

ISOMERS (Same molecular formula)

Structural Isomers (Different connectivity among atoms)

Different carbon skeletons :



Different functional groups :



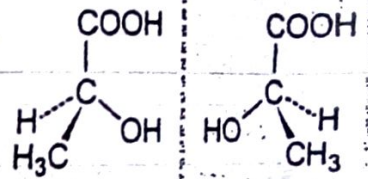
Different position of functional groups :



Stereoisomers (Same connectivity, different arrangement in space)

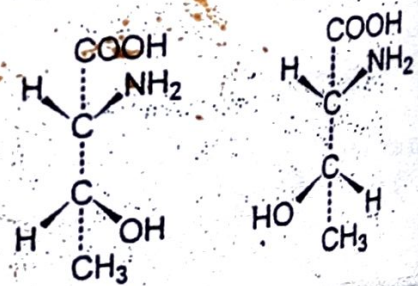
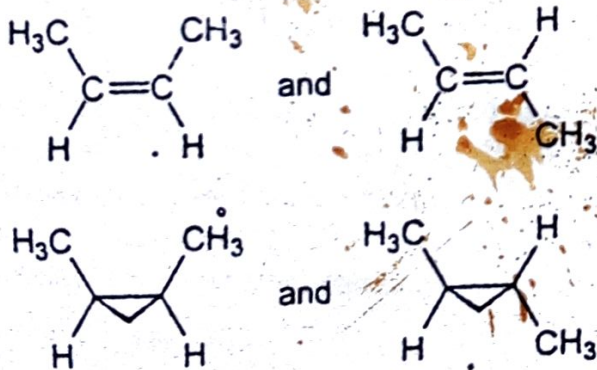
Diastereomers (Nonsuperimposable, non-mirror images)

Enantiomers (Nonsuperimposable, mirror images)



Cis-Trans Isomers (Double bond or Ring)

Chiral Diastereomers (Multiple Chiral centers)



STRUCTURAL ISOMERISM (Constitutional Isomerism)

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

(1) Chain Isomerism

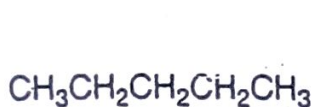
Chain isomers have the same molecular formula but differ in the order in which the carbon atoms are bonded to each other.

Example : *n*-Butane and Isobutane

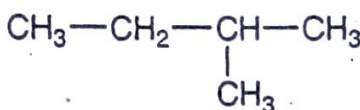
CH₂



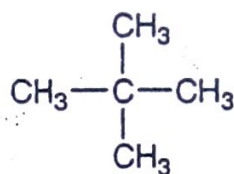
Example 2. 2-Methylbutane and 2,2-Dimethylpropane



n-Pentane



2-Methylbutane



2,2-Dimethylpropane

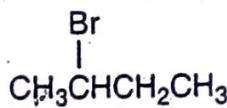
(2) **Position Isomerism**

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

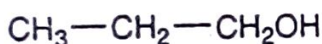


1-Bromobutane

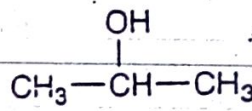


2-Bromobutane

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



n-Propyl alcohol

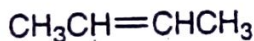


Isopropyl alcohol

Example 3. 1-Butene and 2-Butene

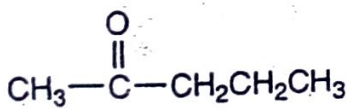


1-Butene

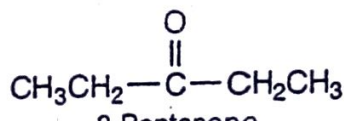


2-Butene

Example 4. 2-Pentanone and 3-Pentanone

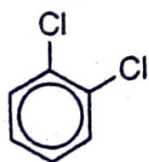


2-Pentanone

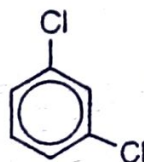


3-Pentanone

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



o-Dichlorobenzene



m-Dichlorobenzene

(3) **Functional Isomerism**

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

Example 1. Ethyl alcohol and Dimethyl ether

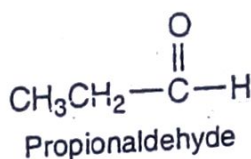
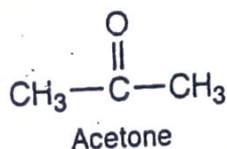


$\text{CH}_3\text{CH}_2\text{OH}$
Ethyl alcohol

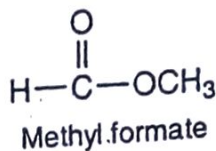
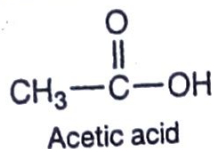
$\text{CH}_3-\text{O}-\text{CH}_3$
Dimethyl ether



Example 2. Acetone and Propionaldehyde



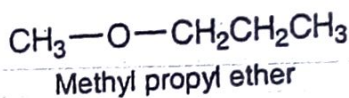
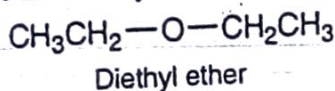
Example 3. Acetic acid and Methyl formate



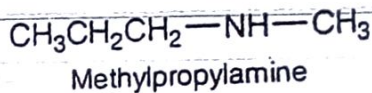
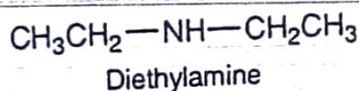
(4) Metamerism

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.

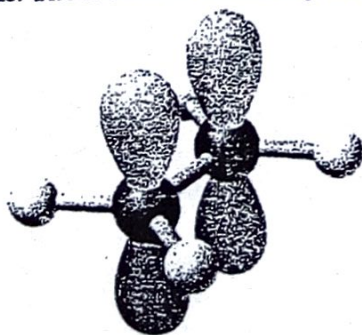


GEOMETRIC ISOMERISM (CIS-TRANS ISOMERISM)

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

GEOMETRIC ISOMERISM IN ALKENES

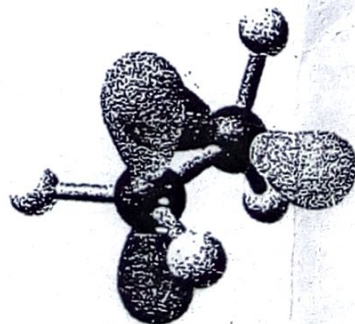
The carbon atoms of the carbon-carbon double bond are sp^2 hybridized. The carbon-carbon double bond consists of a σ bond and a π bond. The σ bond is formed by the overlap of sp^2 hybrid orbitals. The π bond is formed by the overlap of p orbitals.



π -bond

p -orbital overlap

Rotate 90° around
double bond
 \rightarrow
62 kcal/mol



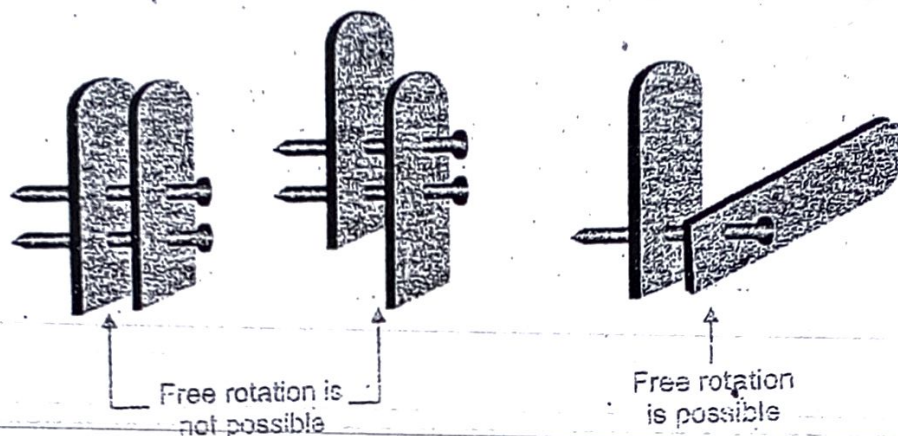
Broken π -bond

p -orbital overlap

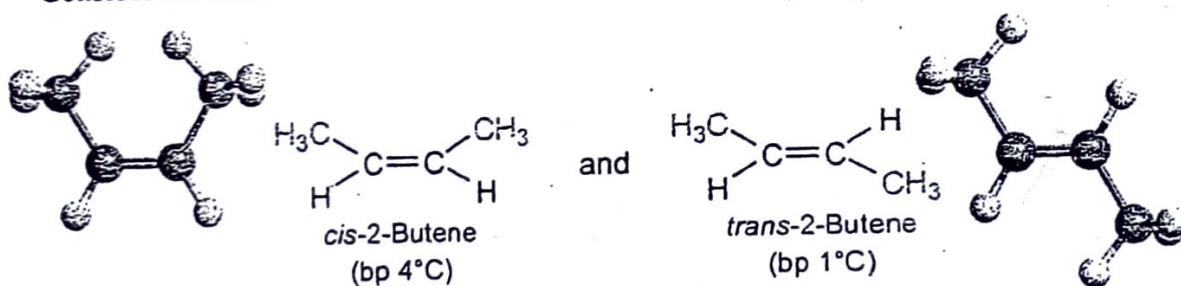
could break the π -bond

The presence of the π bond locks the molecule in one position. The *two* carbon atoms of the $C=C$ bond and the *four* atoms that are attached to them lie in one plane and their positions in space are *fixed*. Rotation around the $C=C$ bond is not possible because rotation would break the π bond (Fig 4.1).

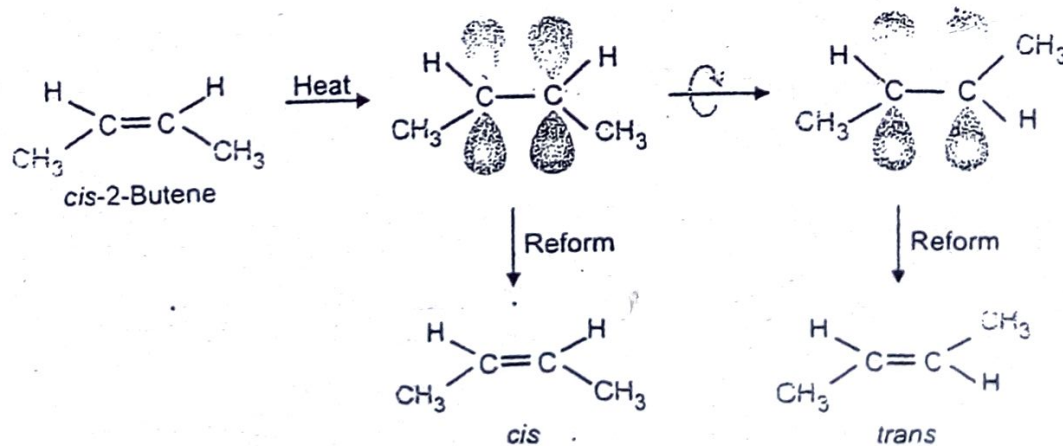
This restriction of rotation about the carbon-carbon double bond is responsible for the geometric isomerism in alkenes. A popular analogy for this situation is based upon two boards and two nails. Driving one nail through two boards will not prevent free rotation of the two boards. But once a second 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 geometric 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. Geometric isomers are stereoisomers, because they have the same structural formula but different spacial arrangement of atoms.



The conversion of *cis*-isomer into *trans*-isomer or *vice versa* is possible only if either isomer is heated to a high temperature or absorbs light. The heat supplies the energy (about 62 kcal/mole) to break the π bond so that rotation about σ bond becomes possible. Upon cooling, the reformation of the π bond can take place in two ways giving mixture of *trans*-2-butene plus *cis*-2-butene.

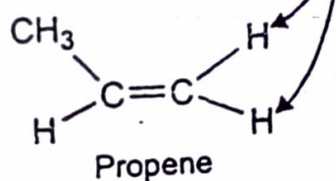
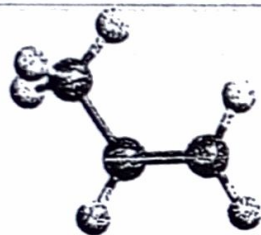
The *trans* isomers are more stable than the corresponding *cis* isomers. This is because, in the *cis* isomer, the bulky groups are on the same side of the double bond. The steric repulsion of the groups makes the *cis* isomer less stable than the *trans* isomer in which the bulky groups are far apart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

The geometric 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 geometric isomerism. Geometric 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 geometric isomers.

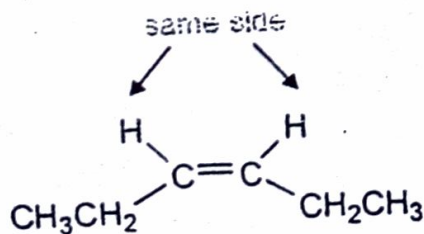
Example 1. Consider the case of Propene

No geometric 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.

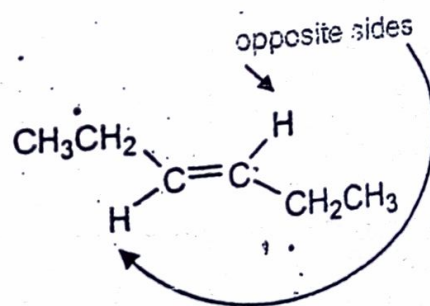


Example 2. Consider the case of 3-Hexene

Geometric 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 :



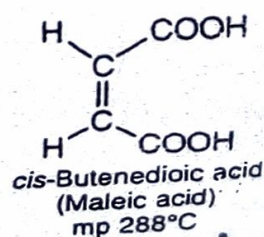
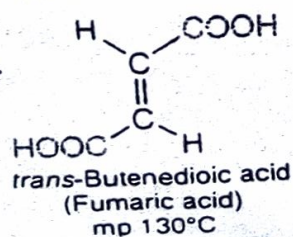
cis-3-Hexene



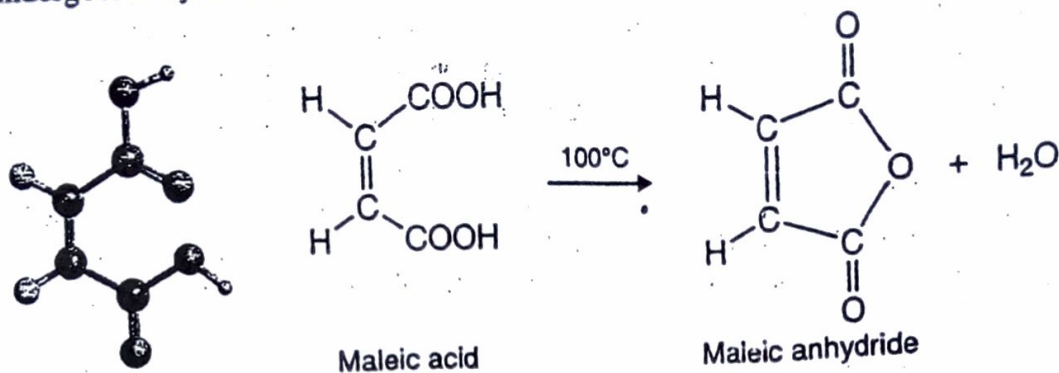
trans-3-Hexene

Example 3. Consider the case of Butenedioic acid

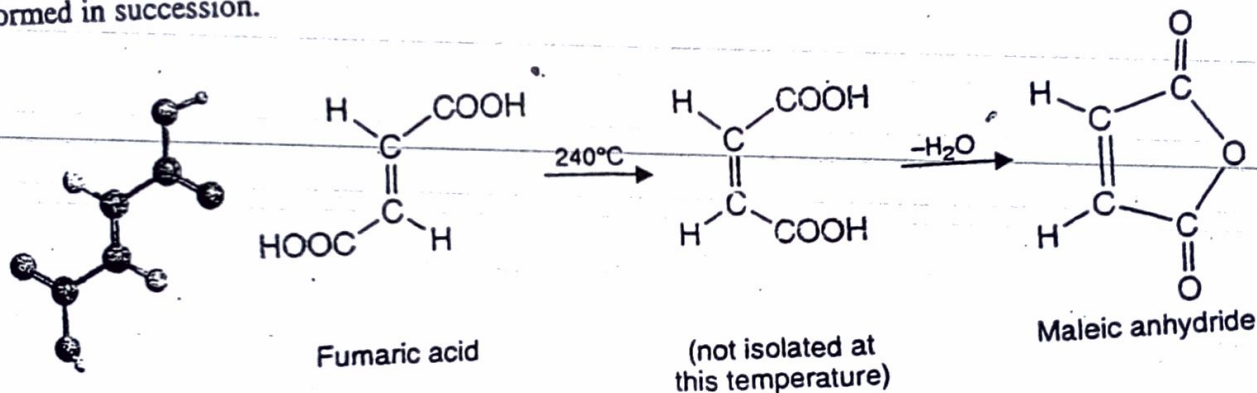
Geometric isomers are possible for butenedioic acid ($\text{HOOC}-\text{CH}=\text{CH}-\text{COOH}$). This is because each double bonded carbon atoms has two different groups attached to it (*H* and *COOH*).



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.



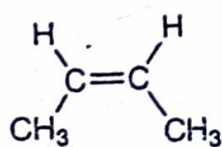
However, the *trans*-acid does not form an anhydride until heated to 240°C. At that temperature there is sufficient thermal energy to break the double bond, so that the *cis*-acid and the anhydride are formed in succession.



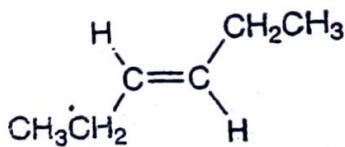
ASSIGNING CONFIGURATIONS TO ALKENES

To designate the configuration of alkenes, we can use the *cis-trans* system or the E-Z system.

Cis-Trans System. The most common method for specifying configuration in alkenes uses the prefixes *cis* and *trans*-. There is no doubt whatsoever which isomers are intended by the name *cis*-2-butene and *trans*-3-hexene.



cis-2-Butene

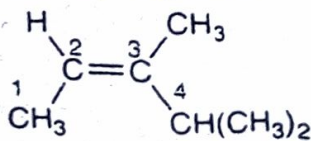


trans-3-Hexene

cis isomers have the substituents on the same side

trans isomers have the substituents on the opposite side

For some alkenes, the assignments of *cis* and *trans* are not as obvious. Following is a structural formula for one *cis-trans* isomer of 3,4-dimethyl-2-pentene.

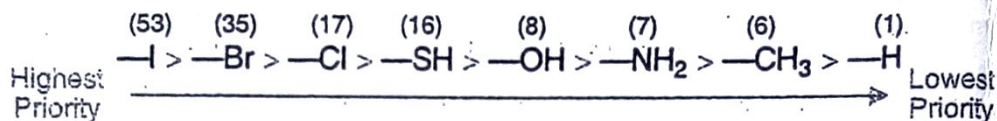


3,4-Dimethyl-2-pentene

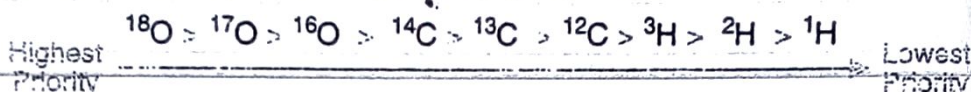
Should it be named *cis*- because carbon atoms 1 and 4 of the parent chain are on the same side of the double bond, or should it be named *trans* because the methyl groups on the double bond are on opposite sides? According to IUPAC rules, it should be named *cis* because of the *cis* orientation of the main carbon chain about the double bond.

E-Z System. The configuration about any carbon-carbon double bond can be specified unambiguously using a set of **Priority Rules** devised in 1964 by R.S. Cahn, C.K. Ingold and V. Prelog. These rules have since been incorporated into the IUPAC system of nomenclature and, when applied to naming alkenes, give what is known as the **E-Z system**.

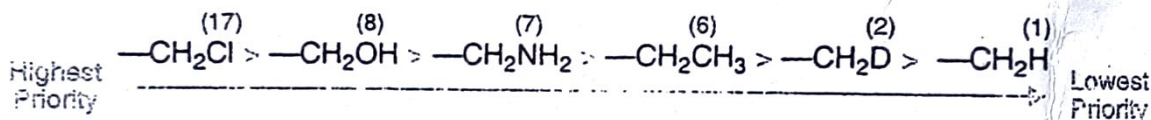
Rule 1. Each atom is assigned a priority. Priority is based on atomic number; the higher the atomic number, the higher the priority. Following are several substituents arranged in order of decreasing priority. The atomic number of the atom determining priority is shown in parentheses.



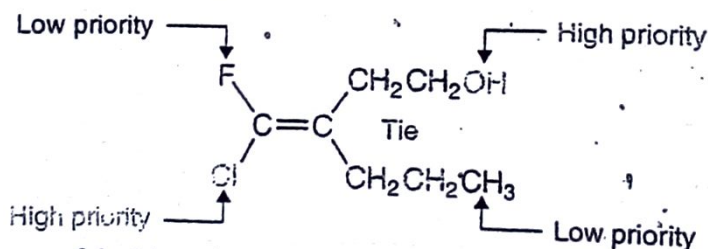
Rule 2. For isotopes, the higher the atomic mass, the higher the priority. Deuterium (Hydrogen-2) for example, has a higher priority than protium (Hydrogen-1).



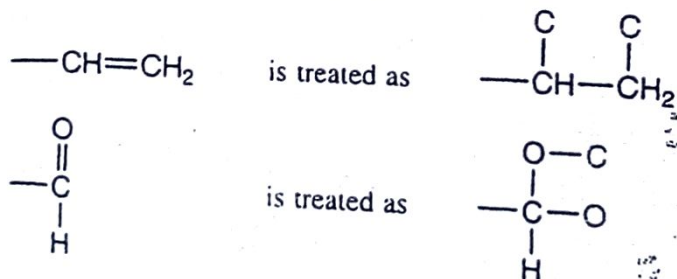
Rule 3. If priority cannot be assigned on the basis of atomic number or atomic mass considering the first atom of a group, then look at the next set of atoms and continue until a priority can be assigned. Priority is assigned at the first point of difference. Following are a series of groups, arranged in order of decreasing priority. Also shown is the atomic number of the atom on which the assignment of priority is based.

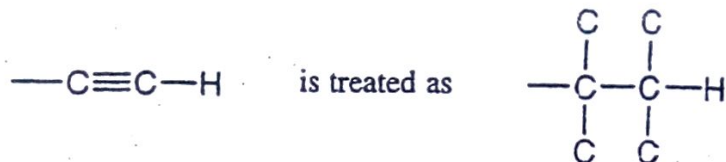


For example,

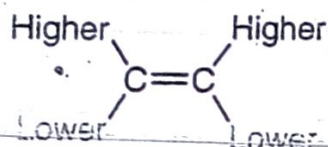
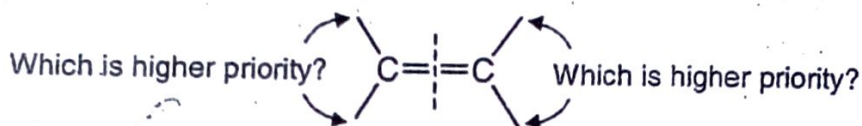


Rule 4. In the case of double and triple bonds, atoms participating in the double or triple bond are considered to be bonded to an equivalent number of similar atoms by single bonds, that is, atoms of double and triple bonds are replicated. For example,

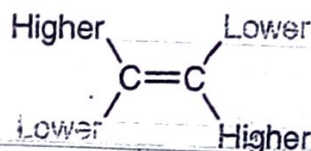




To use the E-Z-system, first assign priority to the two atoms or groups of atoms on one carbon of the double bond, and then repeat the process for the two atoms or groups of atoms on the other carbon. If the groups of higher priority are on the same side of the double bond, the alkene is designated Z (from the German and *zusammen*, together). If the groups of higher priority are on opposite sides of the double bond, the alkene is designated E (from the German word *entgegen*, opposite).



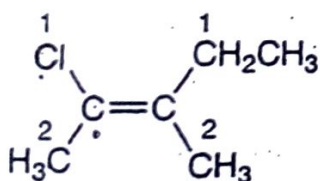
Z (Zusammen)



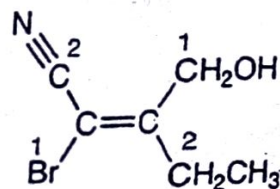
E (Entgegen)

E-alkenes have the groups of highest priority on the *opposite* sides
 Z-alkenes have the groups of highest priority on the *same* sides

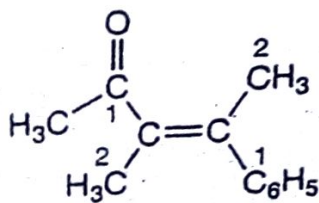
We use the *cis-trans* system for alkenes in which it is clear which is the main carbon chain. We use the E-Z system in all other cases. The following examples show the use of the E-Z system (Numbers on each carbon are given in red to indicate priorities).



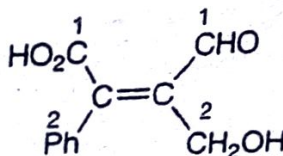
(Z)-2-Chloro-3-methyl-2-pentene



(E)-2-Bromo-3-hydroxymethyl-2-pentenitrile



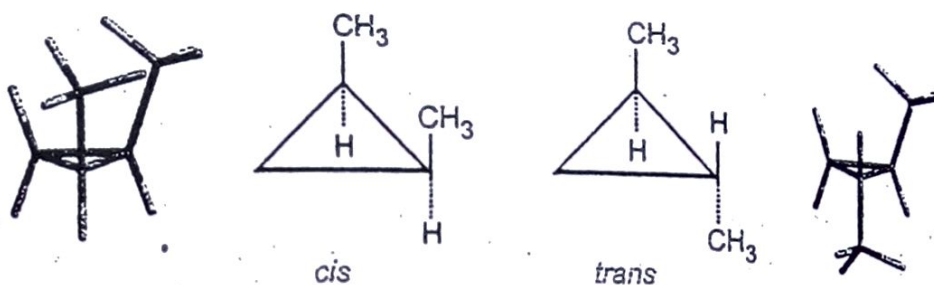
(E)-3-Methyl-4-phenyl-3-penten-2-one



(Z)-3-Hydroxymethyl-4-oxo-2-phenyl-2-butenoic acid

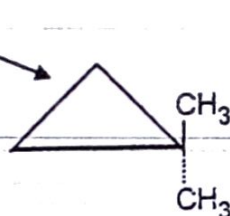
GEOMETRIC ISOMERISM IN CYCLIC COMPOUNDS

Geometric isomerism is also possible in cycloalkanes. 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.

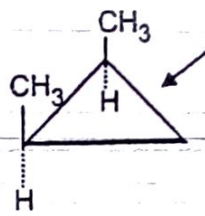


In *cis*-1,2-dimethylcyclopropane, the two methyl groups are on the same side of the ring. In *trans*-1,2-dimethylcyclopropane, they are on opposite sides. A requirement for geometric isomerism in cyclic compounds is that there must be at least two other groups besides hydrogens on the ring and these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

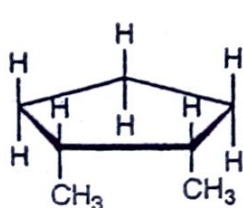
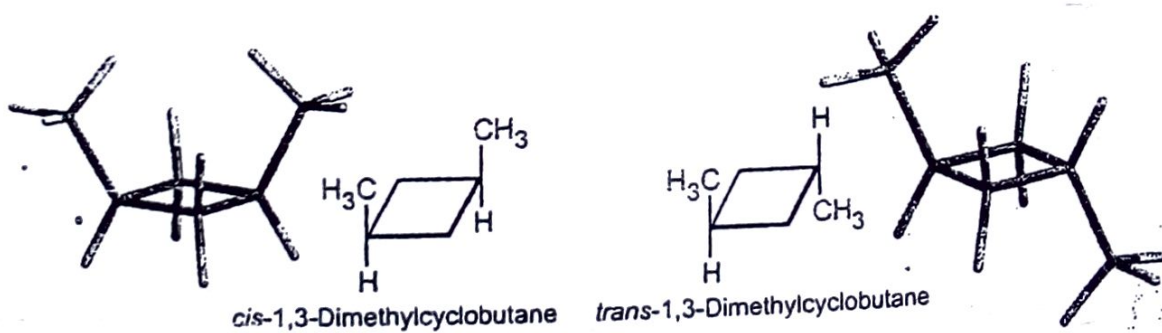
No geometric isomers are possible for this compound



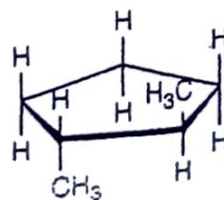
Geometric isomers are possible for this compound



In the above drawings, the cyclopropane ring is shown as a planar triangle viewed through the plane of the ring. The carbon-carbon bond of the ring projecting forward is shown as a heavy line. When viewed from the perspective, substituents attached to the ring project above and below the plane of the ring. More examples of *cis-trans* isomerism are shown below:

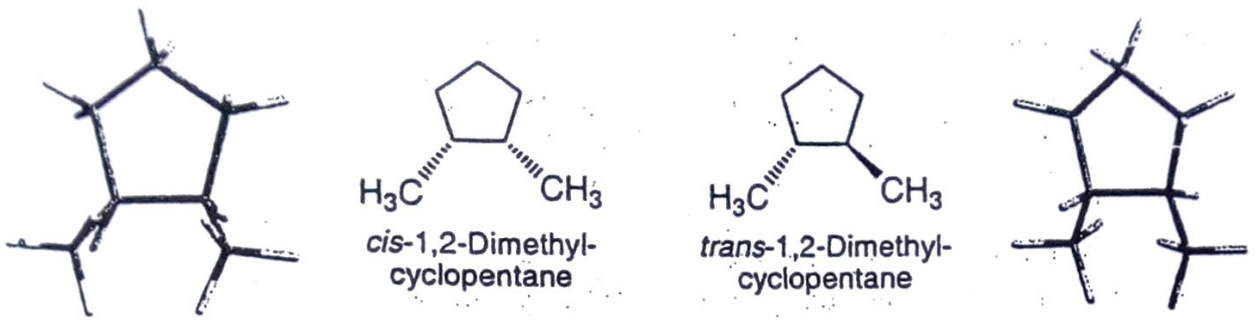


cis-1,2-Dimethylcyclopentane

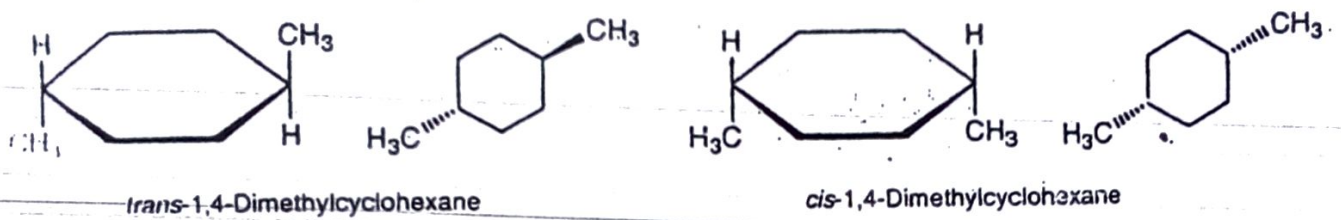


trans-1,2-Dimethylcyclopentane

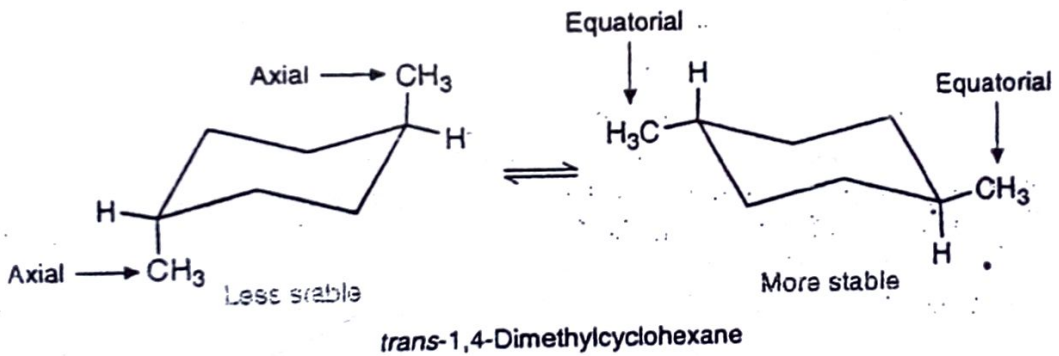
Alternatively, ring can be viewed from above, with the ring in the plane of the paper. Substituents on the ring then either project toward you (that is, they project up above the page) and are shown by solid wedges, or they project away from you (they project down below the page) and are shown by broken wedges. In the following structural formulas, only the two methyl groups are shown (hydrogen atoms of the ring are not shown):



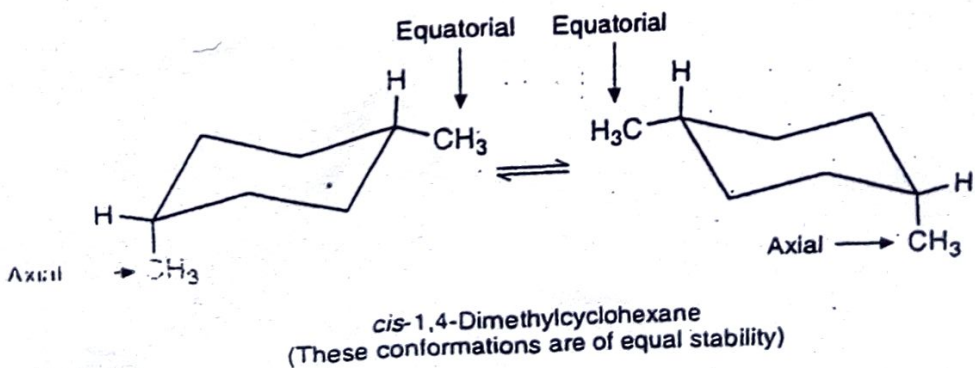
For the purpose of determining the number of *cis-trans* isomers in substituted cycloalkanes, it is adequate to draw the cycloalkane ring as a planar polygon as is done in the following structures for cyclohexane. Two *cis-trans* isomers exist for 1,4-dimethylcyclohexane.



The *cis* and *trans* isomers of 1,4-dimethylcyclohexane can also be drawn as nonplanar chair conformations. In one chair conformation of *trans*-1,4-dimethylcyclohexane the two methyl groups are axial; in the other chair conformation they are equatorial. Of these chair conformations, the one with both methyls equatorial is considerably more stable.

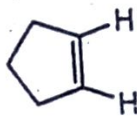


In one chair conformation of *cis*-1,4-dimethylcyclohexane, one methyl group occupies an equatorial position, and the other occupies an axial position. In the other chair, the orientations in space of the CH_3 groups is reversed. The chair conformations of *cis*-1,4-dimethylcyclohexane are of equal energy because in each, one methyl is axial and the other equatorial.

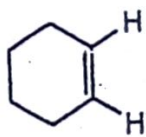


GEOMETRIC ISOMERISM IN CYCLOALKENES

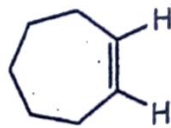
Following are structural formulas for four cycloalkenes:



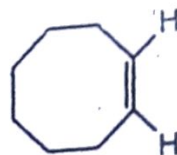
Cyclopentene



Cyclohexene

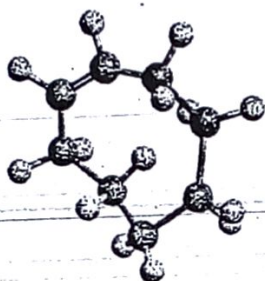


Cycloheptene

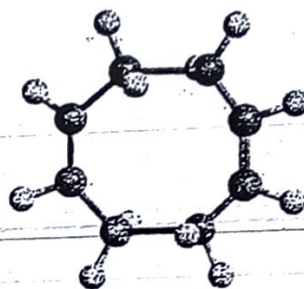


Cyclooctene

In these representations, the configuration about each double bond is *cis*. Because of angle strain, it is not possible to have a *trans* configuration in cycloalkenes of seven or fewer carbons. To date, *trans*-cyclooctene is the smallest *trans*-cycloalkene that has been prepared in pure form and is stable at room temperature. Yet, even in this *trans*-cycloalkene, there is considerable intramolecular strain. *cis*-Cyclooctene is more stable than its *trans* isomer by 9.1 kcal/mol.



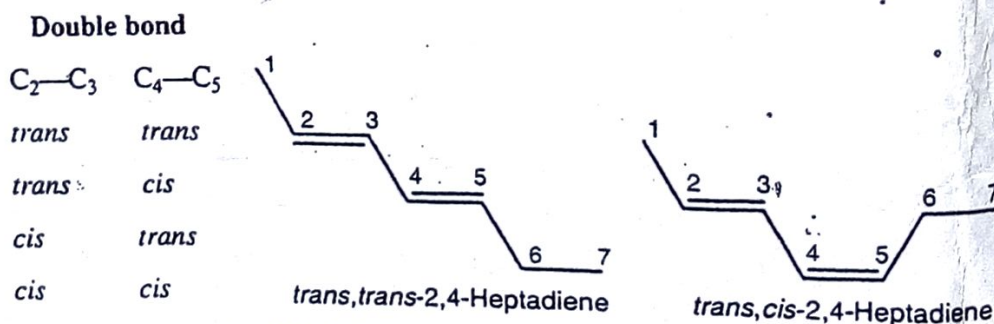
trans-Cyclooctene



cis-Cyclooctene

Thus far, we have considered *cis-trans* isomerism in alkenes containing only one carbon-carbon double bond. For an alkene with one carbon-carbon double bond that can show *cis-trans* isomerism, two *cis-trans* isomers are possible. For an alkene with n carbon-carbon double bonds, each of which can show *cis-trans* isomerism, 2^n *cis-trans* isomers are possible.

Consider the example of 2,4-heptadiene. This molecule has two carbon-carbon double bonds, each of which exhibits *cis-trans* isomerism. As the following table shows, $2^2 = 4$ *cis-trans* isomers are possible (to the right of the table are line angle-formulas for two of these isomers):



Vitamin A is an example of biologically important compound for which a number of *cis-trans* isomers are possible. There are four carbon-carbon double bonds in the chain of carbon atoms bonded to the substituted cyclohexene ring, and each has the potential for *cis-trans* isomerism. Thus, $2^4 = 16$ *cis-trans* isomers are possible for this structural formula. Vitamin A is the *all-trans* isomer.

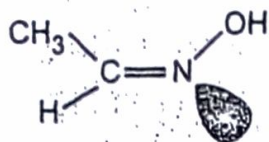


Vitamin A (Retinol)

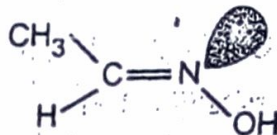
GEOMETRIC ISOMERISM IN OXIMES AND AZO COMPOUNDS

Geometric isomerism is also possible in compounds containing $C=N$ (Oximes) and $N=N$ (Azo compounds). Like alkenes, both double bonded atoms (carbon and nitrogen's) are sp^2 hybridized. The lone-pair of electrons on nitrogen resides in sp^2 hybrid orbital. This fixes the position of all substituents around $C=N$ and $N=N$ double bonds. This results in geometric isomerism. In the past special prefixes have been used to designate these isomers, but this is now satisfactorily achieved by the use of (E) and (Z). For example,

Isomeric Aldoximes :

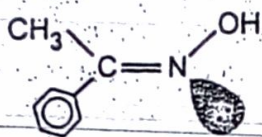


(Z)-Acetoaldoxime

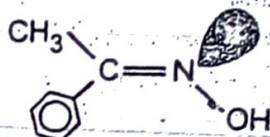


(E)-Acetoaldoxime

Isomeric Ketoximes :



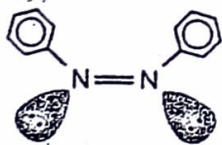
(E)-Acetophenoneoxime



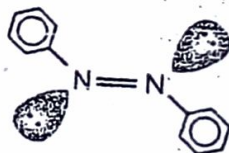
(Z)-Acetophenoneoxime

Symmetrical carbonyl compounds ($R_2C=O$) form oximes which cannot exist as geometric isomers. The only aldehyde to meet this requirement is formaldehyde ($H_2C=O$) but there are many symmetrical ketones of which acetone, $(CH_3)_2C=O$, is the simplest.

Isomeric Azo Compounds :



(Z)-Azobenzene



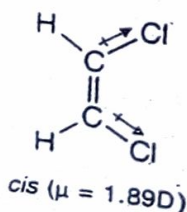
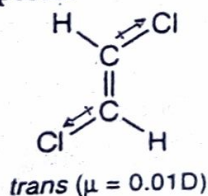
(E)-Azobenzene

DETERMINATION OF CONFIGURATION OF ISOMERS

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

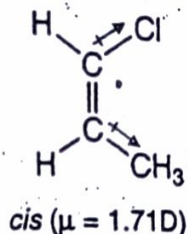
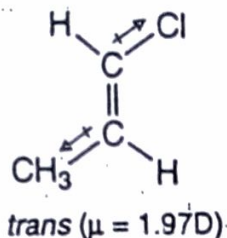
From a study of the physical properties. The difference in the structure of *cis* and *trans* isomers is reflected in their physical properties. Some such properties are illustrated below:

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



In such alkenes which have one polar substituent different from the other, the dipole moment substituent is electron-donating and the other electron-withdrawing, the bond moments are fully additive in *trans* isomer. Thus the *trans* isomer in this case has a higher dipole moment than the corresponding *cis* isomer.

Thus in 1-chloroprene we have,

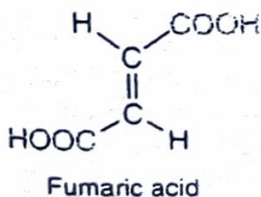
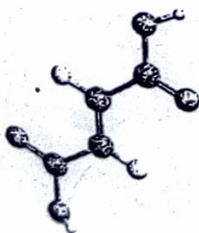
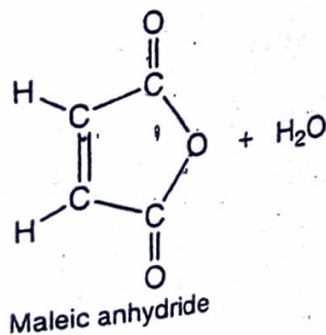
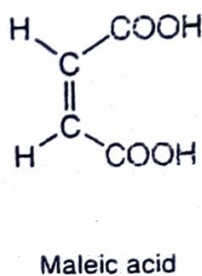
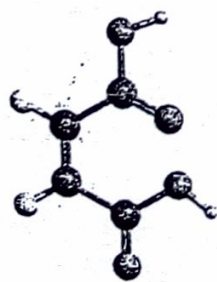


Therefore, it is possible to assign configuration to a pair of isomers on the basis of dipole measurements, provided the nature of substituents is known.

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

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

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



No anhydride is formed at this temperature

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

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.

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**.

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 (*anticlockwise*). 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. 4.2 shows the parts of a polarimeter.

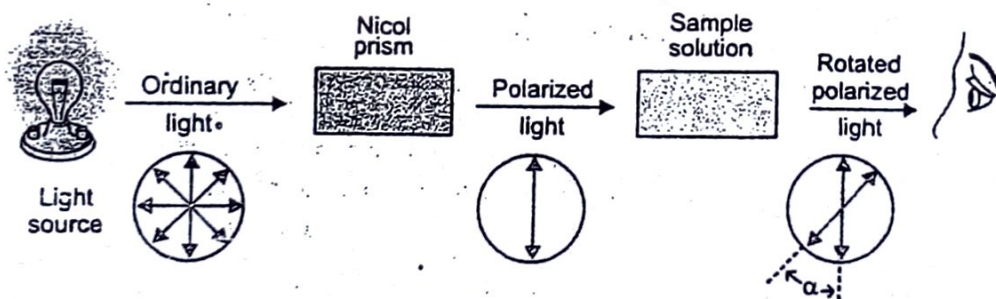
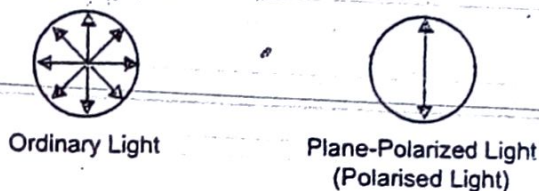
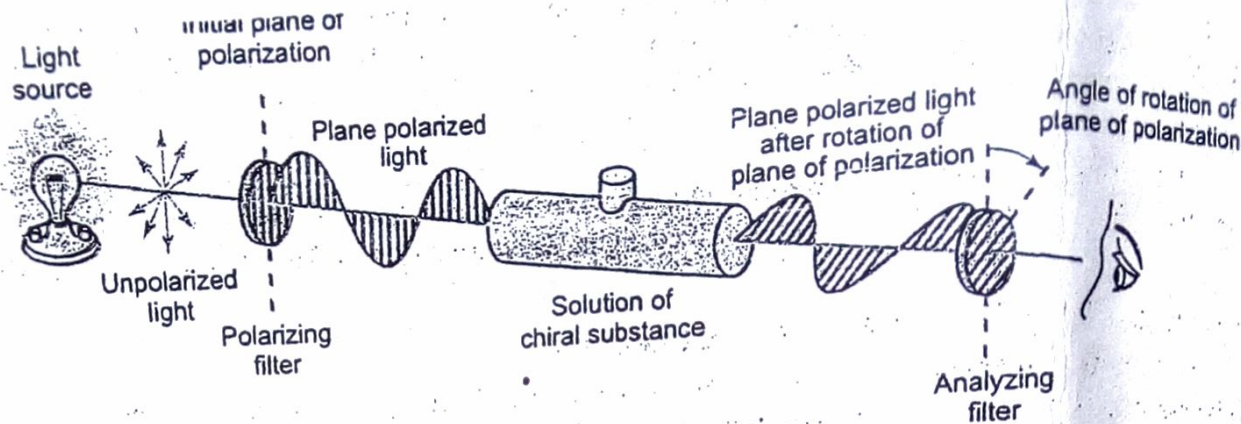


Fig. 4.2. A simple polarimeter in operation.

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 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.



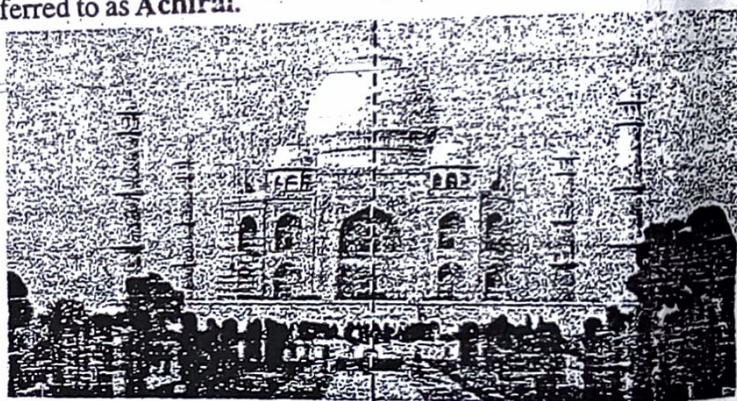
Schematic representation of a polarimeter. Plane-polarized light passes through a solution of optically active molecules, which rotate the plane of polarization.

PLANE OF SYMMETRY

A plane which divides an object into two symmetrical halves, is said to be *plane of symmetry*. For example, a coffee mug has a plane of symmetry (Fig. 4.3). A person's hand or shoes lack a plane of symmetry. An object lacking a plane of symmetry is called **Dissymmetric** or **Chiral** (pronounced as *Ki-ral*). A symmetric object is referred to as **Achiral**.



Plane of symmetry



Plane of symmetry

Fig. 4.3. Planes of Symmetry

A dissymmetric 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. 4.4). 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.

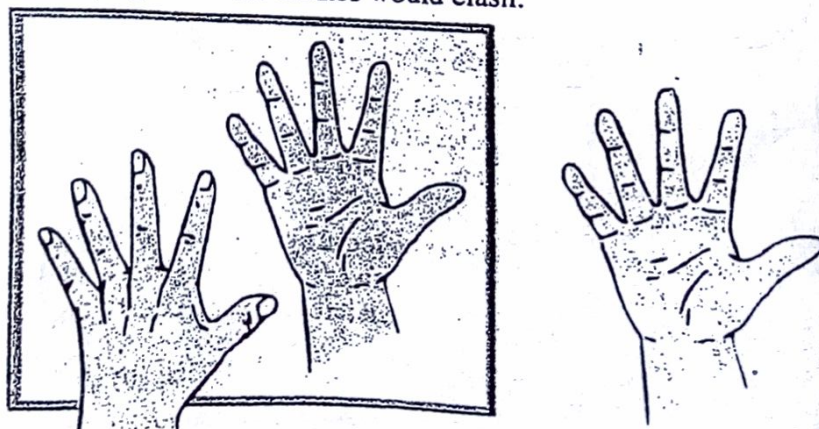
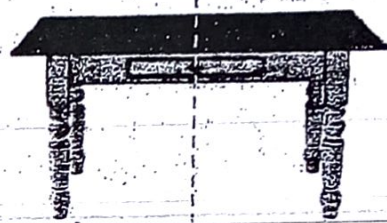


Fig. 4.4. The mirror image relationship of the left and right hand. The right hand is the mirror image of the left hand.



Chiral objects,

A chiral molecule has at least one asymmetric centre and does not have a plane of symmetry.

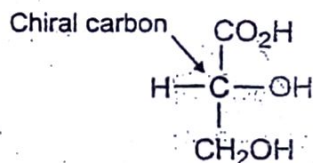
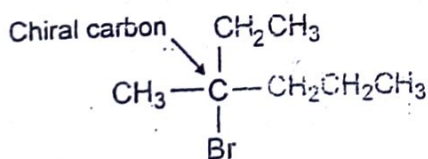


Achiral objects

An achiral molecule has a plane of symmetry.

CHIRAL 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 **Dissymmetric** or **Asymmetric**.

OPTICAL ISOMERISM

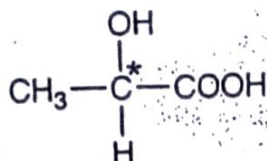
An optically active compound can exist in two isomeric forms which rotate the plane-polarized light in opposite directions. These are called **Optical Isomers** and the phenomenon is known as **Optical Isomerism**.

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. 4.5).

These structures are not identical because they can not 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).

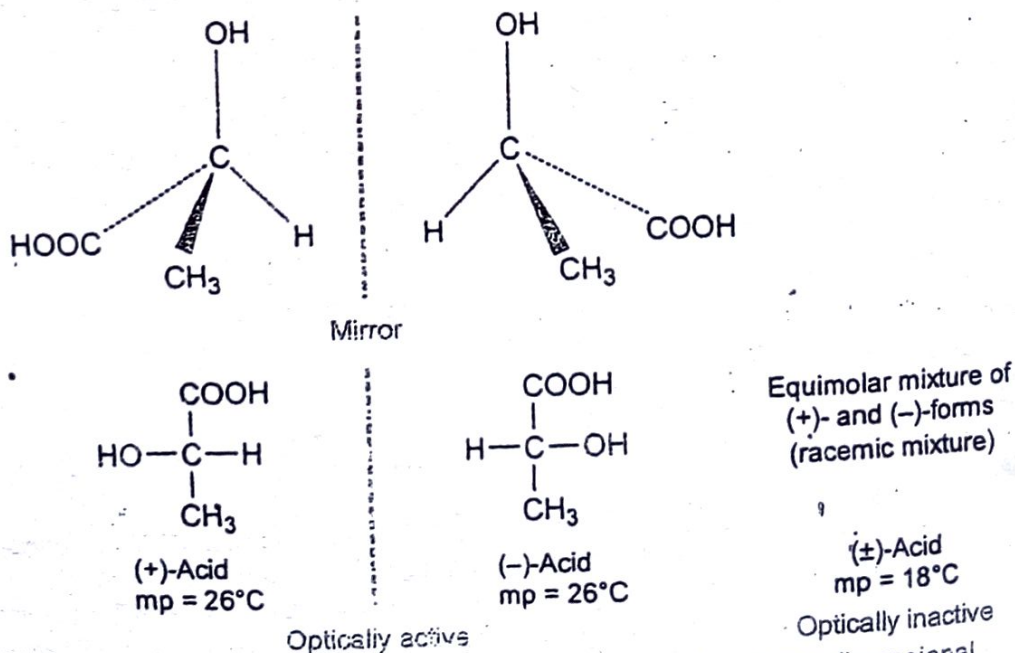


Fig. 4.5. Isomers of Lactic acid. In the upper line two three-dimensional structures are shown. In the lower line a commonly used Fischer projection is given. The vertical lines represent bonds going away from the observer/reader and horizontal lines represent bonds coming toward the observer.

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.

Consider a chiral molecule C_{ABCD} . Fig. 4.6 shows two three dimensional models for this molecule.

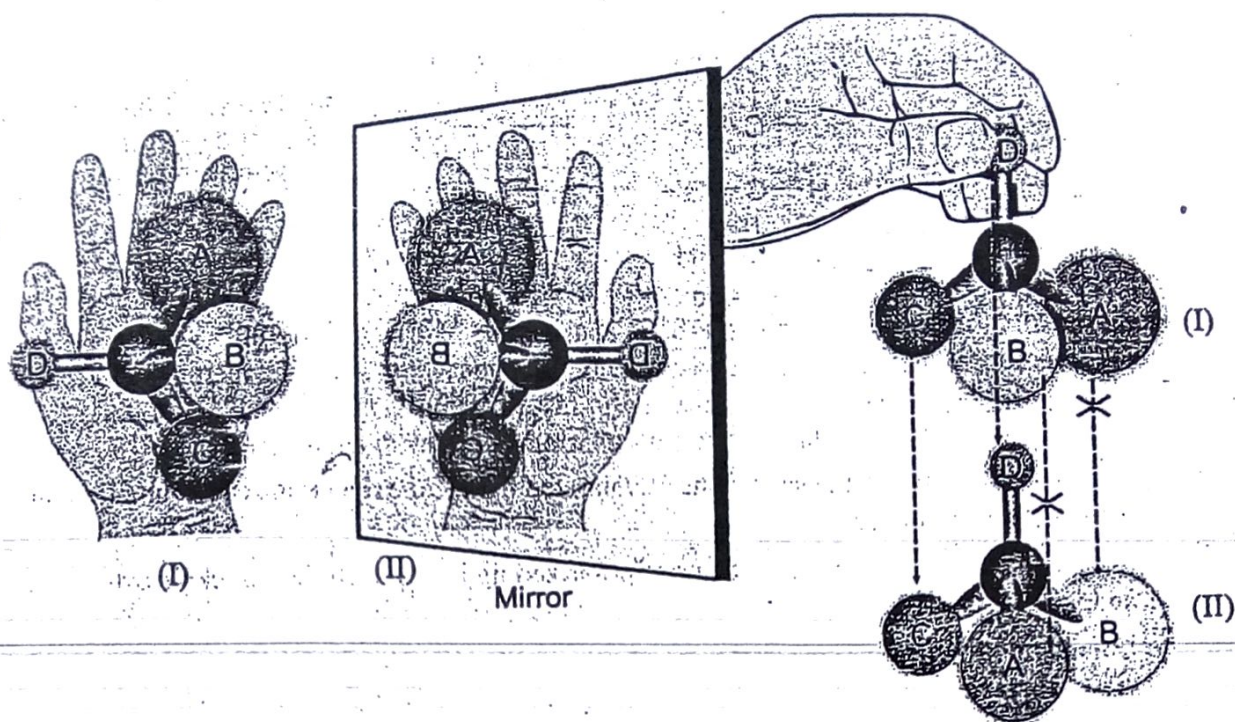


Fig. 4.6. The two forms (I and II) of C_{ABCD} are nonsuperimposable.

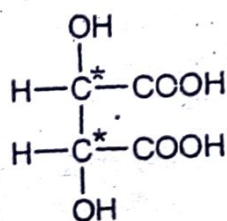
The form (II) is the mirror image of (I) and the two cannot be superimposed. If you try to superimpose the four groups attached to a chiral carbon atom in form (I) and form (II), only two of the four groups coincide, while the other two are in conflict. This shows that the two forms represent different 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 chiral 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 chiral 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. 4.7). 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:

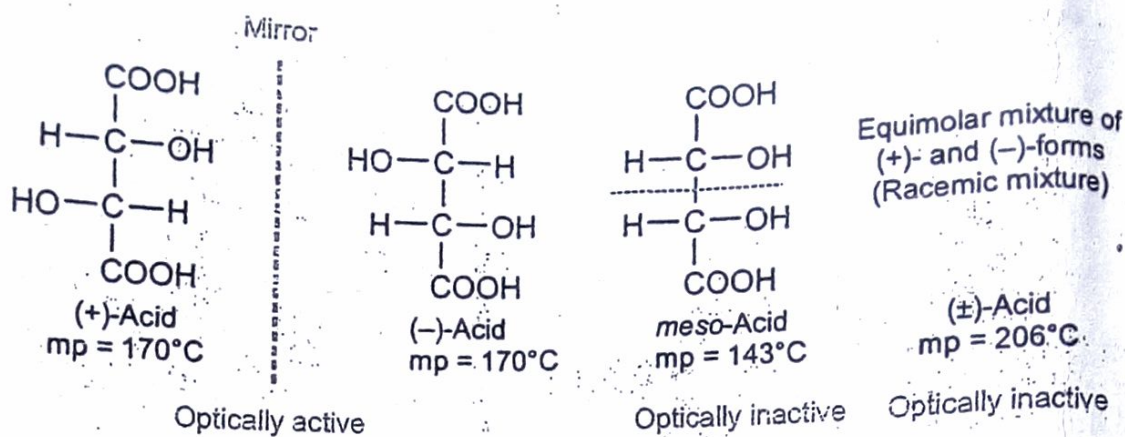


Fig. 4.7. Isomers of Tartaric acid.

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 chiral 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).

TERMS USED TO DESCRIBE OPTICAL ISOMERS

Achiral molecule. An achiral molecule is one that can be superimposed over its mirror image; an achiral molecule is identical to its mirror image. Achiral molecules do not rotate plane-polarized light.

Chiral center. Typically, for a molecule to be chiral it must have at least one chiral center – a carbon with four nonequivalent groups. Any molecule that contains a chiral center will be chiral, unless the molecule has a plane of symmetry, in which case the molecule is achiral (and *meso*).

Chiral molecules. A chiral molecule is one that cannot be superimposed over its mirror image. Chiral molecules rotate plane-polarized light.

Diastereomers. Diastereomers are stereoisomers that are not mirror images of each other. For a molecule to have a diastereomer, it must typically have more than one chiral center.

Enantiomers. Molecules that are mirror images of each other are called enantiomers.

Meso compounds. A *meso* compound is a molecule that contains a chiral center, but is achiral as a result of having a plane of symmetry in the molecule.

Optically active. An optically active compound (such as a pure solution of a single enantiomer of a molecule) has the ability to rotate plane-polarized light.

Racemic mixtures. A racemic mixture is a 50:50 mixture of two enantiomers. Racemic mixtures do not rotate plane-polarized light.

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. 4.8). Notice that (A) is the mirror image of (B). They are a pair of enantiomers.

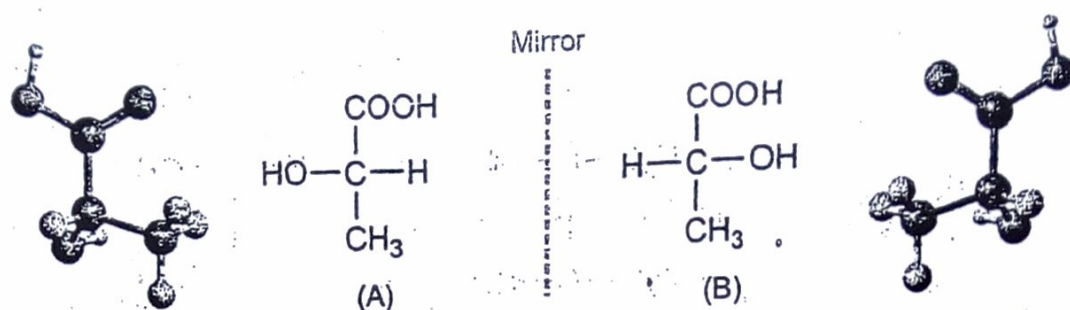


Fig. 4.8. Two isomers of Lactic acid.

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. 4.9 shows the four isomers of 3-bromo-2-butanol, which has *two* chiral carbon atoms.

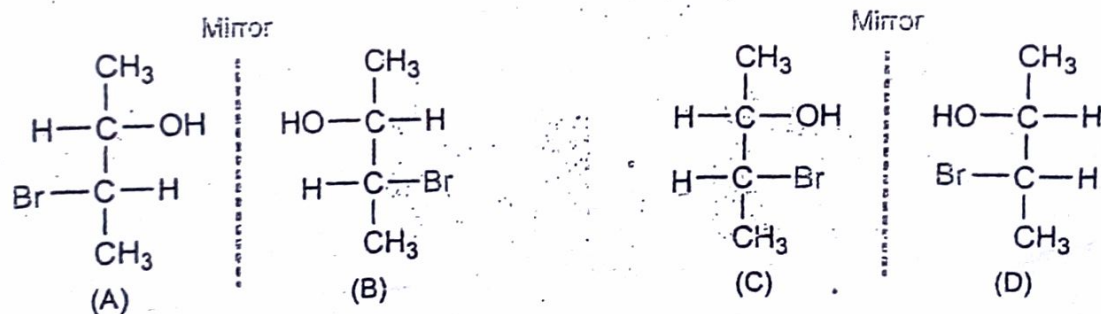


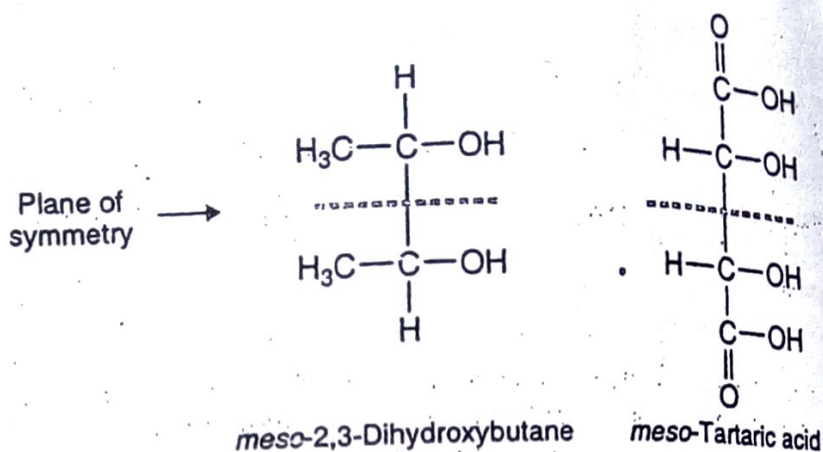
Fig. 4.9. Four isomers of 3-Bromo-2-butanol.

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**.

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. 4.10 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 centers. Neither will rotate the plane polarized light.

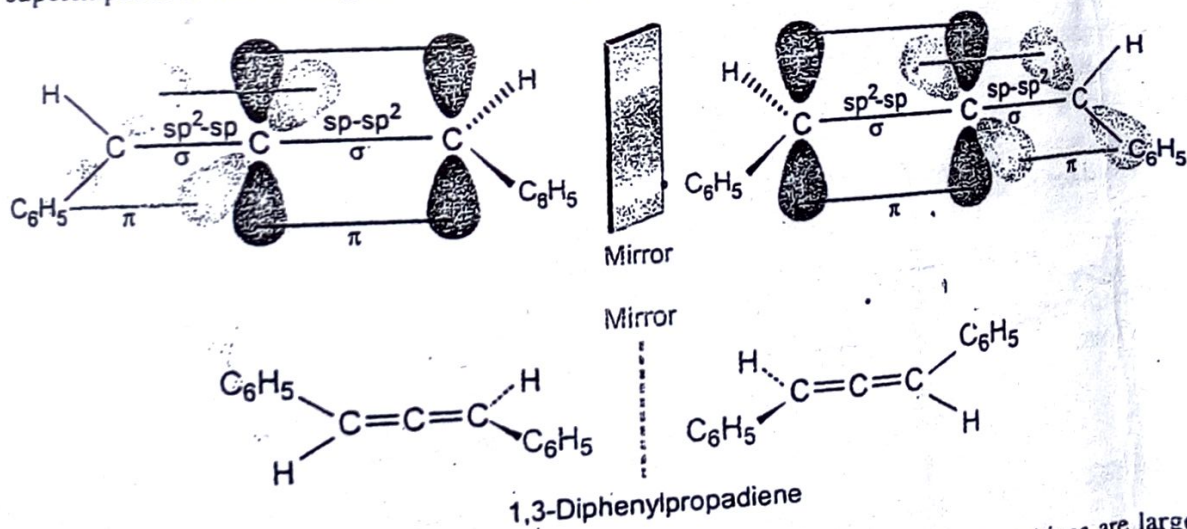
Fig. 4.10. Examples of *meso* compounds.

OPTICAL ACTIVITY WITHOUT ASYMMETRIC CARBONS

Compounds containing a chiral carbon can exist in optically active forms. However, compounds which do not possess a chiral carbon atom can also exist in optically active forms provided that the molecule is dissymmetric. For example,

(1) Allene Derivatives

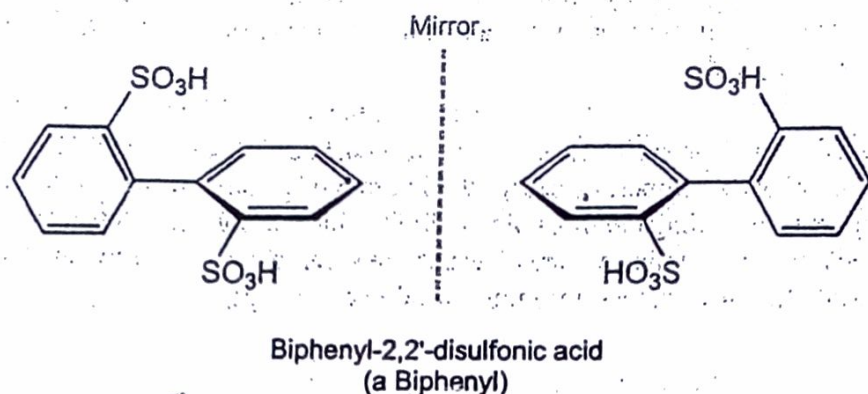
Some derivatives of allene ($\text{CH}_2=\text{C}=\text{CH}_2$) exhibit optical isomerism. Example is 1,3-diphenylpropadiene. In allenes, the central carbon is sp hybridized, and the terminal carbons are sp^2 hybridized. The central carbon forms two $sp-sp^2$ σ bonds. The central carbon also has two p orbitals which are mutually perpendicular. These form π bonds with the p orbitals on the other carbon atoms. As a result, the substituents at one end of the molecule are in a plane which is perpendicular to that of the substituents at the other end, so that the compound exists in two forms which are non-superimposable mirror images and are optically active.



(2) Biphenyl Derivatives

Substituted biphenyls show optical isomerism when substituents in the 2-positions are large enough to prevent rotation about the bond joining the two benzene rings. For example, biphenyl-2,2'-disulfonic acid exists in two forms.

These two forms are non-superimposable mirror images. They do not interconvert at room temperature because the energy required to twist one ring through 180° relative to the other is too high. This in turn is because, during the twisting process, the two $-\text{SO}_3\text{H}$ groups must come into very close proximity when the two benzene rings become coplanar and strong repulsive forces are introduced.



RESOLUTION OF RACEMIC MIXTURES (ENANTIOMERS)

Synthesis of an optically active compound produces a mixture of both (+)– and (–)-isomers in equal amounts. Recall that these optical isomers are nonsuperimposable mirror images and are called **enantiomers**. Such a mixture is called **racemic mixture** or a **racemate**. **The separation of a racemic mixture into its two optically active components (+ and – isomers; enantiomers) is known as Resolution.**

Enantiomers have completely identical physical properties except for the rotation of plane-polarized light one cannot take advantage of differences in boiling point, melting point, or solubility, since enantiomers are identical in each of these aspects. Following are three methods for resolving an enantiomeric pair (racemic mixture).

(1) **Mechanical resolution.** Pasteur's original separation of the sodium ammonium salt of tartaric acid, known as mechanical resolution, is mainly of historical interest. By slow crystallization of this salt, he obtained crystals that existed as two mirror-image forms. Mechanical separation (with tweezers) of the two crystalline forms resulted in the resolution of the racemic mixture. This method is not generally practical because most racemic mixtures do not readily form enantiomorphous crystals. Furthermore, the separation would be extremely tedious.

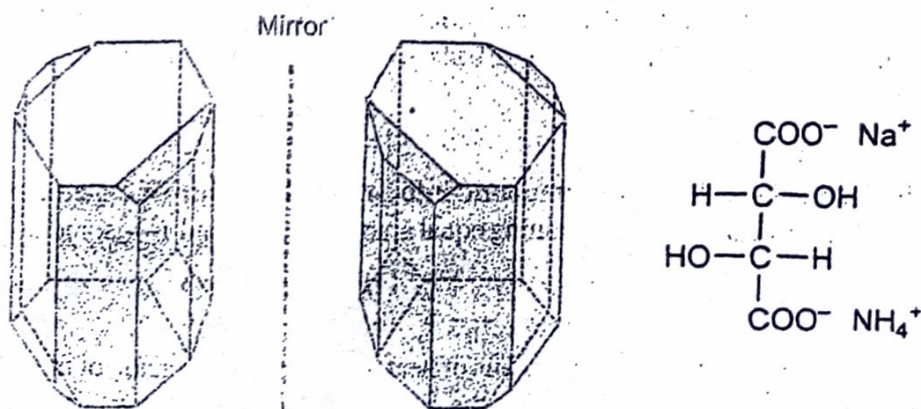


Fig.4.11. Crystals of sodium ammonium tartrate. One of the crystals is dextrorotatory in solution, and the other is levorotatory.

(2) **Biological resolution.** A second method for resolution of enantiomers takes advantage of the varying rates of metabolism of the components of a racemic mixture by microorganisms. Microorganisms produce enzymes that are themselves chiral and consequently react differently with the two enantiomeric forms.

has a better chance of being successful than mechanical resolution and can be applied to a large variety of compounds, it suffers in that one enantiomeric form is lost (metabolized) and the other is often obtained in poor yield.

(3) **Resolution through diastereomers.** The most generally useful (and theoretically successful) method for separating enantiomers involves converting them into diastereomers. Whereas enantiomers are identical in all physical properties except the rotation of plane-polarized light, diastereomers differ in all properties, including melting point, boiling point, and solubility. If an enantiomeric pair can be converted into a pair of diastereomers, which are separable, and the separated diastereomers converted back into the enantiomers, resolution would be accomplished.

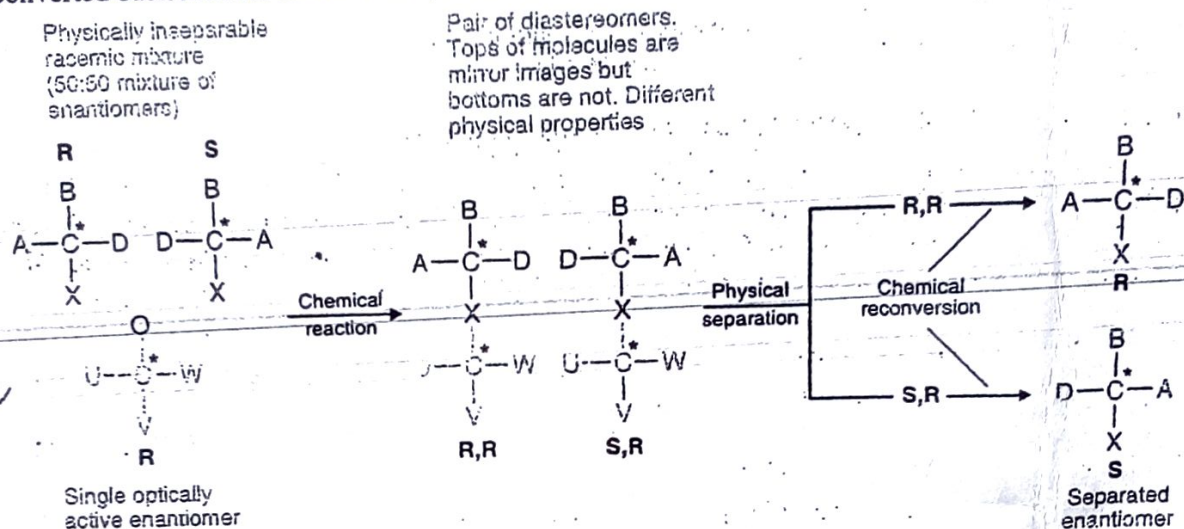


Fig.4.12. Resolution of enantiomers through the use of diastereomers. Asterisk (*) denotes chiral atoms.

Take the physically inseparable pair of enantiomers in Fig.4.12. If group **X** on each enantiomer reacts with group **O** of a single enantiomer (optically active) from another source, a pair of diastereomers (optical isomers that are not mirror images) is formed. The diastereomers are separated by physical means such as distillation, fractional crystallization or chiral chromatography. The separated diastereomers are then individually converted back to the original enantiomers, which are now isolated from one another.

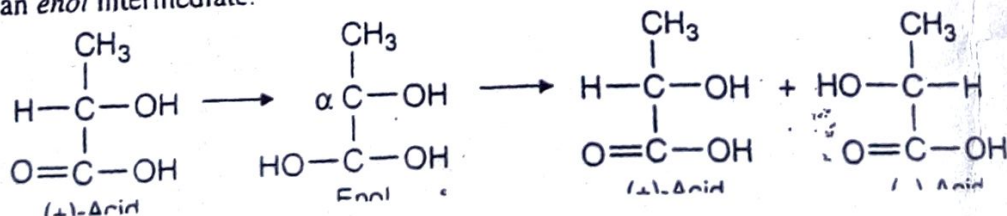
RACEMIZATION

Conversion of an optically active compound into a racemic mixture is called Racemization.

Recall : Racemic mixture is a mixture containing equal amounts of (+)- and (-)-isomers. Thus,



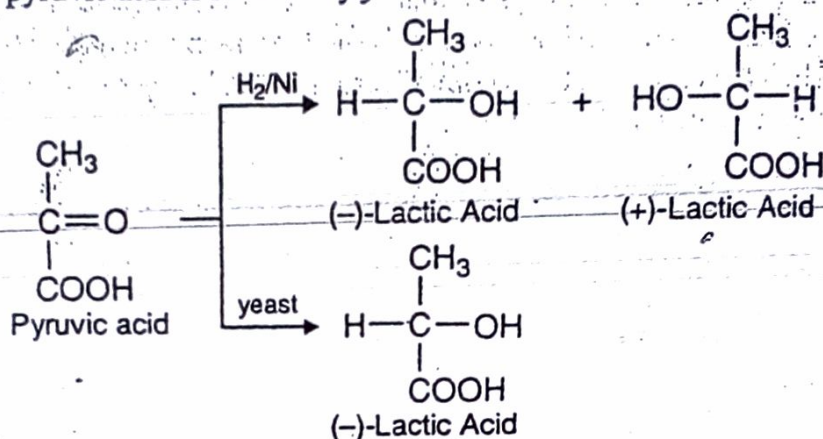
Racemization can be accomplished by means of heat, light, or by conversion of the isomer into an optically inactive intermediate which reverts to the racemic mixture. The conversion of either of the optically active lactic acids into a racemic mixture by heating its aqueous solution may proceed through an *enol* intermediate.



When the proton migrates back to the carbon atom, the process can involve the opening of either of the two linkages of the double bond and can produce either the original configuration or the opposite of it.

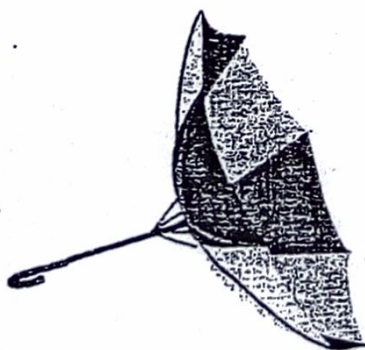
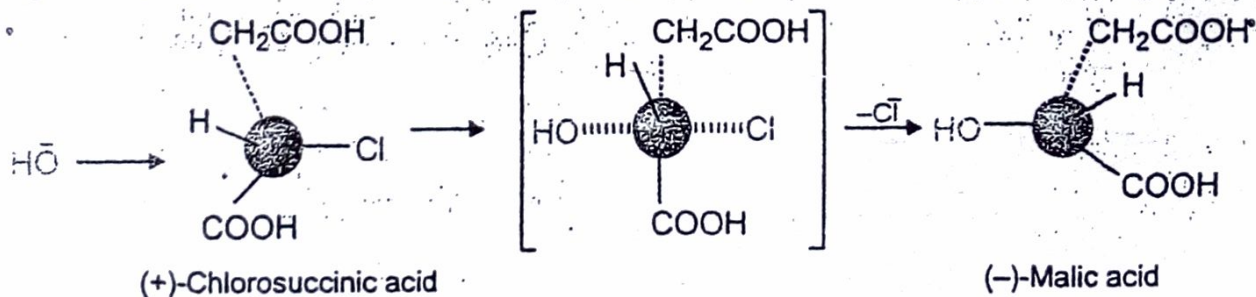
CHIRAL SYNTHESIS

When a compound containing a chiral carbon atom is synthesized by ordinary laboratory methods from an achiral compound, the product is a racemic mixture. If, however, such a synthesis is carried under the *chiral influence* of a suitable optically active reagent, only one of the optically active isomers (+ or -) is formed. This process in which a chiral compound is synthesized from an achiral compound to yield the (+)-isomer or (-)-isomer directly is termed **Chiral Synthesis**. For example, the reduction of pyruvic acid, $\text{CH}_3\text{COCO}_2\text{H}$, in the laboratory leads to (\pm)-lactic acid (racemic mixture). On the other hand, pyruvic acid is reduced by *yeast* to (-)-lactic acid only.



WALDEN INVERSION

When a group attached to a chiral carbon atom is replaced, the configuration of the new compound may be opposite to that of the original. That is, the product is the enantiomer (mirror image) of the expected substance. This phenomenon is known as **Walden Inversion**. Factors which determine whether or not an inversion will occur are the nature of the reagent, the nature of the solvent, the temperature, and the nature of the substance being acted upon.



- (1) Approach of the attacking group from the side of the molecule opposite to the position of the group which is later replaced.
- (2) Formation of an intermediate transition state in which three groups and the chiral carbon atom lie in one plane.
- (3) Separation of the group being replaced. This change is analogous to an umbrella being blown inside out. The conversion of (+)-chlorosuccinic acid into (-)-malic acid is an example of Walden inversion.

FISCHER PROJECTIONS : REPRESENTING 3-D STRUCTURES ON PAPER

The most convenient way of viewing molecules with more than one chiral center is with Fischer projections. A Fischer projection is a convenient two-dimensional drawing that represents a three-dimensional molecule. To make a Fischer projection, you view a chiral center so that two substituents are coming out of the plane at you (to hug you), and two substituents are going back into the plane, as Fig.4.13 shows. Then the chiral center becomes a cross on the Fischer projection. Every cross on a Fischer projection is a chiral center.

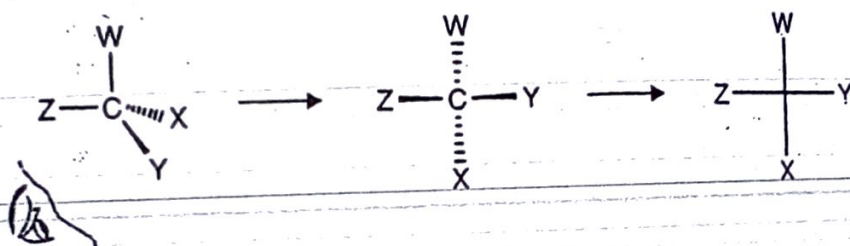
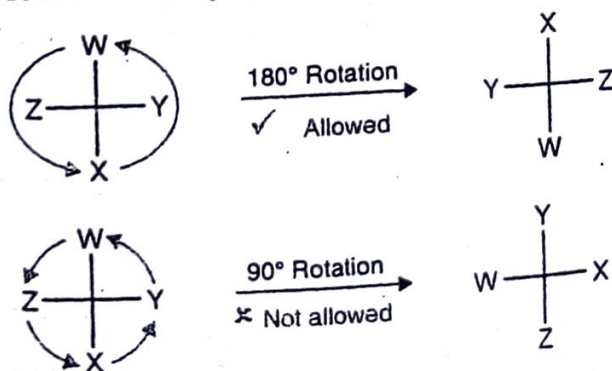


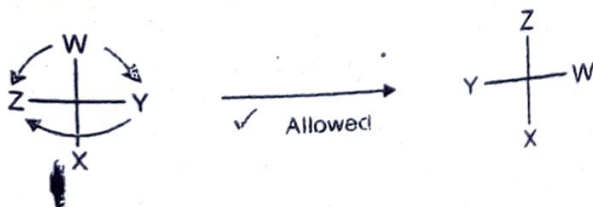
Fig.4.13. Writing a Fischer projection formula. The horizontal bonds are coming out of planes of the paper towards you. The vertical bonds are extending into the plane of the paper.

Rules for using fischer projections. Fischer projections are convenient for comparing the stereochemistries of molecules that have many chiral centers. But these projections have their own sets of rules and conventions for how you can rotate and move them. The two main ways to rotate a Fischer projection are as follows :

- Rule 1. You can rotate a Fischer projection 180° and retain the stereochemical configuration, but you cannot rotate a Fischer projection 90° .



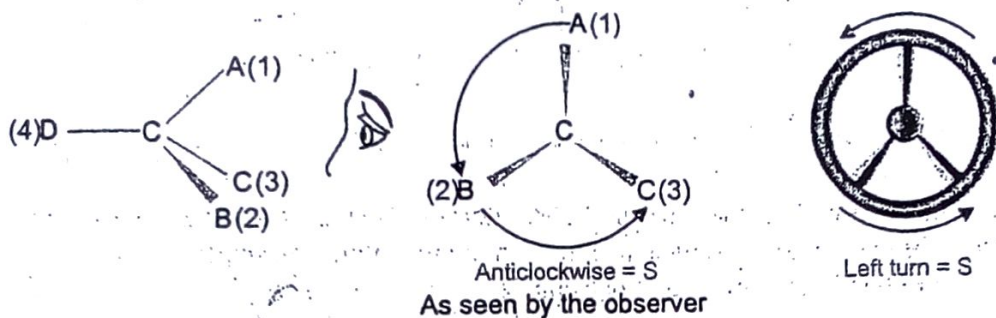
- Rule 2. You can rotate any three substituents on a Fischer projection while holding one substituent fixed and retain the stereochemical configuration.



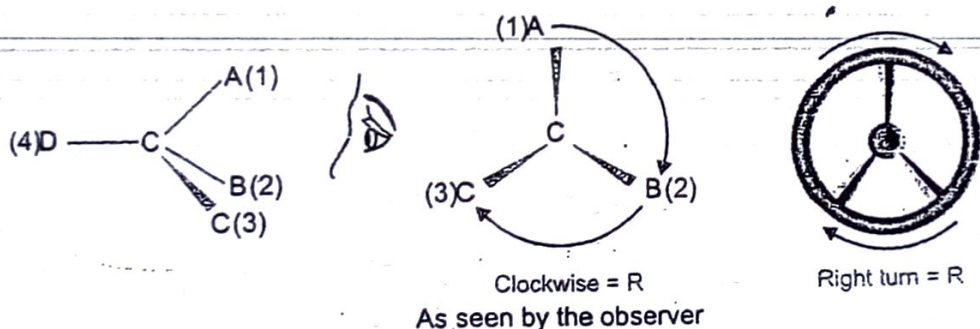
ASSIGNING CONFIGURATIONS TO CHIRAL MOLECULES

The actual 3-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 **Cahn-Ingold-Prelog system** or **CIP 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 carbon with the lowest priority group (4) on the side opposite the observer (group priorities are shown in parentheses):



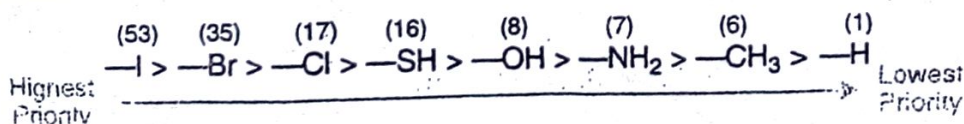
In the above example, A has the highest priority (1); B has the next highest (2); C has the next (3); and D has the lowest priority (4). We now go from high to low priority (1→2→3). To do so we move in an **anticlockwise** direction, and therefore we assign to this structure the **S configuration** (S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



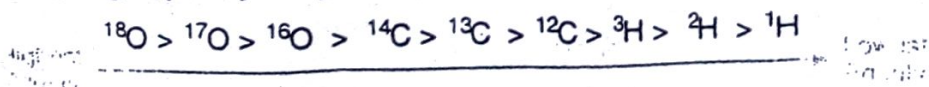
In the structure given above, we go from highest to lowest priority by moving in a **clockwise** direction. We therefore assign to this structure the **R configuration** (R = *rectus* = right).

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

Rule 1. Each atom bonded to chiral carbon is assigned a priority. Priority is based on atomic number; the higher the atomic number, the higher the priority. Following are several substituents arranged in order of decreasing priority. The atomic number of the atom determining priority is shown in parentheses.

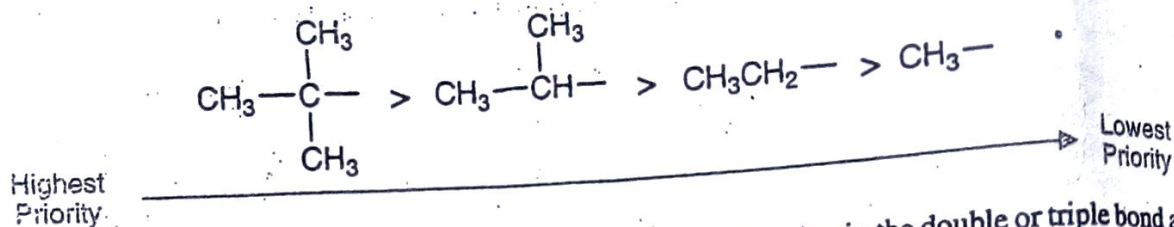
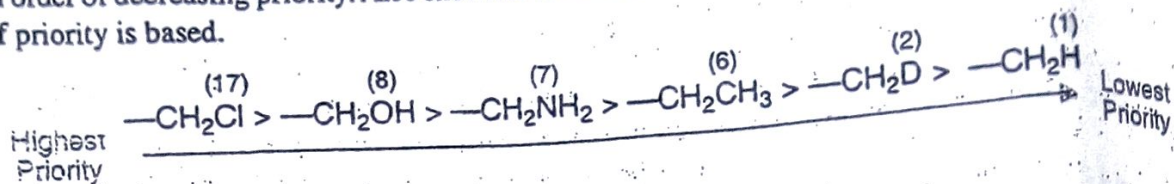


Rule 2. For isotopes, the higher the atomic mass, the higher the priority. Deuterium (Hydrogen-2) for example, has a higher priority than protium (Hydrogen-1).

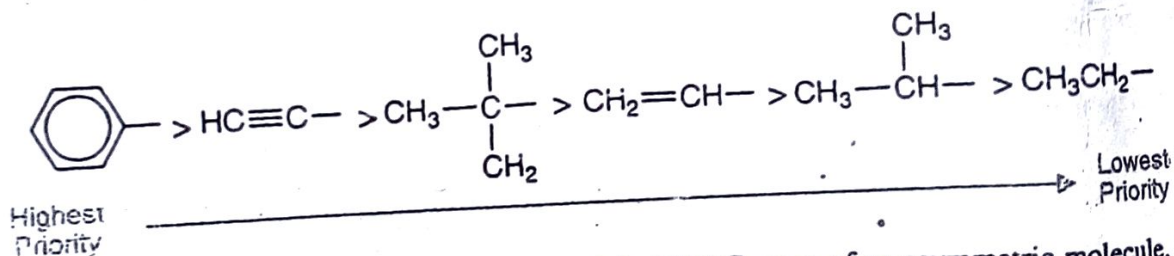
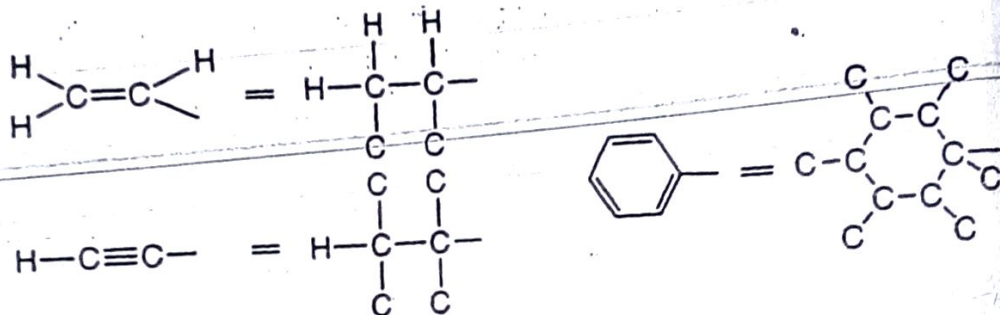


Rule 3. If priority cannot be assigned on the basis of atomic number or atomic mass considering the first atom of a group, then look at the next set of atoms and continue until a priority can be assigned. Priority is assigned at the first point of difference. Following are a series of groups, arranged

in order of decreasing priority. Also shown is the atomic number of the atom on which the assignment of priority is based.

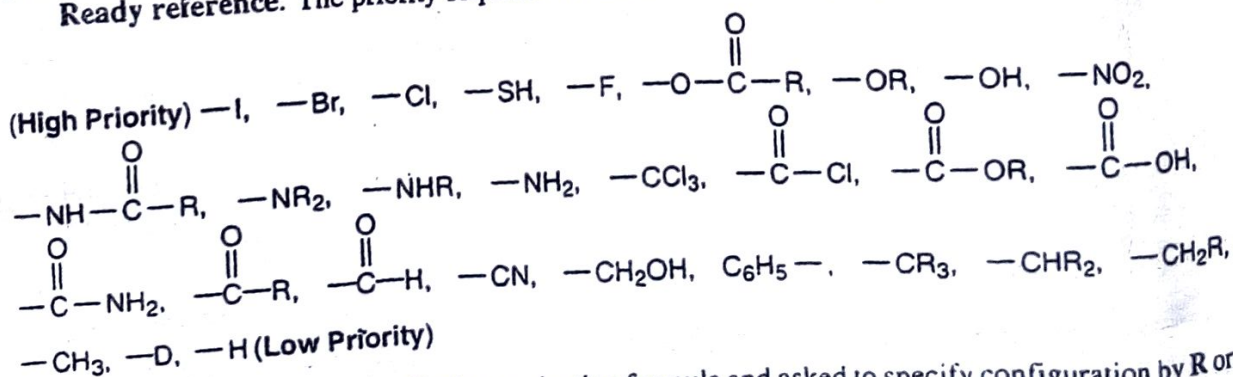


Rule 4. In the case of double and triple bonds, atoms participating in the double or triple bond are considered to be bonded to an equivalent number of similar atoms by single bonds, that is, atoms of double and triple bonds are replicated. For example,

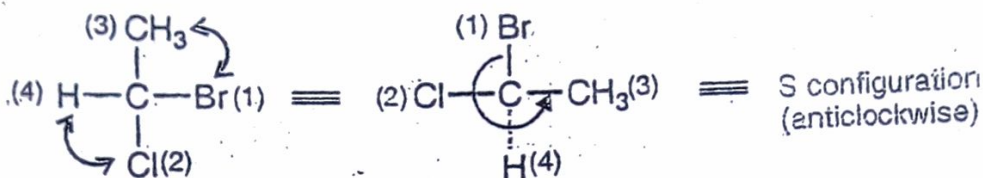


The R and S notations can be used as part of the IUPAC name of an asymmetric molecule, to provide a complete structural description, including configuration. The (R) and (S) designations precede the remainder of the name, separated from it with a hyphen.

Ready reference. The priority sequence for the most common groups and atoms is given below :



Ordinarily you are given a Fischer projection formula and asked to specify configuration by R or S notation. It is easy to do so if you follow the following step-by-step method. Consider the following example :



Order of Priority

- (1) Br (atomic number 79.9) (*Highest*)
- (2) Cl (atomic number 35.5)
- (3) CH₃ (C, atomic number 12)
- (4) 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 :



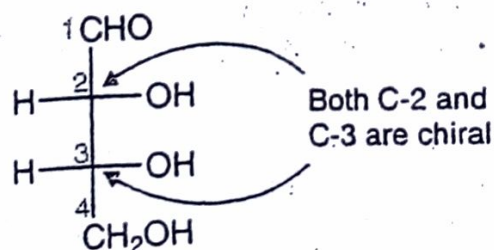
Step 2. Position the lowest priority group (in this case H) down and away from the observer. This is done by interchanging groups bonded to the asymmetric carbon. **Remember that interchanging any pair of groups in a Fischer projection inverts the configuration. Interchanging two pairs of groups retains the original configuration. Thus, the interchange operation must always be done in pairs or twice chiral to avoid a configuration change.**

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

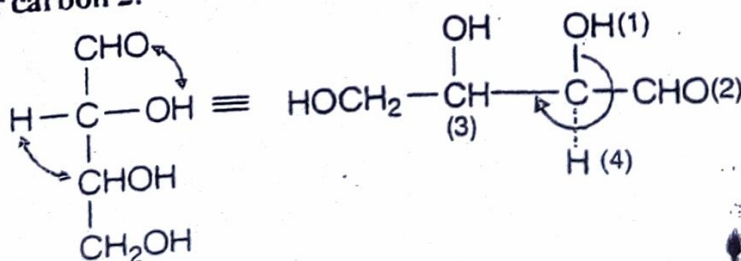
Step 3. Specify the direction of decreasing priority of the three groups (1→2→3). Ignore the lowest priority group. **If the groups 1, 2, and 3 are arranged in clockwise fashion, the configuration is R. If the groups occur in anticlockwise fashion, the configuration is S.**

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

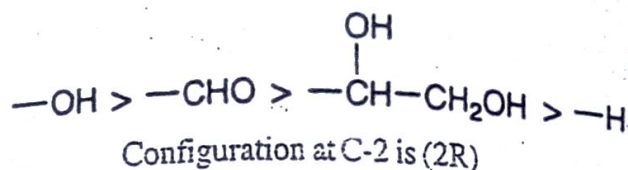
The configuration of compounds with more than one chiral center can also be specified by the R-S system. The configuration of each chiral carbon is determined individually, using the same rules as for compounds with one chiral center. The configuration of all chiral centers are then specified before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



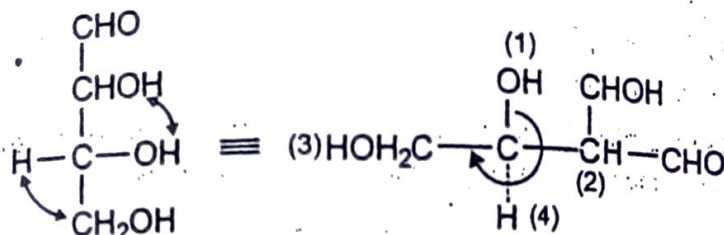
Configuration for carbon 2:



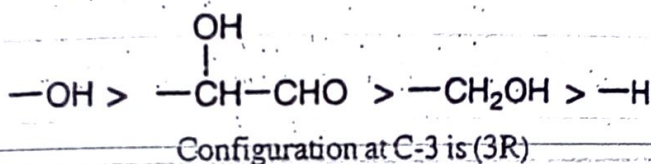
Order of priority is:



Configuration for carbon 3:



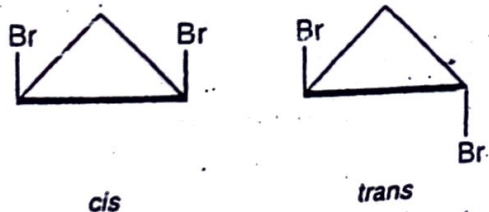
Order of priority is:



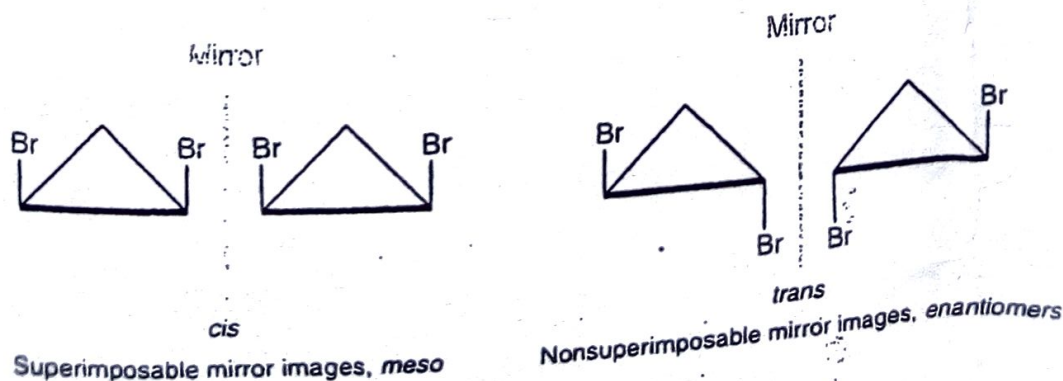
The name of the above compound is therefore (2R,3R)-2,3,4-trihydroxybutanal. Note that parentheses refer to the configurations around two chiral centers in one molecule.

OPTICAL ISOMERISM IN CYCLIC COMPOUNDS

Cyclic compounds can exhibit optical isomerism as well as geometric isomerism. Using 1,2-dibromocyclopropane as an illustration, we find that the *cis* isomer has its two bromines on the same side of the planar ring while the *trans* isomer has one above and one below the ring.

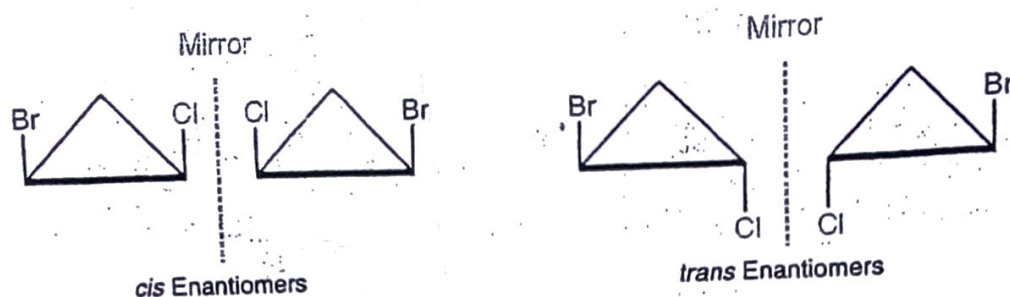


1,2-Dibromocyclopropane has two chiral carbons (the carbons bonded to bromines) and should have a maximum of *four* optical isomers. Let us draw the mirror images of the *cis* and *trans* isomers and test for superimposability.



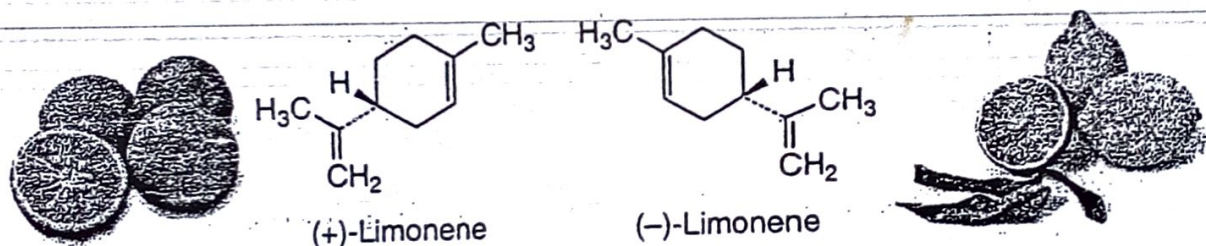
cis-1,2-Dibromocyclopropane is superimposable on its mirror image. Therefore the molecule is not chiral (it is achiral) and it is an optically inactive *meso* structure. The *trans* isomer is not superimposable on its mirror image; it exists as an enantiomeric pair.

The compound 1-bromo-2-chlorocyclopropane has two dissimilar chiral carbons and thereby two pairs of enantiomers.

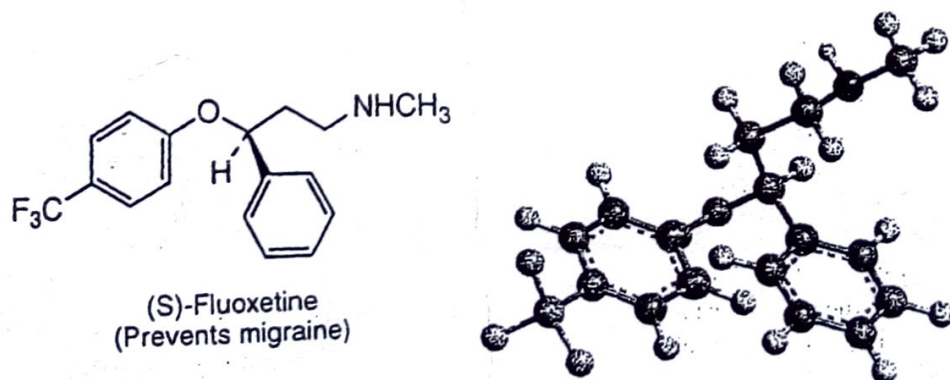


OPTICAL ISOMERISM IN NATURE

Just as different stereoisomeric forms of a chiral molecule have different physical properties, they usually have different biological properties as well. For example, the (+) enantiomer of limonene has the odor of *oranges*, but the (-) enantiomer has the odor of *lemons*.



More dramatic examples of how a change in chirality can affect the biological properties of a molecule are found in many drugs, such as fluoxetine, a commonly prescribed medicine for migraine. Racemic fluoxetine is an effective antidepressant, but it has no activity against migraine. The pure *S* enantiomer, however, works remarkably well in preventing migraine.



Why do different stereoisomers have different biological properties? To exert its biological action, a chiral molecule must fit into a chiral receptor at a target site, much as a hand fits into a glove. But just as a right hand can fit only into a right-hand glove, so a particular stereoisomer can fit only into a receptor having the proper complementary shape. Any other stereoisomer will be a misfit, like a right hand in a left-handed glove. A schematic representation of the interaction between a chiral molecule and a chiral biological receptor is shown in Fig. 4.14. One enantiomer fits into the receptor perfectly, but the other does not.

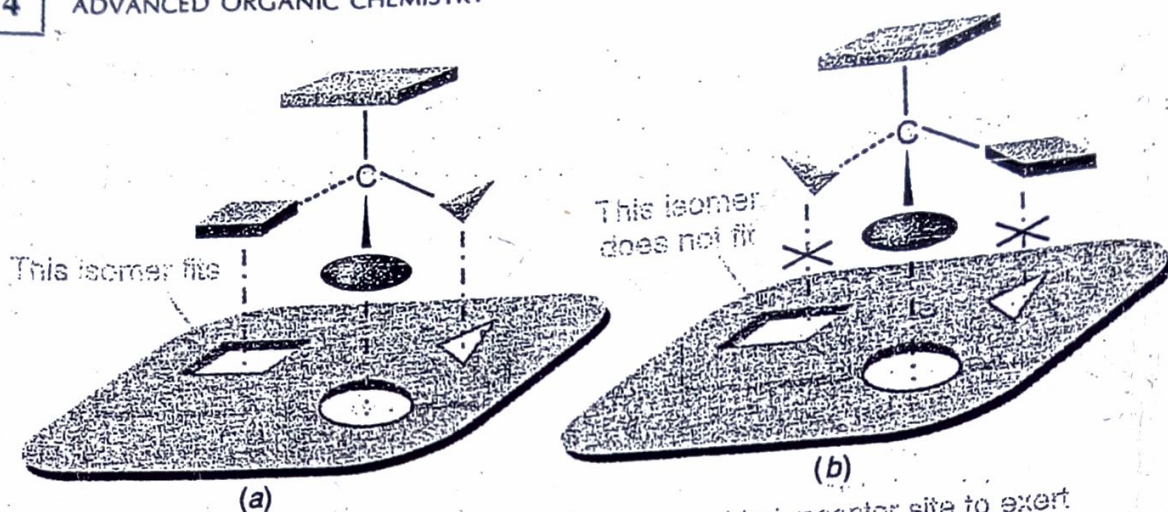
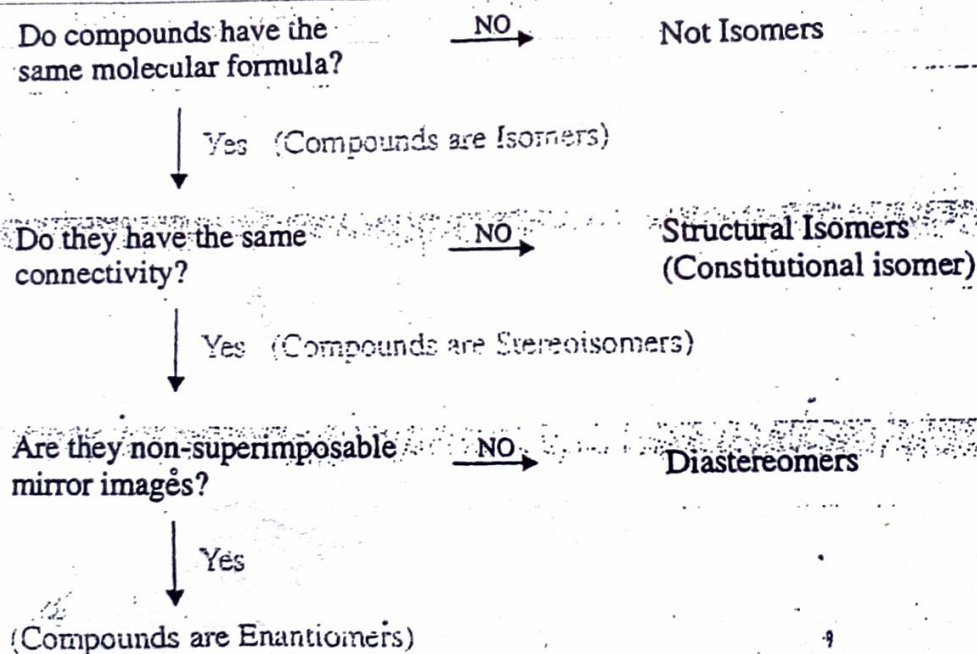


Fig. 4.14. (a) One enantiomer fits easily into a chiral receptor site to exert its biological effect, but (b) the other enantiomer can't fit into the same receptor.

SUMMARY OF ISOMERISM

The following flowchart summarizes the relationships between different types of isomerism:



STUDY PROBLEMS

- Define or explain the following terms :

(a) Structural isomerism	(b) Stereoisomerism
(c) Geometric isomerism	(d) Optical isomerism
(e) Chiral carbon	(f) Chiral center
(g) Chiral molecule	(h) Enantiomers
(i) Diastereomers	(j) Meso compounds
(k) Racemic mixture	
- Write a note on : Structural isomerism
- Write notes on :
 - Chain isomerism
 - Position isomerism

(c) Functional isomerism

(d) Metamerism

4. Which of the following statements is false about tautomers ?

(a) Tautomers are structural isomers

(b) Tautomers are structural isomers which exist in dynamic equilibrium

(c) Tautomerism involves movement of atoms

(d) Tautomers have independent existence

Answer. (d)

5. Write a note on : Geometric isomerism.

6. State the necessary conditions for a compound to show Geometric isomerism. Illustrate your answer with examples.

7. Describe the isomerism exhibited by maleic and fumaric acids.

8. Which of the following compounds show geometric isomerism?

(a) 2-Butene

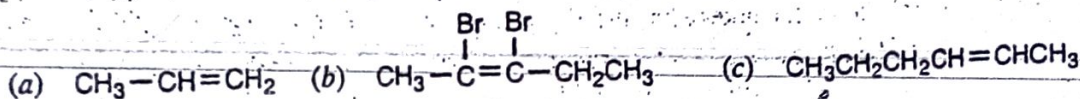
(b) 2-Methyl-2-butene

(c) 2-Pentene

(d) 1,2-Dichloropropane

Answer. (a) and (c)

9. Which of the following compounds show geometric isomerism :



Answer. (b) and (c)

10. Which of the following compounds exhibit *cis-trans* isomerism ?

(a) 1-Pentene

(b) 2-Methyl-2-pentene

(c) 2-Pentene

(d) 2-Methyl-2-butene

Answer. (c)

11. Which of the following compounds show *cis-trans* isomerism.

(a) $(\text{CH}_3)_3\text{N}$

(b) $\text{CH}_3\text{CH}=\text{CH}_2$

(c) $(\text{CH}_3)_2\text{NH}$

(d) $\text{CH}_3\text{CH}=\text{CHCH}_3$

Answer. (d)

12. Which of the following compounds will show *cis-trans* isomerism ?

(a) $\text{CH}_2=\text{CHCl}_2$

(b) $\text{ClCH}=\text{CHBr}$

(c) $\text{CH}_2=\text{CHCl}$

(d) $\text{Cl}_2\text{C}=\text{CBr}_2$

Answer. (b)

13. Which of the following compounds will not show geometric isomerism ?

(a) $\text{BrCH}=\text{CHBr}$

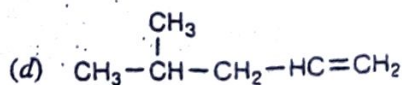
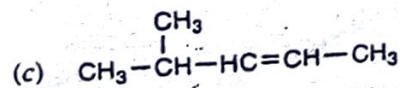
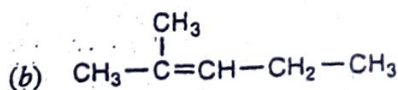
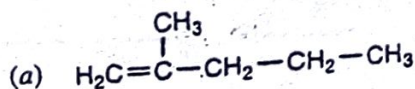
(b) $\text{BrCH}=\text{CHCl}$

(c) $\text{CH}_3-\overset{\text{Br}}{\underset{|}{\text{C}}}=\text{CHBr}$

(d) $\text{CH}_3-\overset{\text{CH}_3}{\underset{|}{\text{C}}}=\text{CHCH}_3$

Answer. (d)

14. Which of the following alkenes show *cis-trans* isomerism? For each that does, draw structural formulas for the isomers.



Answer. *Cis-trans* isomerism is possible only for (c). Each other alkene has two identical substituents on one of the carbons of the double bond. Following are the *cis-trans* isomers for (c).