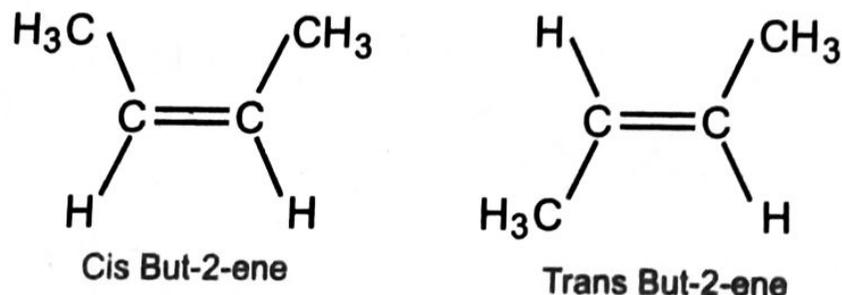


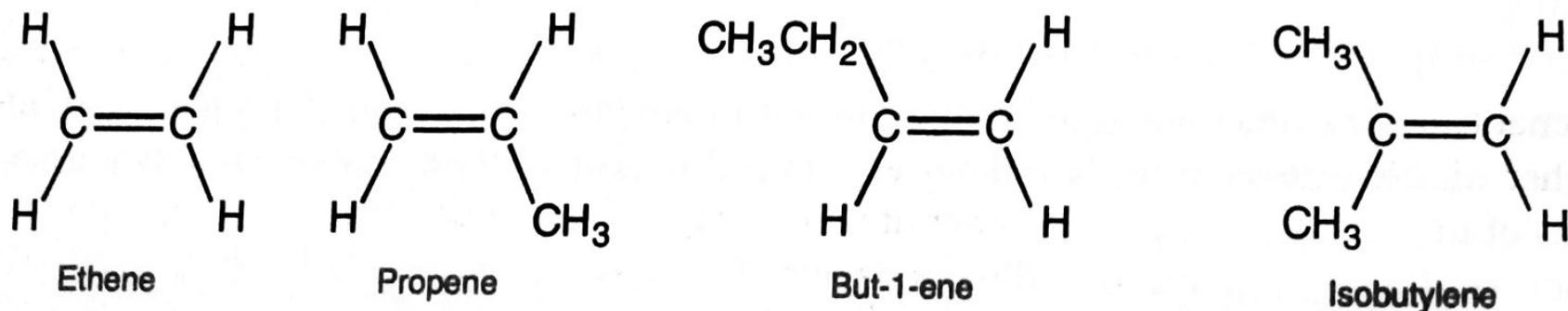
BASIC CONDITIONS FOR GEOMETRICAL ISOMERISM :

The necessary conditions for geometrical isomerism are :

- (i) Presence of atleast one double bond
- (ii) Each carbon atom of the double bond should be linked to two different atoms or groups. For example,



No geometrical isomerism is observed when similar atoms or groups are attached to any of the doubly bonded carbon. For example, ethene, but-1-ene and isobutylene do not show geometrical isomerism.



(No Geometrical isomerism)

METHODS FOR DETERMINATION OF CONFIGURATION OF GEOMETRICAL ISOMERS

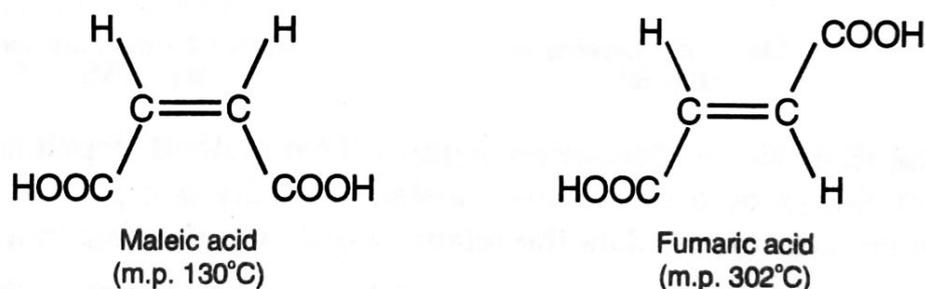
There are no general methods to ascertain the configuration of geometrical isomers. The methods employed depend on the nature of compound under consideration. It has been found that geometrical isomers show different physical properties. These isomers also differ in some of their chemical properties. These facts are used to ascertain the configuration of the isomers. The following methods are employed to determine whether a given compound is a cis or a trans-isomer.

I. **By studying their physical properties.** By studying their physical properties it has been found that generally a cis isomer has **low melting point, high boiling point, higher density, greater solubility in organic solvents, higher heat of combustion and hydrogenation, higher refractive index, higher viscosity and higher dissociation constant (if an acid) than a trans-isomer.**

Some of these important physical properties and their applications in ascertaining the configurations are discussed below :

(1) **Melting points.** The trans-isomer, in general has a higher melting point than the corresponding cis isomer. This is due to the fact that in the cis-isomer, the two similar atoms or groups are on the same side of the double bond. Therefore, these molecules are unsymmetrical and hence do not show close packing in the crystal lattice. On the other hand, trans isomer is more symmetrical as the two similar atoms or groups lie on the opposite side of the double bond. Therefore, these molecules pack well in the crystal lattice. As a result, the intermolecular forces of attraction of trans isomer are much stronger than those holding the cis isomer. Hence the melting point of trans isomer is higher than that of the corresponding cis isomer.

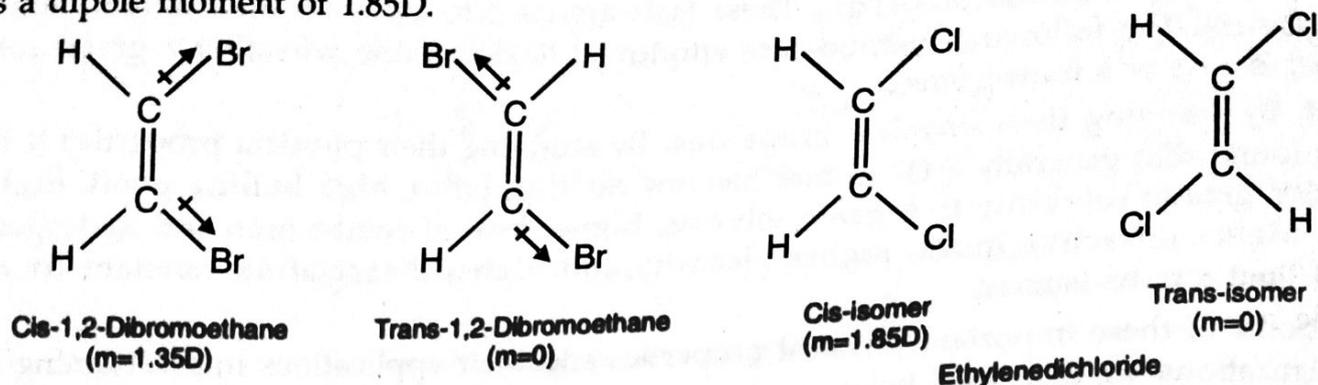
For example, maleic acid (cis-isomer) has a melting point of 130°C while Fumaric acid (trans-isomer) melts at 302°C . This is in accordance with the above discussion.



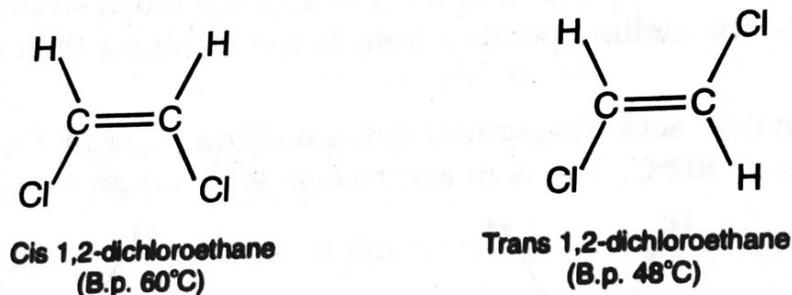
(2) **Solubility.** As discussed above, molecules of cis-isomer are less closely packed and thus have weak intermolecular forces of attraction in the crystal lattice than the corresponding trans-isomer. Therefore cis isomers should have higher solubility than that of the corresponding trans-isomer. This is evident from the solubility (in water at 20°C) of maleic acid ($79.0\text{ g}/100\text{ ml}$) and fumaric acid ($0.7\text{ g}/100\text{ ml}$).

(3) **Dipole moments.** It has been found that generally cis isomers have higher dipole moments as compared to trans isomers which have zero or nearly zero dipole moments. The higher dipole moments of cis isomer as compared to that of trans isomer is due to orientations of the two dipoles of cis isomer at some angle. The two dipoles in a trans-isomer on the other hand are in the opposite directions and thus they cancel out. As a result, cis isomer will have some finite value of dipole moments but trans isomer will have zero dipole moments.

Thus, this is an important physical property which helps a lot in establishing configuration of geometrical isomer. It is also evident from the dipole moment of ethylene dibromide that trans isomer has zero dipole moment as compared to cis isomer which has a dipole moment of 1.35D. Similarly, trans ethylenedichloride has zero dipole moment while the cis isomer has a dipole moment of 1.85D.



(4) Boiling points. In general, the boiling point of a cis isomer is higher than that of the corresponding trans isomer. It is due to the more polar nature (due to higher dipole moments) of cis isomer than the corresponding trans isomer, which results in comparatively stronger intermolecular attractions. For example, cis dichloroethene boils at $60^{\circ}C$ where as trans isomer boils at $48^{\circ}C$. However, there are a few exceptions to these generalizations. For example *trans-1, 2-diiodoethene has higher boiling point than the corresponding cis isomer.*

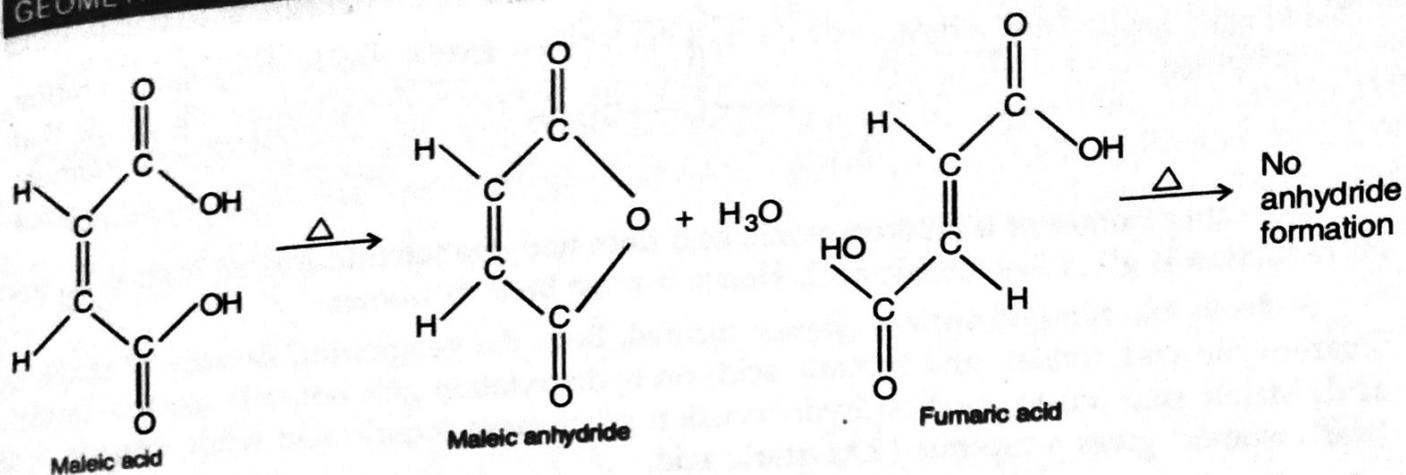


(5) Studying their X-ray diffraction pattern. This method depends upon the fact that the diffraction of X-rays by a crystalline substance produces a pattern on a photographic plate, which can be used to calculate the relative positions of atoms in a molecule.

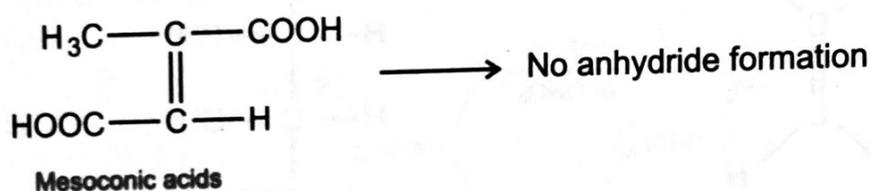
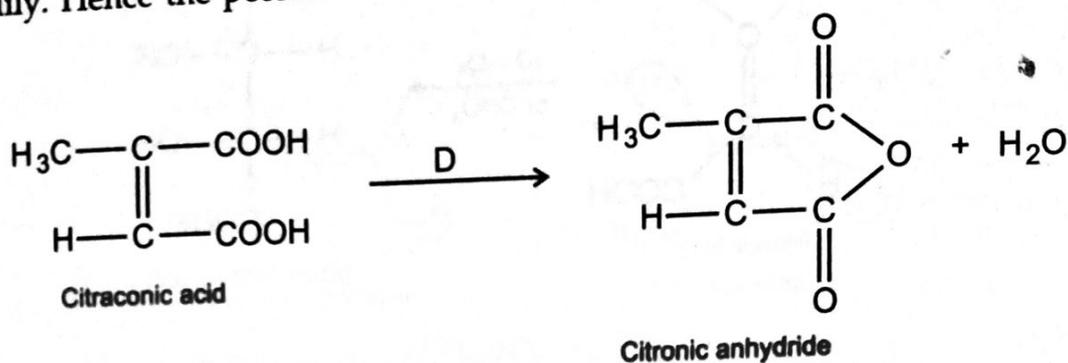
II. By studying their chemical properties. Chemical properties of the cis and trans isomers are related to the relative positions of the two groups on each of the two doubly bonded atoms. These provide more dependable results than those provided by physical properties. Some of the methods are :

(1) By cyclization method. Cyclization occurs easily if the two reactive groups are close together. Since in cis-isomer the reacting groups are quite near to each other, they result in the formation of cyclic compound. But in trans-isomer the two reactive groups are far apart and, therefore are unable to react mutually to form a cyclic derivative. This fact is utilized to assign configuration to cis- and trans-isomers. For example, when maleic acid is heated, it forms maleic anhydride. Anhydride formation does not take place with fumaric acid.

GEOMETRICAL ISOMERISM

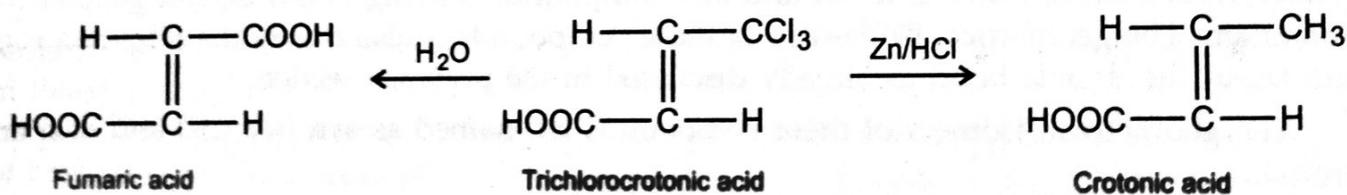


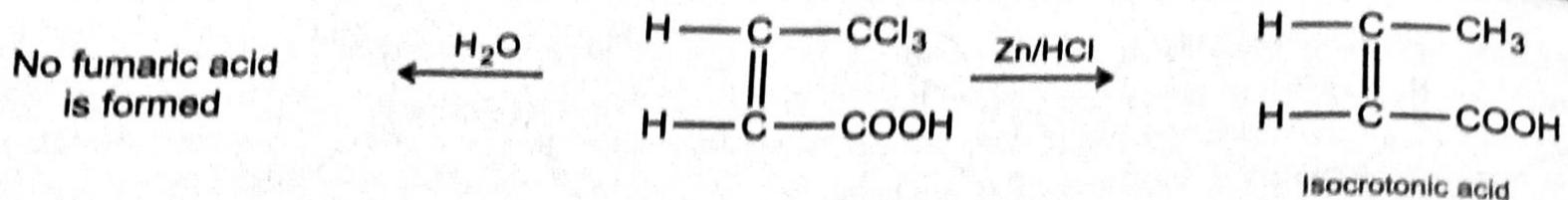
Similarly out of the citraconic acid and mesoconic acids, the former gives a cyclic anhydride readily. Hence the possible structures are :



2. By converting into compounds of known configuration. In some cases a geometrical isomer can be changed into a compound of known configuration. It is presumed that during such a change there is no isomerisation.

For example, trichlorocrotonic acid can be converted into fumaric acid on hydrolysis. hence the trichlorocrotonic acid must be a trans-isomer. It further gives crotonic acid on reduction.





The other isomer of trichlorocrotonic acid does not give fumaric acid on hydrolysis and on reduction it gives isocrotonic acid. Hence it must be a cis-isomer.

3. From the type of optical isomer formed. Both the geometrical isomers of ethylene dicarboxylic acid, (maleic and fumaric acid) on hydroxylation give optically inactive tartaric acid. Maleic acid (cis-isomer) on hydroxylation gives meso tartaric acid while fumaric acid (trans isomer) gives a racemic (\pm) tartaric acid.

