B.SC PART II SUBSIDARY PAPER ORGANIC

TOPIC:- Optical Isomerism

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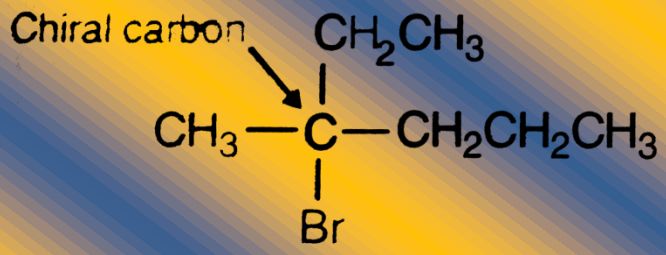
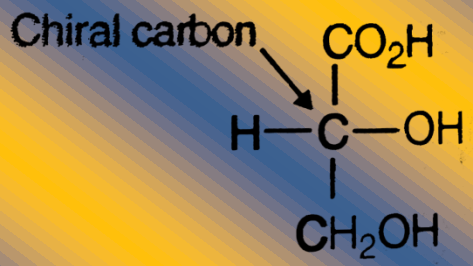
CHIRAL (OR ASYMMETRIC) CARBON ATOM

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

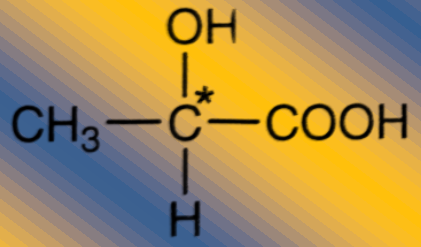
A substance which has the ability to rotate the plane of polarized light is said to be optically active and exhibits optical isomerism. Optical isomers are isomers that are identical in all properties except for their effect on plane of polarized light.

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 rotator 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.

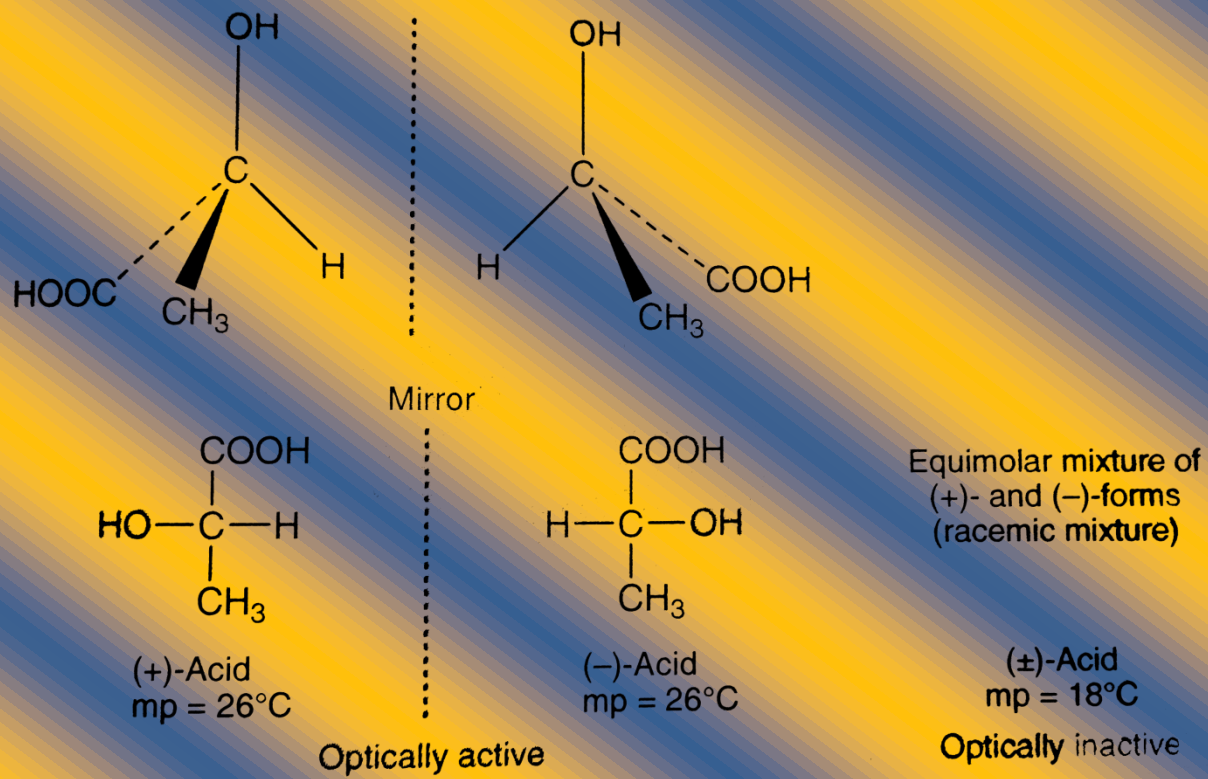
These structures are not identical because they cannot be superimposed on each other. One is the mirror image of the other. Such nonsuperimposable mirror image forms are optical isomers and are called enantiomers. Thus, three forms of lactic acid are known. Two are optically active and the third is optically

Inactive.

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

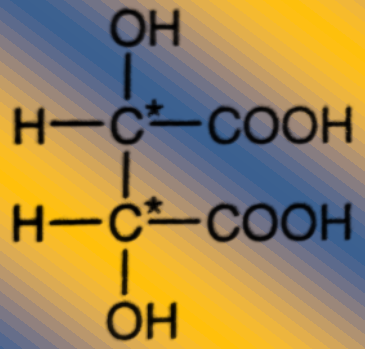
2. (-)-Lactic Acid- It rotates the plane of polarized light to the left (anticlockwise direction) and is called levoratatory. (-)-Lactic acid is the mirror image of (+)-lactic acid and vice versa.

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)



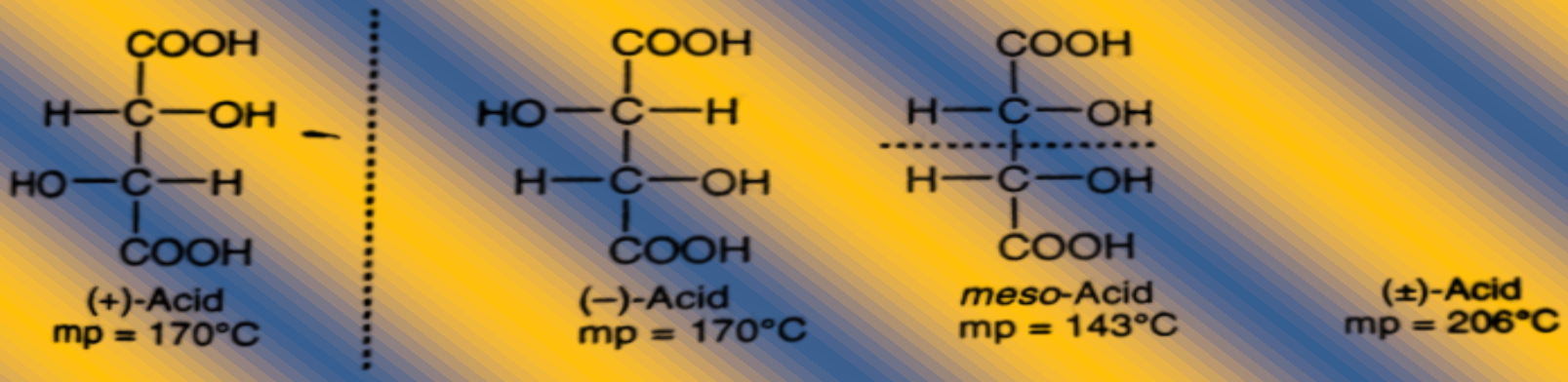
OPTICAL ISOMERISM OF TARTARIC ACID

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 . 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.

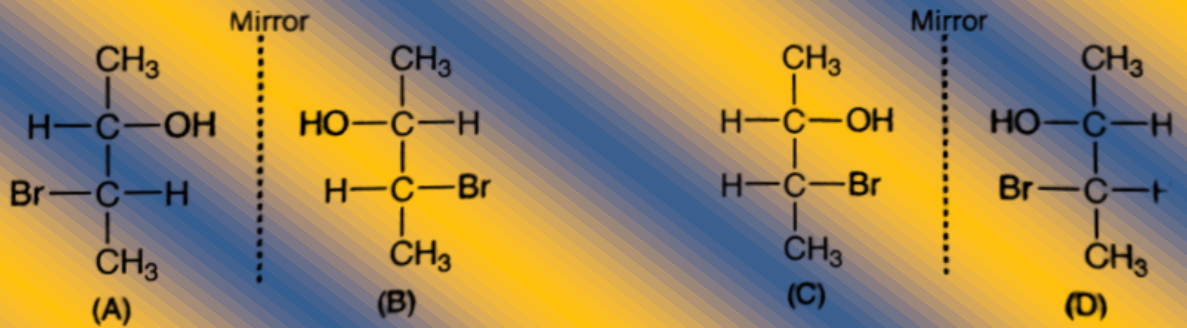


Isomers of tartaric acid.

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 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 centers 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 3-bromo-2-butanol.

It has two chiral carbon atoms but no plane of symmetry.



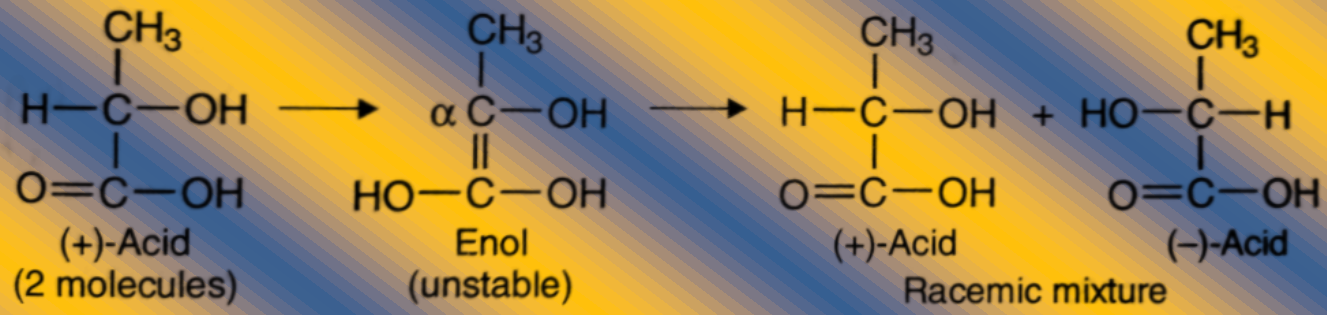
Four isomers of 3-Bromo-2-butanol.

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,

$$2(+)\text{-A} \longrightarrow (+)\text{-A} + (-)\text{-A}$$
$$2(-)\text{-A} \longrightarrow (+)\text{-A} + (-)\text{-A}$$

Racemization can be accomplished by mean 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 though an enol intermediate.

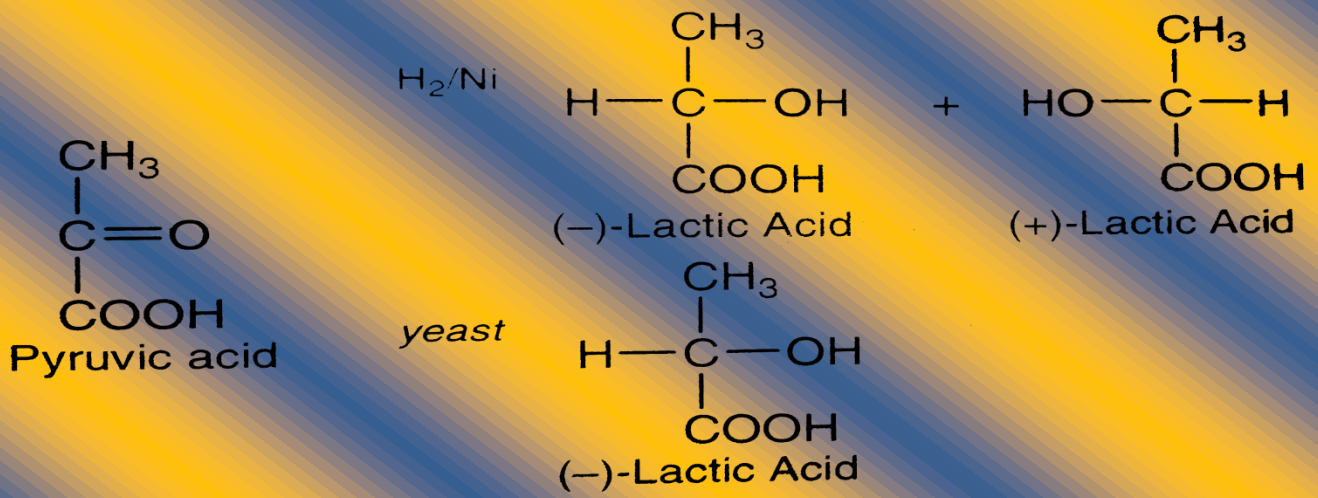


When the proton migrates back to the carbon atom, the process can involve the opening of either of the two linkages of the double bond and can produce either the original configuration or the opposite of it.

CHIRAL SYNTHESIS

When a compound containing a chiral carbon atom is synthesized by ordinay laboratory methods from a symmetric compound, the product is a racemic mixture. If, however, such a synthesis is carried under the asymmetric influence of a suitable optically active reagent, only one of the optically active isomers(+ or-) is formed.

This process in which a chiral compound is synthesized from a symmetric compound to yield the (+)-isomer or (-)-isomer directly is termed Chiral Synthesis. For example, the reduction of pyruvic acid, $CH_3COCOOH$,in the laboratory leads to (±) lactic acid (Racemic mixture). On the other hand, pyruvic acid is reduced by yeast to (-)-lactic acid only.



WALDEN INVERSION

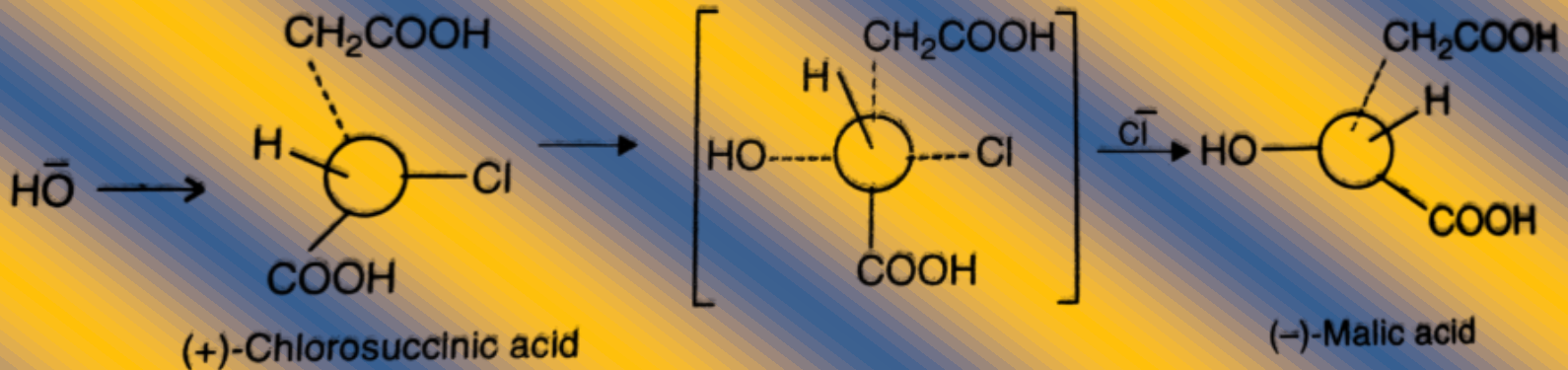
When a group attached to a chiral carbon atom is replaced, the configuration of the new compound may be opposite to that of the original. That is, the product is the enantiomer (mirror image) of the expected substance. This phenomenon is known as **Walden Inversion**. Factors which determine whether or ot 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.

The mechanism of Walden inversion involves three steps:

(1) Approach of the attacking group from the side of the molecule opposite to 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.



Thank You