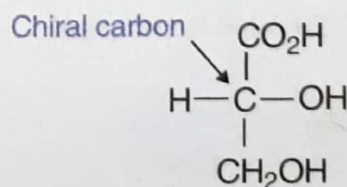
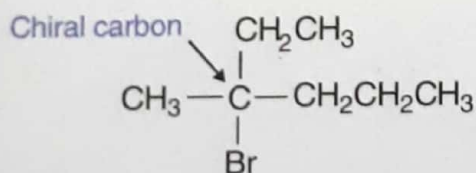


Fig. 7.4. The mirror image relationship of the left and right hands. Notice that right hand is the mirror image of the left hand.

CHIRAL (OR ASYMMETRIC) CARBON ATOM

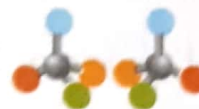
A carbon atom which is bonded to four different groups is called a **Chiral (or Asymmetric) Carbon Atom**. For example,



The term **chiral** (Greek **handedness**; pronounced **kairal**) carbon atom means that a carbon atom is bonded to four different groups and that a molecule of this type lacks a plane of symmetry. Such a molecule is also called **Asymmetric** or **Dissymmetric**.

OPTICAL ISOMERISM

A substance which has the ability to rotate the plane of polarized light is said to be *optically active* and exhibits *optical isomerism*. **Optical isomers are isomers that are identical in all properties except for their effect on plane of polarized light.**

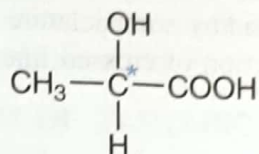


The isomer which rotates the plane of polarized light to the right (clockwise direction) is known as **Dextrorotatory Isomer** or (+)-isomer. The isomer which rotates the plane of polarized light to the left (anticlockwise direction) is known as the **Levorotatory Isomer** or (-)-isomer. The optical rotatory powers of two isomers are equal in magnitude but opposite in sign. An equimolar mixture of the two isomers, therefore, will not rotate the plane of polarized light at all and is said to be **Racemic Mixture**.

Optical isomers have the same physical properties : melting point, boiling point, density, etc. They have the same specific rotation but with opposite signs.

OPTICAL ISOMERISM OF LACTIC ACID

Lactic acid (2-Hydroxypropanoic acid) is an example of a compound which shows optical isomerism. It contains one chiral carbon atom.



Lactic acid. The chiral carbon is shown by an asterisk.

Two three dimensional structures are possible for Lactic acid (Fig. 7.5).

These structures are not identical because they cannot be superimposed on each other. One is the mirror image of the other. Such nonsuperimposable mirror image forms are optical isomers and are called *enantiomers*. Thus, three forms of lactic acid are known. Two are optically active and the third is optically inactive.

1. **(+)-Lactic Acid**. It rotates the plane of polarized light to the right (clockwise direction) and is called dextrorotatory.

2. **(-)-Lactic Acid**. It rotates the plane of polarized light to the left (anticlockwise direction) and is called levorotatory. (-)-Lactic acid is the mirror image of (+)-lactic acid and *vice versa*.

3. **(±)-Lactic Acid**. It does not rotate the plane of polarized light. That is, it is optically inactive. It is an equimolar mixture of (+)-and (-)-forms (racemic mixture).

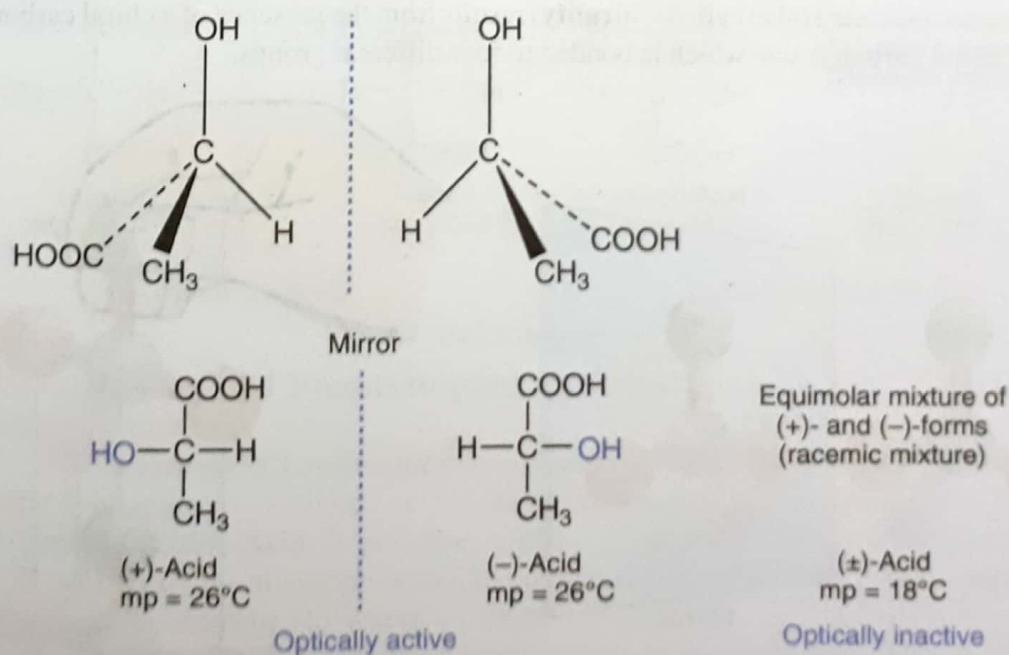


Fig. 7.5. Isomers of Lactic acid. In the upper line two three-dimensional structures are shown. In the lower line a commonly used Fischer projection is given. The vertical lines represent bonds going away from the observer/reader and horizontal lines represent bonds coming toward the observer.

FISHER PROJECTIONS

Fischer projections provide an easy way to draw three-dimensional molecules on paper. All atoms are projected onto one plane. The Fischer projection of one of the enantiomers of lactic acid is shown below :



Fischer projection of (+)-Lactic acid.

The **Fischer rules** for showing the arrangement around a chiral carbon are as follows:

1. The carbon chain of the compound is arranged vertically, with the most oxidized carbon at the top. Or, put the carbon number 1 (as defined by nomenclature rules) at the top.
2. Represent the chiral carbon(s) at the intersection of crossed lines. Some teachers like to show the chiral carbon also.



3. Groups attached to the vertical lines are understood to be going back behind the plane of the paper. That is, the vertical lines represent bonds going away from the observer. The chiral carbon is in the paper plane.
4. Groups attached to the horizontal lines are understood to be coming forward out of the paper plane. That is, the horizontal lines represent bonds coming toward the observer.

CONDITION FOR OPTICAL ISOMERISM

The necessary condition for a molecule to exhibit optical isomerism is that it should be *dissymmetric*. That is, the molecule should not be superimposable on its mirror image. In simple molecules, the dissymmetry (also called **Chirality**) results from the presence of a chiral carbon atom. Recall that a chiral carbon is one which is bonded to four different groups.

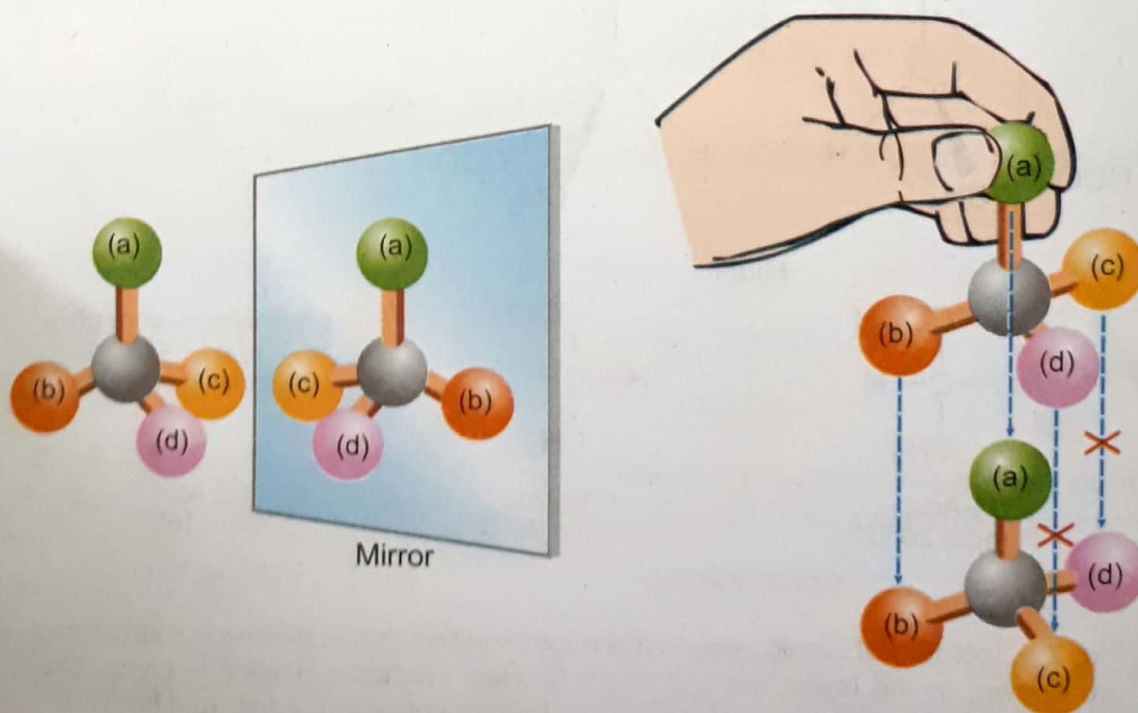


Fig. 7.6. The two forms (I and II) of C_{abcd} are nonsuperimposable.



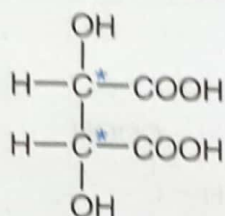
Consider a chiral molecule C_{abcd} . Fig. 7.6 shows two three dimensional models for this molecule. The form (II) is the mirror image of (I) and the two cannot be superimposed. If you try to superimpose the four groups attached to a chiral carbon atom in form (I) and form (II), only two of the four groups coincide, while the other two are in conflict. This shows that the two forms represent different compounds.

The nonsuperimposable mirror image forms of a chiral molecule are called **Enantiomers** (Greek, *enantio* = opposite). They represent two optical isomers : (+) and (-). Their opposite rotatory powers are due to the opposite arrangements of groups around the asymmetric carbon atom.

It is true that most of the compounds which contain chiral carbon atoms show optical isomerism. But it is not always so. There are some compounds (such as *meso*-tartaric acid) which have asymmetric carbons but being *achiral*, do not show optical isomerism. On the other hand, there are certain compounds (such as substituted allenes and biphenyls) which have no chiral carbons but being dissymmetric, show optical isomerism.

OPTICAL ISOMERISM OF TARTARIC ACID

Tartaric acid (2,3-Dihydroxybutanedioic acid) contains two chiral carbon atoms.



Tartaric acid. The two chiral carbons are shown by asterisks.

Four forms of tartaric acid are known (Fig. 7.7). Two of them are optically active and two are optically inactive. The optically active forms are related to each other as an object to its mirror image. That is, they are *enantiomers*.

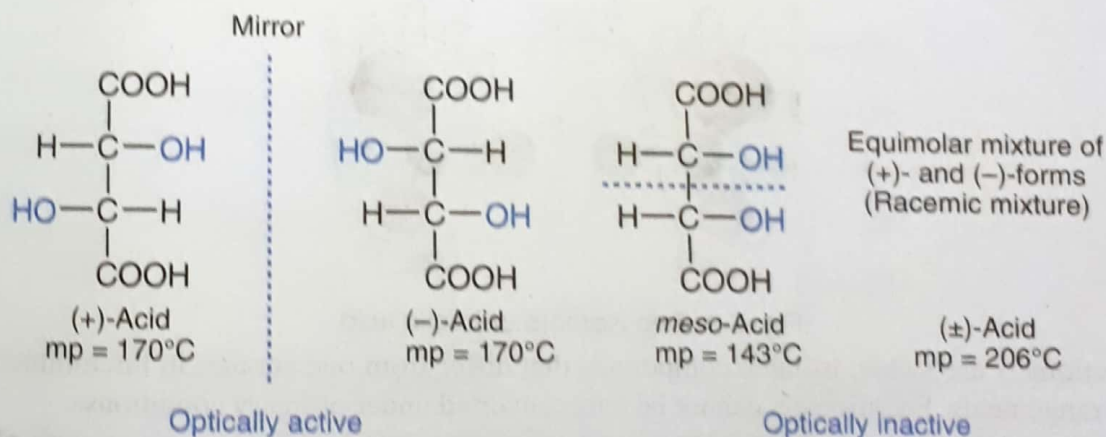


Fig. 7.7. Isomers of tartaric acid.

1. **(+)-Tartaric Acid.** It rotates the plane of polarized light to the right (clockwise direction) and is called dextrorotatory.
2. **(-)-Tartaric Acid.** It rotates the plane of polarized light to the left (anticlockwise direction) and is called levorotatory. (-)-Tartaric acid is the mirror image of (+)-tartaric acid and *vice versa*.
3. ***meso*-Tartaric Acid.** It possesses a plane of symmetry and is consequently optically inactive. This optically inactive form is said to be *internally compensated* (Optical rotation of one asymmetric carbon is cancelled by that of the other).
4. **(±)-Tartaric Acid.** It does not rotate the plane of polarized light. That is, it is optically inactive. It is an equimolar mixture of (+)- and (-)-forms (racemic mixture).

A molecule containing n chiral centres can give rise to a maximum of 2^n optical isomers, unless the compound has a *meso* form, in which case it is $2^n - 1$. For example, *four* optical isomers are possible for 2-bromo-2-butanol. It has *two* chiral carbon atoms but no plane of symmetry (Fig. 7.8).

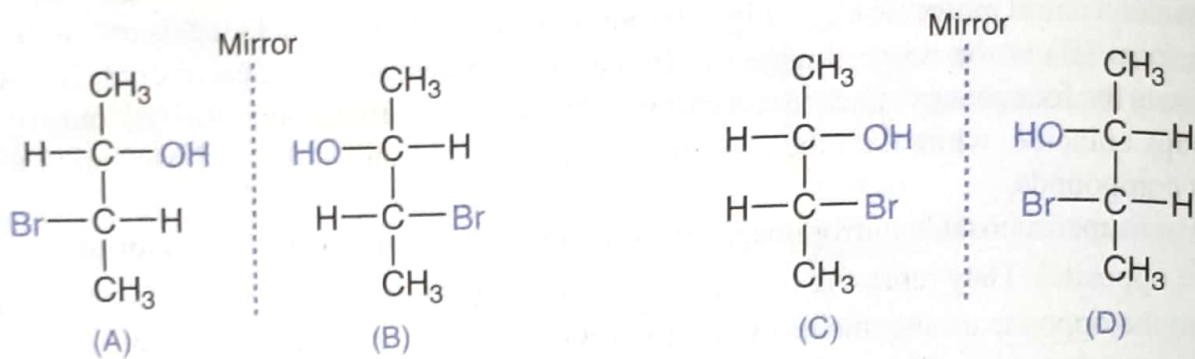


Fig. 7.8. Four isomers of 3-Bromo-2-butanol.

Optical isomers which are not enantiomers (mirror images) such as (A) and (C) or (B) and (D) of the above example, are known as **Diastereomers**.

PROPERTIES OF ENANTIOMERS

Optical isomers that are mirror images are called **Enantiomers**. These always exist as discrete pairs. For example, there are two optical isomers of lactic acid (Fig. 7.9). Notice that (A) is the mirror image of (B). They are a pair of enantiomers.

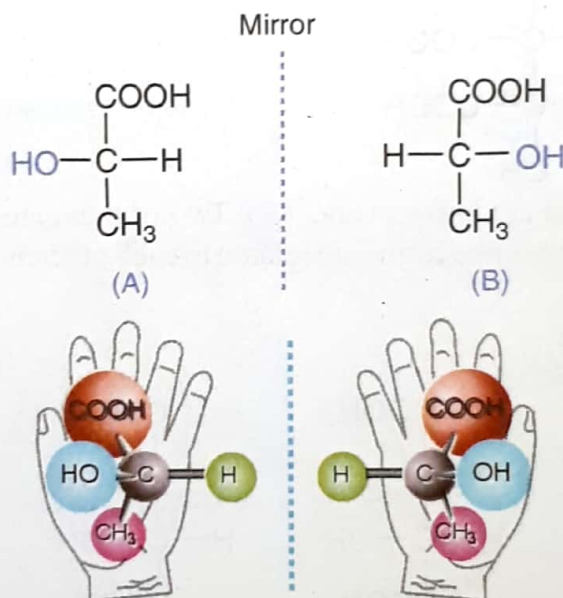


Fig. 7.9. Two isomers of Lactic acid.

Enantiomers are stable, isolable compounds that differ from one another in three-dimensional spatial arrangements. Enantiomers cannot be interconverted under ordinary conditions.

Enantiomers have identical properties in all respects except in their interaction with plane of polarized light. Enantiomers have the same melting point, density, solubility, color, and reactivity toward acids and bases. They differ, however, in the direction in which they rotate the plane of polarized light. Both rotate the plane of polarized light to exactly the same extent (same angle) but one rotates the plane to the right (clockwise; called *dextrorotatory*), while the other rotates the plane to the left (anticlockwise; called *levorotatory*).

A mixture of equal amounts of two enantiomers is called a **Racemic Mixture**. Such a mixture is optically inactive (does not rotate the plane of polarized light) because the two components rotate the plane of polarized light equally in opposite directions and cancel one another.

PROPERTIES OF DIASTEREOMERS

In general, each chiral carbon atom in a molecule doubles the number of theoretically possible isomers. Hence, molecule with n chiral carbon atoms should have 2^n stereoisomers. Fig. 7.10 shows the four isomers of 3-bromo-2-butanol, which has two chiral carbon atoms.



Notice that (A) is the mirror image of (B); (C) is the mirror image of (D). Thus the four isomers are two pairs of *enantiomers*. Now compare (A) with (C). They are neither superimposable nor are they mirror images. They are called *diastereomers*. (A) and (D) are also diastereomers, as are (B) and (C), and (B) and (D). Stereoisomers that are not mirror images of each other are called **Diastereomers**.

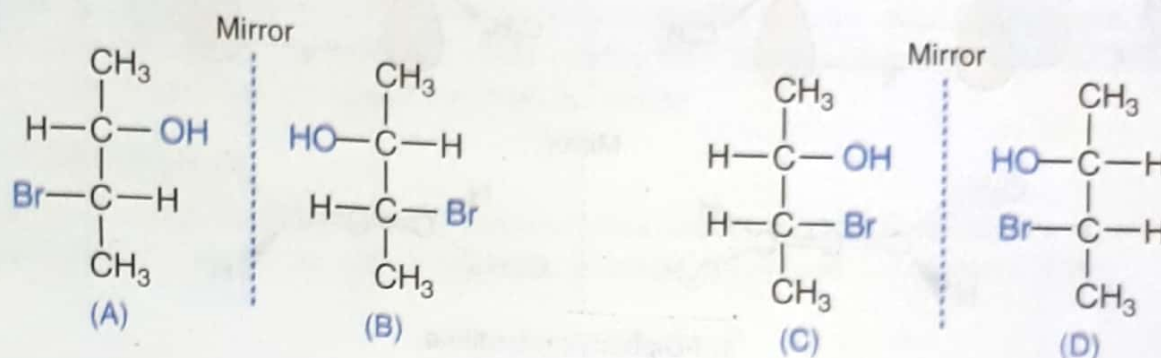


Fig. 7.10. Four isomers of 3-bromo-2-butanol.

Diastereomers have different properties. Two diastereomers will have different melting points, boiling points, and solubilities. They will have different chemical reactivities toward most reagents.

PROPERTIES OF MESO COMPOUNDS

A compound with two or more chiral carbon atoms but also having a plane of symmetry (a mirror plane) is called the **Meso Compound**. Fig. 7.11 shows two meso compounds. These molecules have planes of symmetry dividing them midway between the two chiral carbons in each. Notice that one-half of the molecule is the mirror image of the other. Both molecules are optically inactive, even though each has two chiral centres. Neither will rotate the plane polarized light.

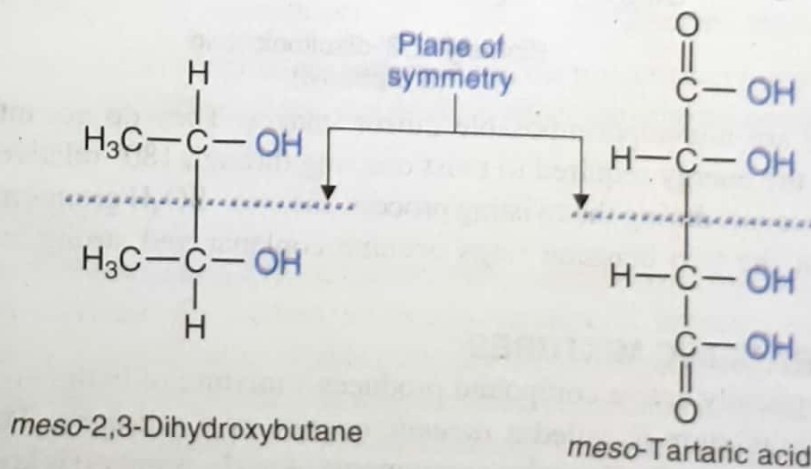
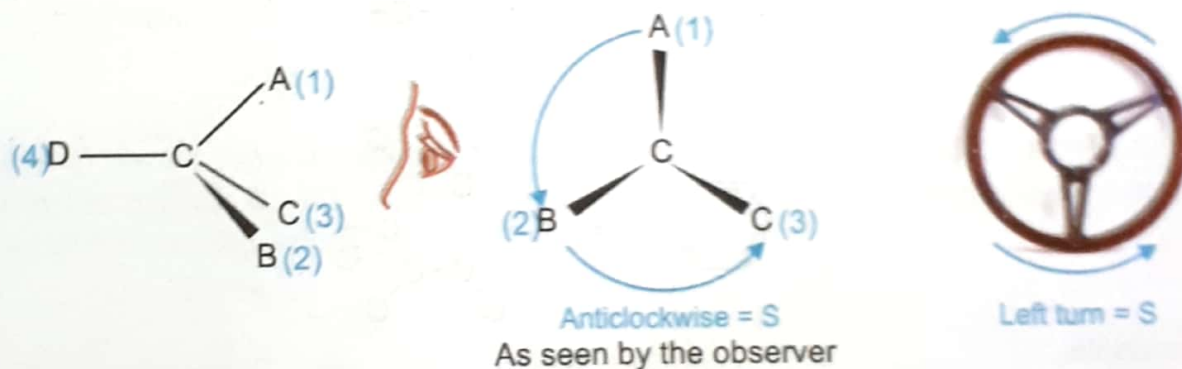


Fig. 7.11. Examples of meso compounds.

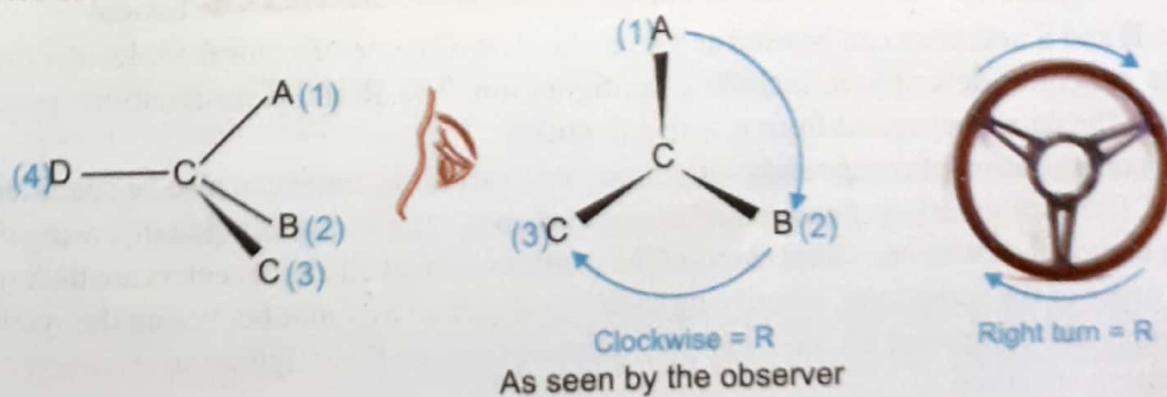
R,S SYSTEM OF SPECIFYING CONFIGURATIONS

The actual three-dimensional arrangement of groups in a chiral molecule is called its **Absolute Configuration**. We can specify the configuration by using the **R,S System**. The R,S system is also called the **Cahn-Ingold-Prelog System** (named after its inventors).

In the R,S system, we arrange the four groups attached to the chiral carbon in decreasing order of priority (1, 2, 3, 4) by applying the rules given below. We then view the chiral center with the lowest priority group (4) on the side opposite the observer (group priorities are shown in parentheses):

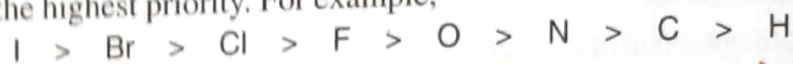


In the above example, **A** has the highest priority (1); **B** has the next highest (2); **C** has the next (3); and **D** has the lowest priority (4). We now go from high to low priority (1→2→3). To do so we move in an *anticlockwise* direction, and therefore we assign to this structure the **S Configuration** (*S* = *sinister* = left). In the structure given below, we go from highest to lowest priority by moving in a *clockwise* direction. We therefore assign to this structure the **R Configuration** (*R* = *rectus* = right).



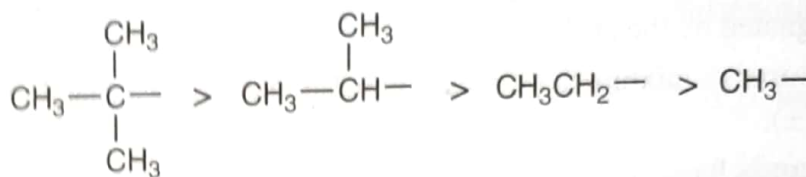
To establish the *group priorities* we use the following **Sequence Rules** :

Rule 1. Of the atoms attached directly to the chiral carbon atom, the one with the highest atomic number has the highest priority. For example,



Highest  Lowest

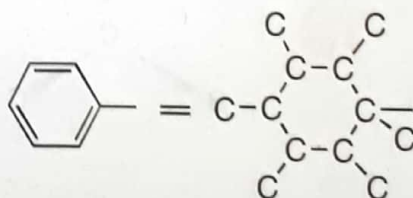
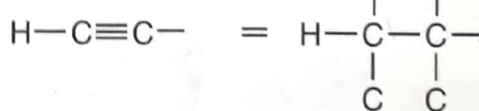
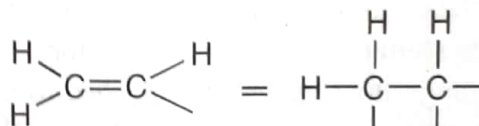
Rule 2. If the atoms attached to the chiral carbon atom are the same, we determine priority by going to the next atom away from the chiral carbon atom. For example,



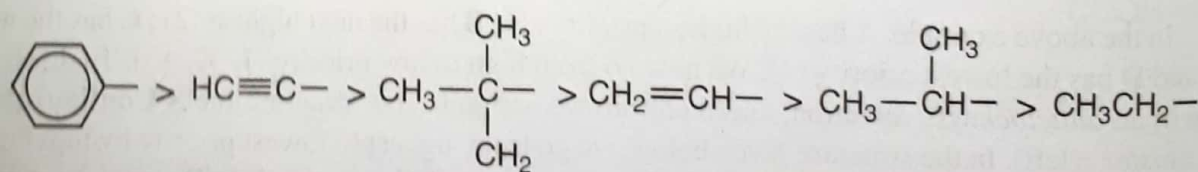
Highest  Lowest

Ethyl has a higher priority than methyl because the ethyl group has (CHH attached to the first carbon, whereas the methyl carbon has only hydrogens (HHH), and C has priority over H. Isopropyl is of higher priority than ethyl because it has two carbons attached to the first carbon and ethyl has only one. If there is no difference at the second atom in the chain, we go to the next atom and so forth.

Rule 3. A double bond is treated as though each atom of the double bond were bonded to two atoms:



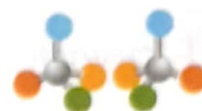
For example,



Highest  Lowest

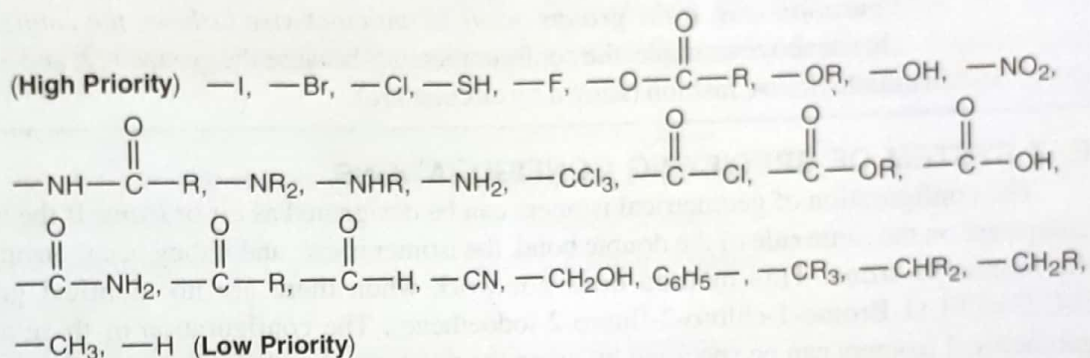
The **R** and **S** notations can be used as part of the IUPAC name of a chiral molecule, to provide a complete structural description, including configuration. The **R** and **S** designations precede the remainder of the name, separated from it with a hyphen.

The configuration of compounds with more than one chiral center can also be specified by the **R,S** system. The configuration of each chiral center carbon is determined individually, using the same rules as for compounds with one chiral carbon. The configuration of all chiral centers are then specified before the name of the compound, identifying each chiral carbon by a number before the symbol **R** or **S**. For example, the compound **2R,3S**-3-chloro-2-pentanol has the **R** configuration at carbon 2 and the **S** configuration at carbon 3.

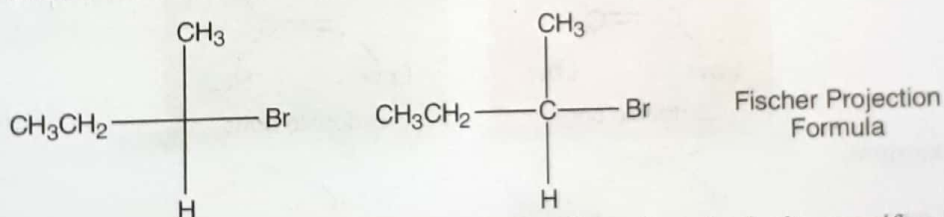


Points to Remember

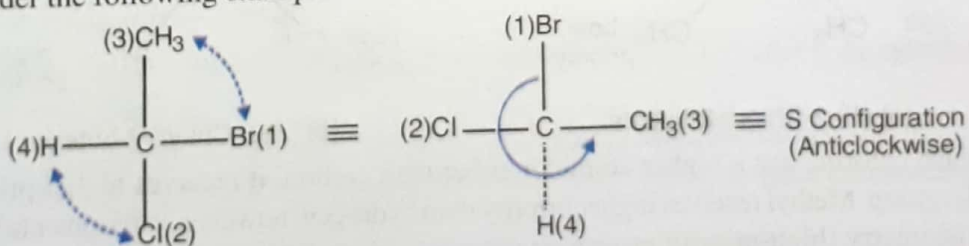
- Most errors in designating the configurations of molecules by R,S system come from a failure to point the lowest priority group away from the observer. You can easily assign the wrong configuration to a molecule if you do not point the lowest priority group away from yourself.
- The priority sequence for the most common atoms and groups is as follows :



- The Fischer projection formula is commonly used to show configuration without going to the trouble of drawing three-dimensional structure. In this convention the chiral center and the bonds to it are represented by crossed vertical and horizontal lines. It is understood that **groups attached by vertical bonds point away from the observer ; those bonded horizontally point toward the observer.** Some chemists show chiral carbon also.



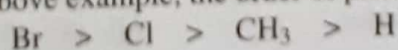
- In exam you are ordinarily given a Fischer projection formula and asked to specify configuration using the symbols **R** and **S**. It is easy to do so if you follow the following *step-by-step* method. Consider the following example :



Order of Priority

- Br (atomic number 79.9) (Highest)
- Cl (atomic number 35.5)
- CH₃ (C, atomic number 12)
- H (atomic number 1) (Lowest)

- Step 1.** Determine the priority of groups attached to the chiral carbon atom. Apply the sequence rules carefully. In the above example, the order of priority is :



- Step 2.** Position the lowest priority group (in this case H) down and away from the observer. This is done by interchanging groups bonded to the asymmetric carbon. Remember that interchanging any pair of groups in a Fischer projection inverts the configuration.

Interchanging two pairs of groups retains the original configuration. Thus, the interchange operation must always be done in pairs to avoid a configuration change.

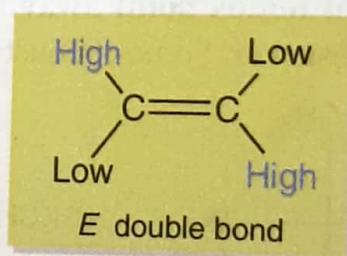
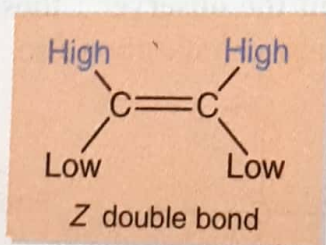
In the above example, a dotted line has been used to highlight a bond between the chiral carbon and the lowest priority group (H). The interchange operations have been shown by dotted double-headed curved arrows.

Step 3. Specify the direction of decreasing priority of the three groups (1→2→3). Ignore the lowest priority group. If the groups 1, 2, and 3 are arranged in clockwise fashion, the configuration is *R*. If the groups occur in anticlockwise fashion, the configuration is *S*.

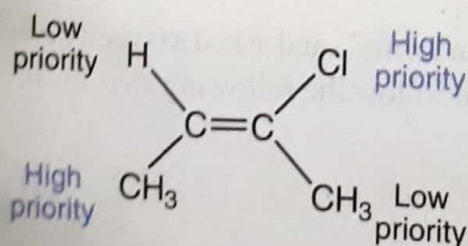
In the above example, the configuration is *S* because the groups 1, 2, and 3 are arranged in anticlockwise fashion (shown by circular arc).

E, Z SYSTEM OF SPECIFYING CONFIGURATIONS

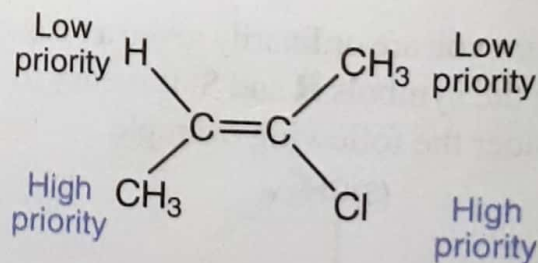
The configuration of geometrical isomers can be designated as *cis* or *trans*. If the two identical groups are on the same side of the double bond, the isomer is *cis*; and if they occur on opposite sides, the isomer is *trans*. This method does not work when there are no identical groups, as in BrCIC=CFI (1-Bromo-1-chloro-2-fluoro-2-iodoethene). The configuration of these and all other geometrical isomers can be specified by using the notations *Z* and *E*. To do this, first determine the group of highest priority on each carbon. If the two high-priority groups are together on the same side, the configuration is *Z* (German, *zusammen* = together). If they are on opposite sides, the configuration is *E* (German, *entgegen* = opposite).



For example,



(a) (*E*)-2-Chloro-2-butene



(b) (*Z*)-2-Chloro-2-butene

Because chlorine has a higher atomic number than carbon, it receives higher priority than a methyl (CH_3) group. Methyl receives higher priority than hydrogen, however, and isomer (a) is therefore assigned *E* geometry (high-priority groups on opposite sides of the double bond). Isomer (b) has *Z* geometry (high-priority groups on "zed zame zide" of the double bond).