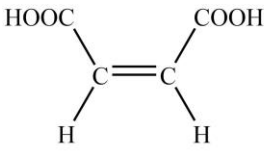
❖ Methods of Determining the Configuration

After studying the geometrical isomerism in alkenes, it's time to discuss the route by which know their configurations. The methods of determining the configuration of geometrical isomers are based upon either physical or chemical properties.

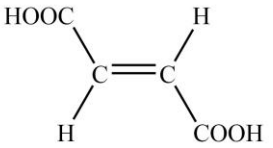
➢ *Determination of Configuration Using Physical Properties*

The geometrical isomers of alkenes can be identified with various kinds of physical properties like melting point, solubility, dipole moment, or boiling point, etc. Some of the important physical methods for determining the configuration of geometrical isomers are given below.

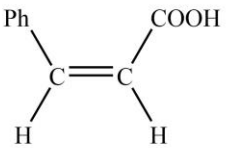
1. Melting point: The melting points of trans-isomers are generally higher than that of cis-isomers, which makes it a suitable tool for configuration prediction. The reason for such behavior is the fact that trans-isomers are symmetrical, and consequently, are well packed to give stronger intermolecular forces than cis-isomers.



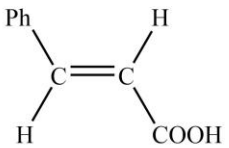
Maleic acid
melting point = 403 K



Fumaric acid
melting point = 575 K

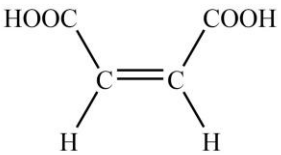


Allocinnamic acid
melting point = 341 K

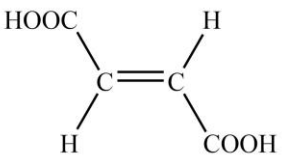


Cinnamic acid
melting point = 406 K

2. Solubility: The solubility of cis-isomers are generally higher than that of trans-isomers, which makes it a suitable tool for configuration prediction. The reason for such behavior is the fact that cis-isomers are unsymmetrical, and consequently, are not well packed, giving weaker intermolecular forces than trans-isomers.

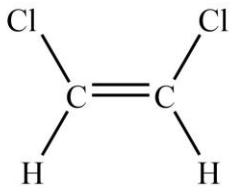


Maleic acid
Solubility = 790g per liter water

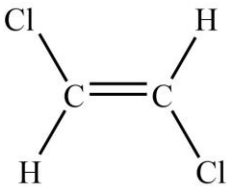


Fumaric acid
Solubility = 7g per liter water

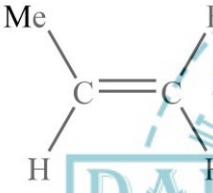
3. Dipole moment: The dipole moments of cis-isomers are generally higher than that of trans-isomers, which makes it a suitable tool for configuration prediction. The reason for such behavior is the fact that trans-isomers have individual dipoles in the exact opposite direction which may or may not get canceled completely.



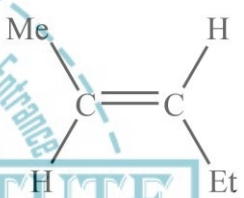
cis-dichloroethene
Dipole moment = 1.85D



trans-dichloroethene
Dipole moment = 0D

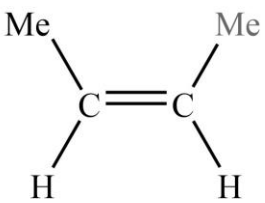


(*Z*)-pent-2-ene
More polar
Higher dipole moment



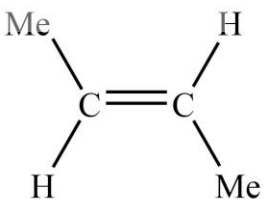
(*E*)-pent-2-ene
Less polar
Lower dipole moment

4. Boiling Point: The boiling points of cis-isomers are generally higher than that of trans-isomers, which makes it a suitable tool for configuration prediction. The reason for such behavior is the fact that the boiling points are typically the function of dipole moments, which are higher for cis-isomers.



(*Z*)-but-2-ene

Boiling point = 277K
Dipole moment = 0.4 D



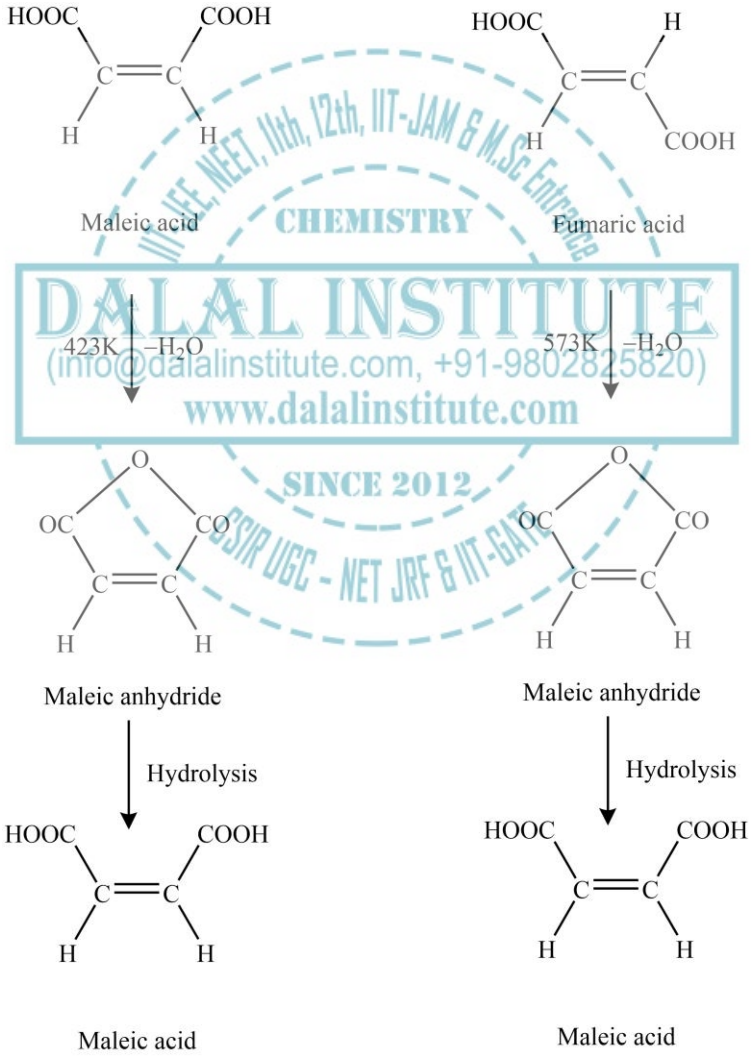
(*E*)-but-2-ene

Boiling point = 274K
Dipole moment = 0.0 D

➢ ***Determination of Configuration Using Chemical Properties***

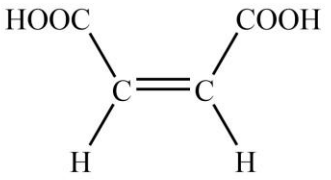
The geometrical isomers of alkenes can be identified with various kinds of chemical properties like the formation of cyclic compounds, or the optical properties of the stereoisomers formed during bromination and hydroxylation reactions, etc. Some of the important chemical methods for determining the configuration of geometrical isomers are given below.

1. Generation of cyclic systems: Since the reactive groups of the substrate are on the same side in cis-isomer, the formation of cyclic systems will be an easy task. Conversely, if the reactive groups of the substrate are on the opposite side (in trans-isomer), the formation of cyclic systems will be much more difficult to carry out. This can be illustrated by the case of maleic acid and fumaric acid where the generation of maleic anhydride requires much more temperature for the later substrate.

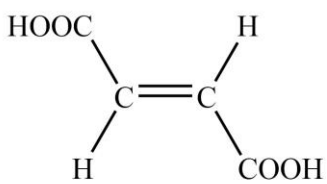


Furthermore, it is also worthy to note that the hydrolysis of maleic anhydride gives back only maleic acid and no fumaric acid.

2. Optical properties of stereoisomers formed: The geometrical isomers of alkenes can be identified with the optical properties of the stereoisomers formed during bromination and hydroxylation reactions. Since the alkene's hydroxylation with dilute $KMnO_4$ or OsO_4 is cis-addition, we should get a meso-product with cis-isomer and racemic mixture for trans-substrate.



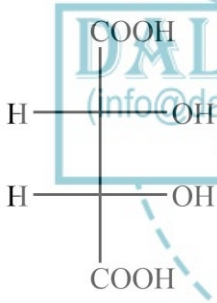
Maleic acid
(*cis*-isomer)



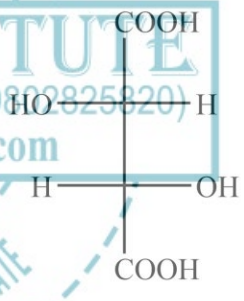
Fumaric acid

Aq. $KMnO_4$
or OsO_4

Aq. $KMnO_4$
or OsO_4

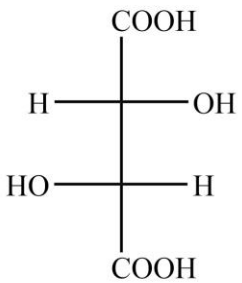


meso-Tartaric acid



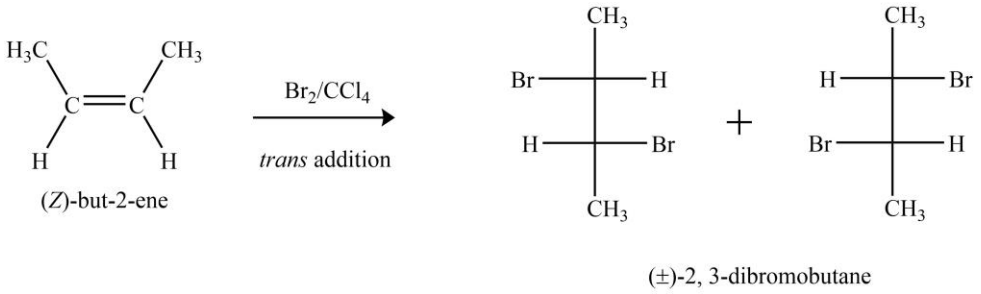
(+)-Tartaric acid

&



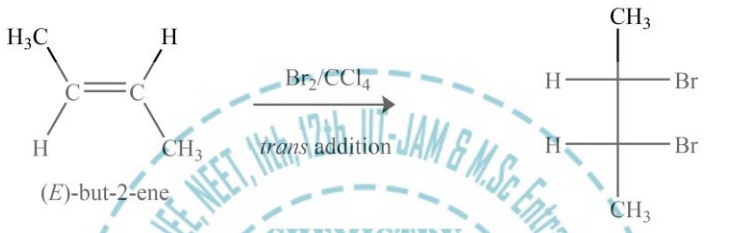
(–)-Tartaric acid

On the other hand, the alkene's bromination with CCl_4 is trans-addition, we should get a meso-product with trans-isomer and racemic mixture for cis-substrate.



(*Z*)-but-2-ene

(±)-2, 3-dibromobutane



(*E*)-but-2-ene

meso-dibromobutane

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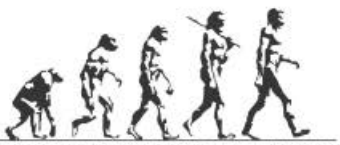

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