

# STEREOCHEMISTRY

1.

Degree-II (Hons.), Paper-IV, Group-B

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## Geometrical Isomerism Due to C=C bond

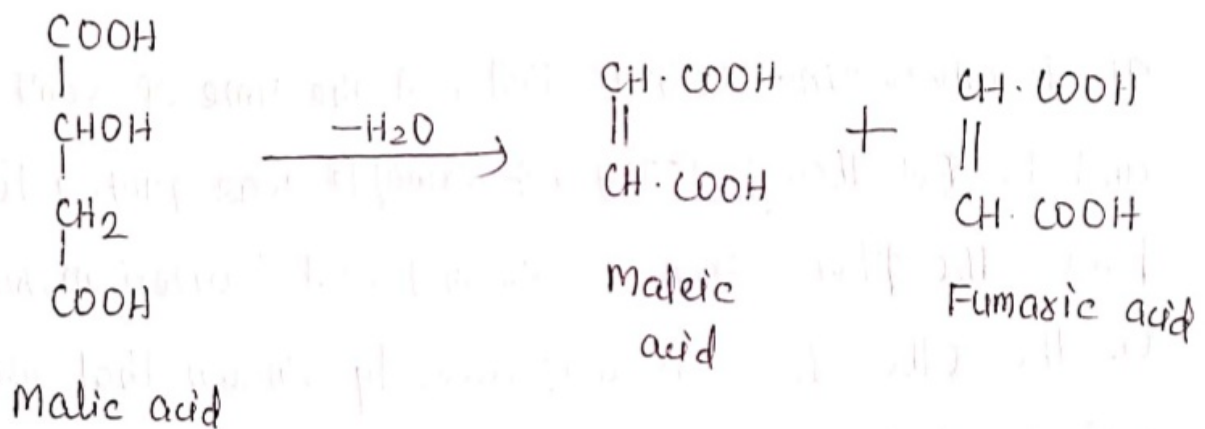
- \* Maleic acid and fumaric acid (compounds having C=C bonds) were the first examples to show the phenomenon of geometrical isomerism.
- \* It is interesting to note that, at the time of van't Hoff and Le Bel theory (1875) no example was quoted to prove the phenomenon of Geometrical isomerism, but on the other hand it was already known that malic acid on dehydration gives two different dibasic acids having the following similar properties: -
  - (i) Both acids (Maleic and fumaric) have same molecular formula  $C_4H_4O_4$ .
  - (ii) On reduction, both of them gives succinic acid.
  - (iii) Both of them add one molecule of HBr to form bromosuccinic acid.

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iv) Both of them add one molecule of water and bromine to form malic and dibromosuccinic acids respectively.

v) Both of them are oxidised by alkaline  $KMnO_4$  to tartaric acid.

\* The above similarities indicates that the two acids are structurally identical, and their formation may be represented as below.

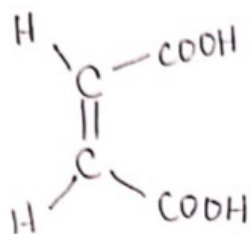


On the other hand, the two acids differ from each other in many of their physical and some chemical properties. eg; boiling point, density, solubility, action of heat etc.

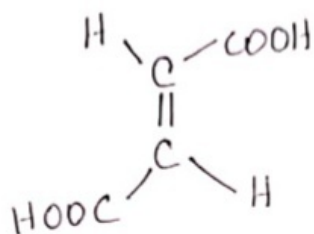
\* The isomerism in the above two acids is due to the presence of olefinic linkage.

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So, on the basis of Van't Hoff and Le-Bel theory, the isomeric acids may now be represented as below -



Maleic acid  
(cis)



Fumaric acid  
(trans)

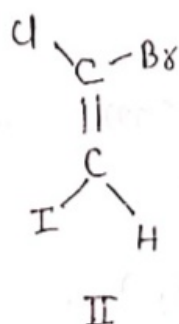
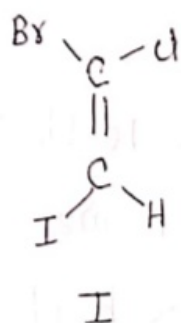
- \* If similar group on same side of  $C=C$  double bond = cis isomer
- \* If similar group on opposite side of  $C=C$  bond = Trans isomer.

## Nomenclature Of Geometrical Isomerism

- \* The simple cis-trans nomenclature is not applicable when the ethylenic carbon atoms possess four different groups and of course, in such cases nomenclature is somewhat complicated.
- \* It has been suggested that in such cases the prefix cis and trans should indicate the disposition of the first two groups named.

4.

For example, the two geometrical isomers of 1-bromo-1-chloro-2-iodo-ethylene.



I and II may be named as cis-1-bromo-2-iodo-1-chloro-ethylene  
or

trans-1-chloro-2-iodo-1-bromo ethylene

and

cis-1-chloro-2-iodo-1-bromo ethylene.

or

trans-1-bromo-2-iodo-1-chloroethylene respectively.

**Continued in next lecture...**