

RELATIVE CONFIGURATION
and
CONFORMATION OF CYCLIC COMPOUNDS

①

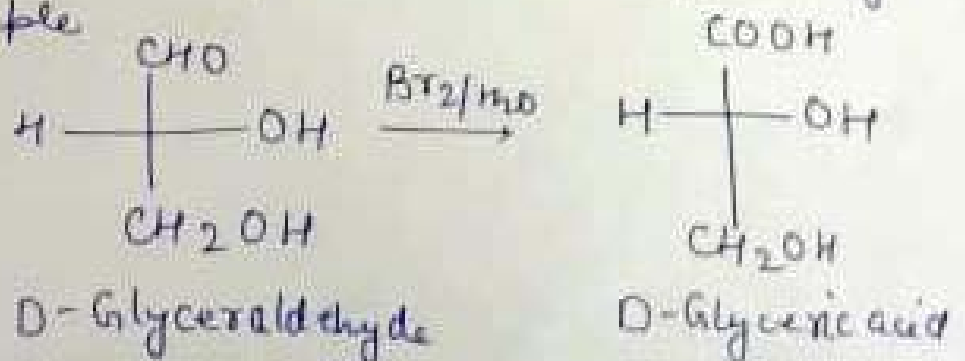
Relative Configuration

This means the arrangement of atoms or groups in space of stereoisomer of a compound relative to the atoms or groups of another compound chosen as an arbitrary standard.

For example sugars can be said D or L sugars if they can be related with D or L - Glyceraldehyde. Here D or L - Glyceraldehyde is the arbitrary standard.

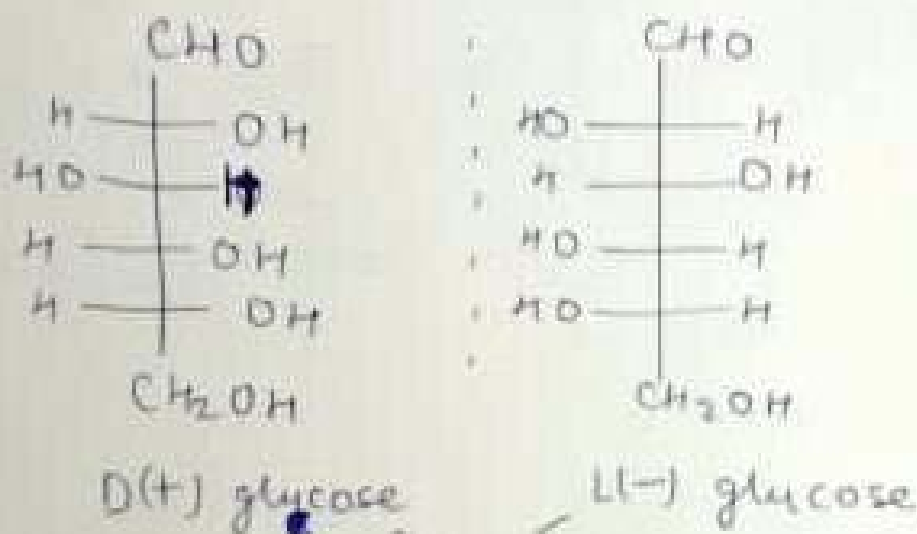
Any compound that can be prepared from D or L glyceraldehyde without breaking at the chiral centre or by even number of Walden inversion occurring at chiral centre has D or L - configuration respectively.

For example



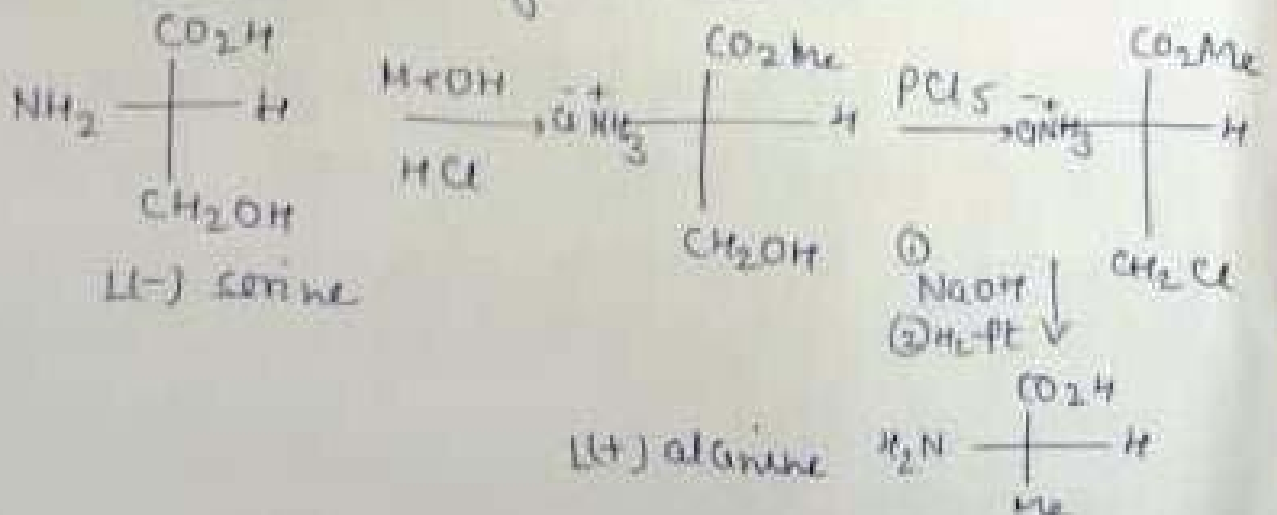
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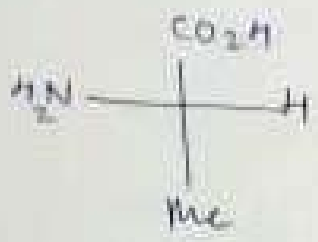
D or L denote relative configuration it has nothing to do with (+) or (-) sign which represents sign of rotation. However D-glyceraldehyde & L-glyceraldehyde are enantiomers. Similarly



enantiomeric relationship

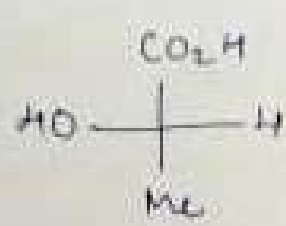
Similarly L(-) serine has been chosen as standard for correlating the configuration of amino acids.



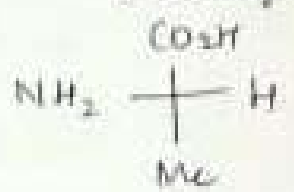
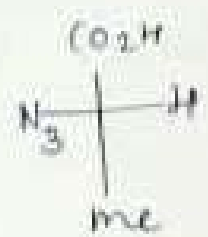
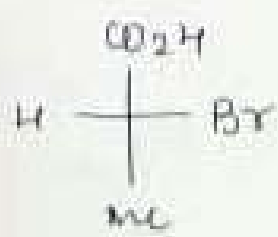


can be correlated to L(+)
Lactic acid

L(+)
alanine



means
inversion

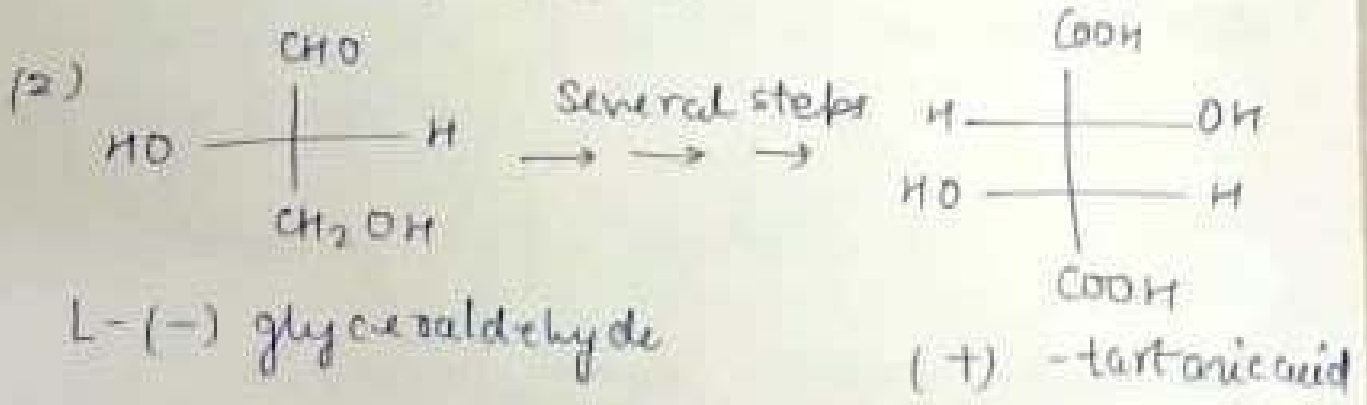
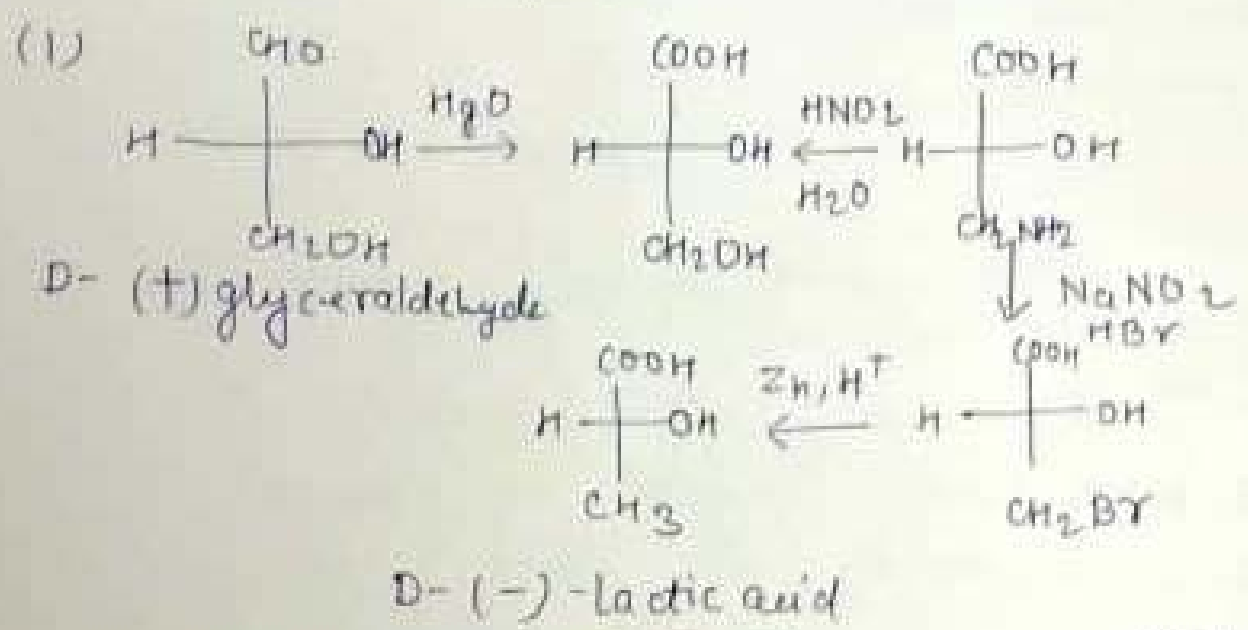


L(+)
alanine

Background of relative configuration
 Until 1951 the absolute configuration of glyceraldehyde was not known whether it has R or S configuration so arbitrarily the ^D(+) glyceraldehyde was assumed to have OH on the right side any compound which could be correlated to it through

reactions without involving breaking at chiral centre or by then no of Walden inversion said to have D-configuration.

For example



When X-ray crystallography gave the absolute configuration of (+) tartaric acid as R,R.

(5)

Since R-R tartaric acid can be synthesised from L(-)-glyceraldehyde so it was confirmed that L(-)-glyceraldehyde was S and had OH on the left side so the assumption was correct.

Once we know whether the compound is R or S that means we know its absolute configuration.

Absolute Configuration R, S

The actual arrangement of the groups in space around a chiral centre with its stereochemical description R or S is called Absolute Configuration.

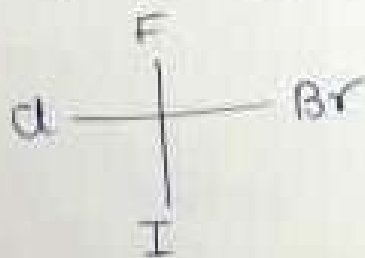
Limitation of D, L - system

- ① Sometimes same compound can be assigned as D and L depending on different series of reactions leading to D & L standard.

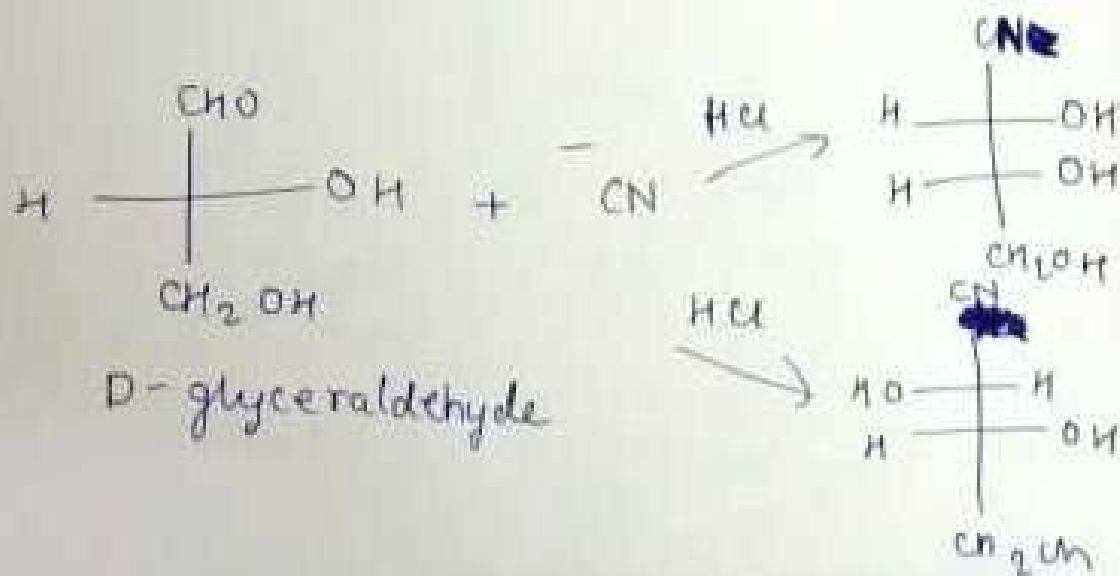
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(2) (+) Tartaric acid may be assigned as L w.r.t. the bottom chiral C & D w.r.t. top chiral C.

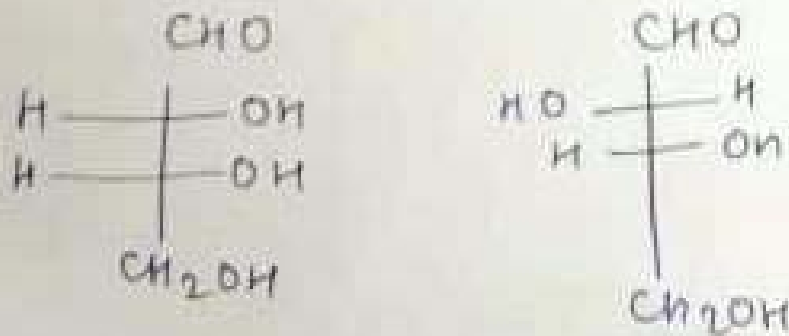
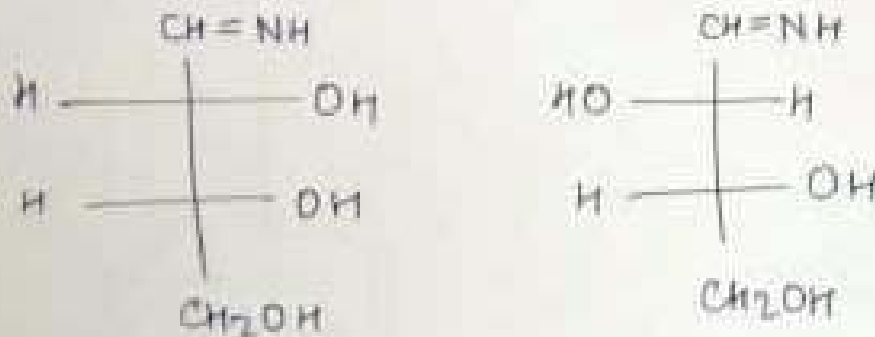
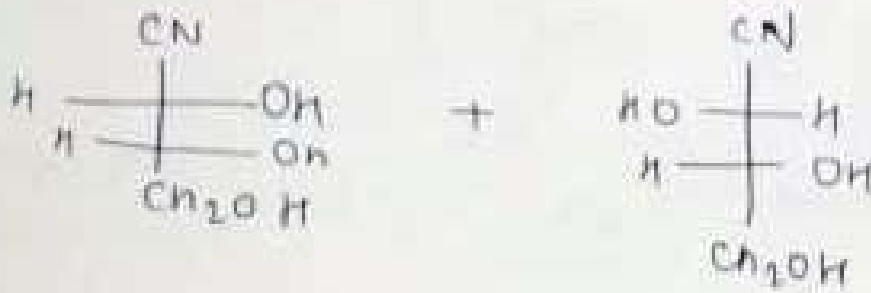
(3) D, L can't be applied on e.g.



(4) In sugars D & L refers to only last chiral C configuration. On other chiral C of the chain can't be known.



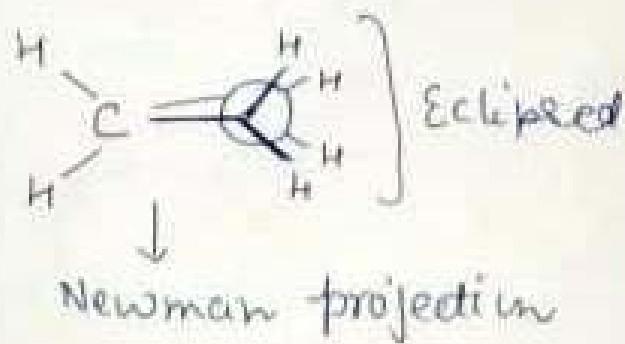
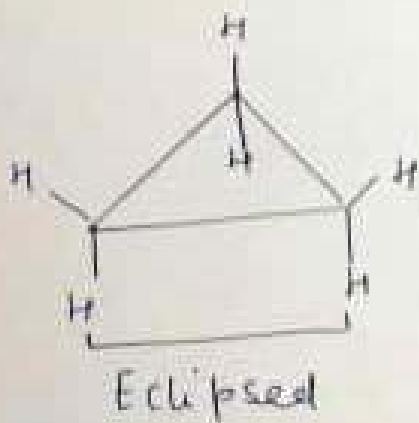
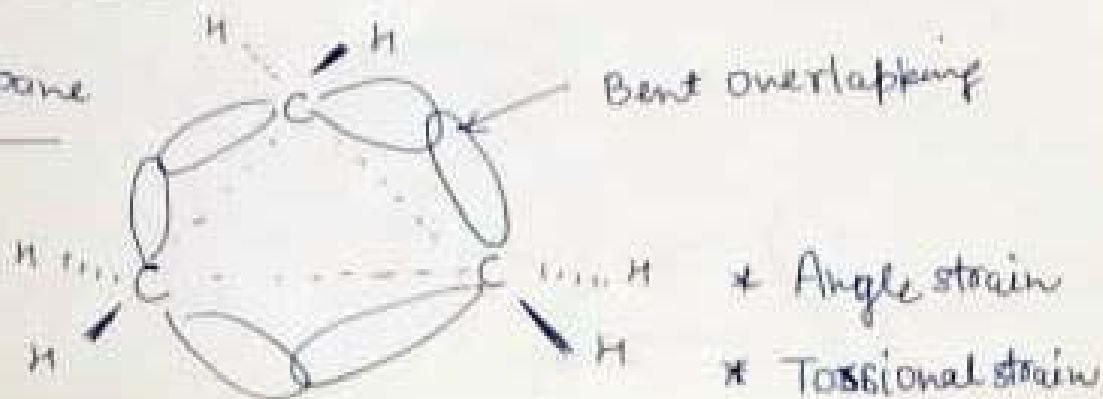
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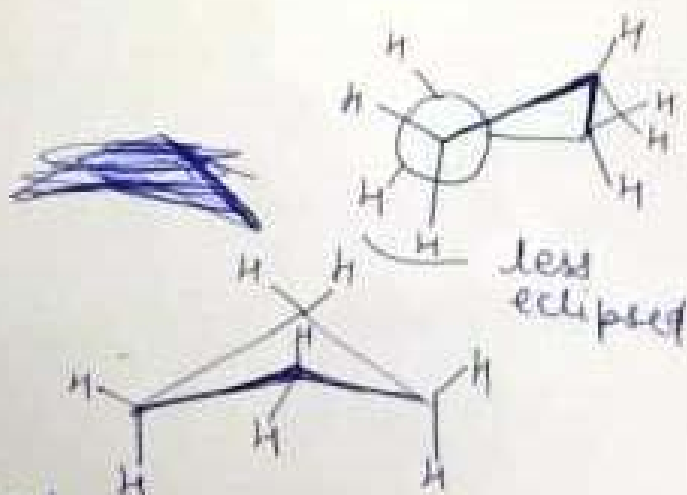
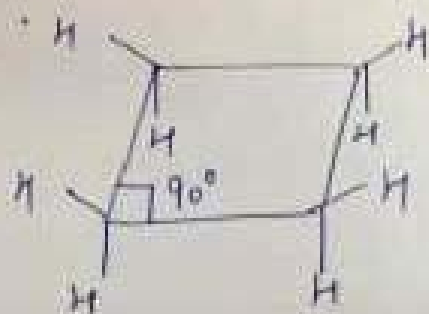
Chain elongation in sugar
without disturbing last Chiral centre
so both are D-sugars.

Conformation of cyclic hydrocarbon

Cyclopropane

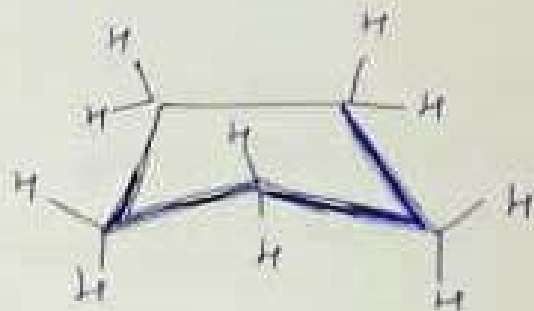
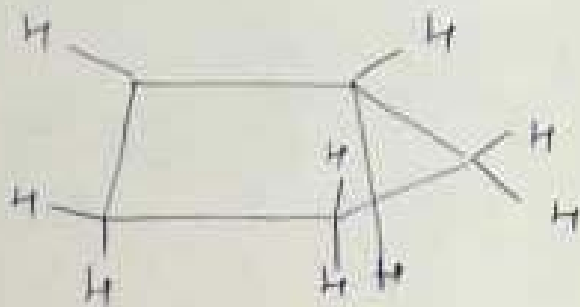


Cyclobutane

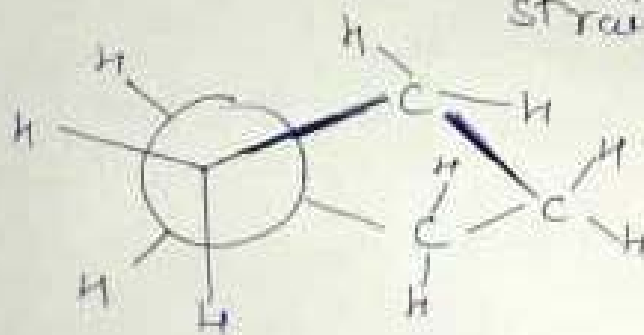


Puckered

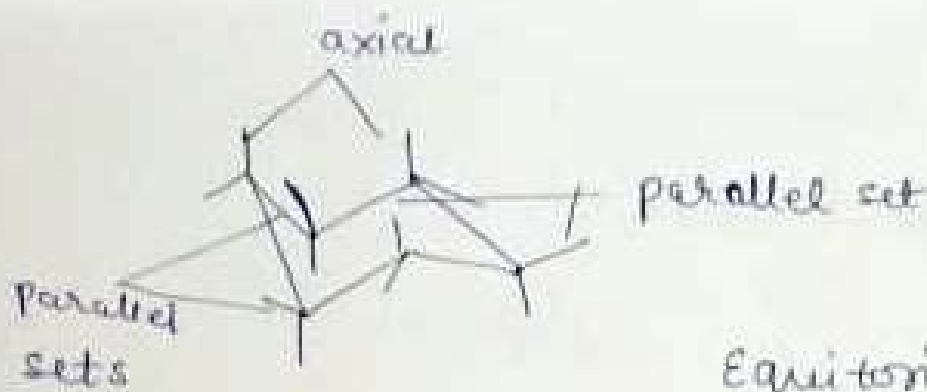
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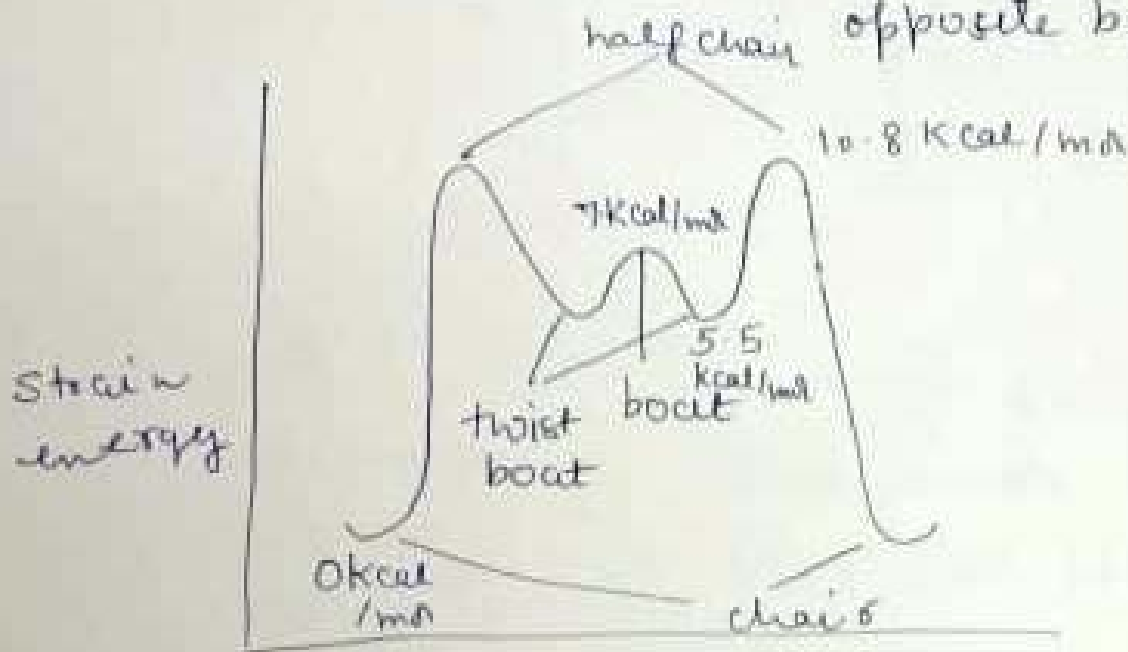
(Envelope conformation
Relieved torsional
strain)



Stability of cyclohexane was explained by Sachse & Mohr on the basis of stable non planar, puckered conformations which are strain free.



Equatorial bonds are parallel to opposite bonds.



Flat cyclohexane > 20 kcal/mol

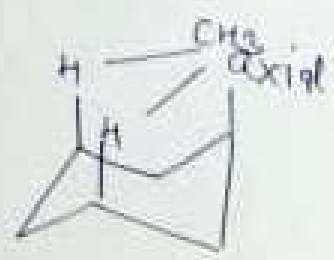
Ring flipping
or ring inversion
or chair chair
interconversion

Axial substituents become equatorial



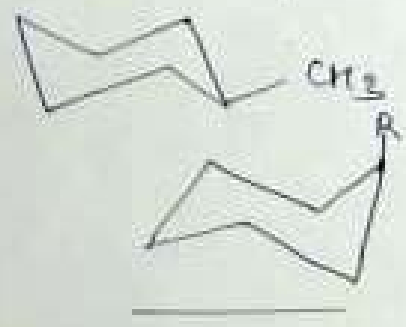
Conformational change to
homomers

(11)



1, 3 - diaxial interaction
less stable

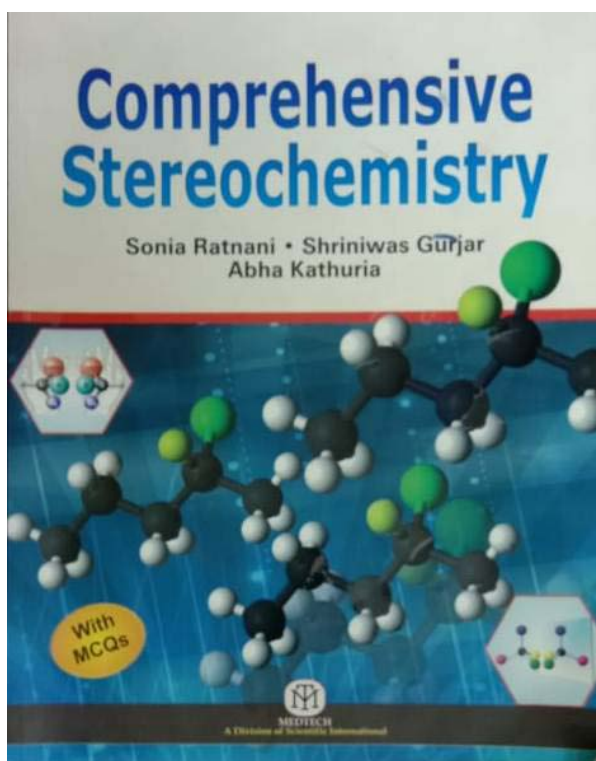
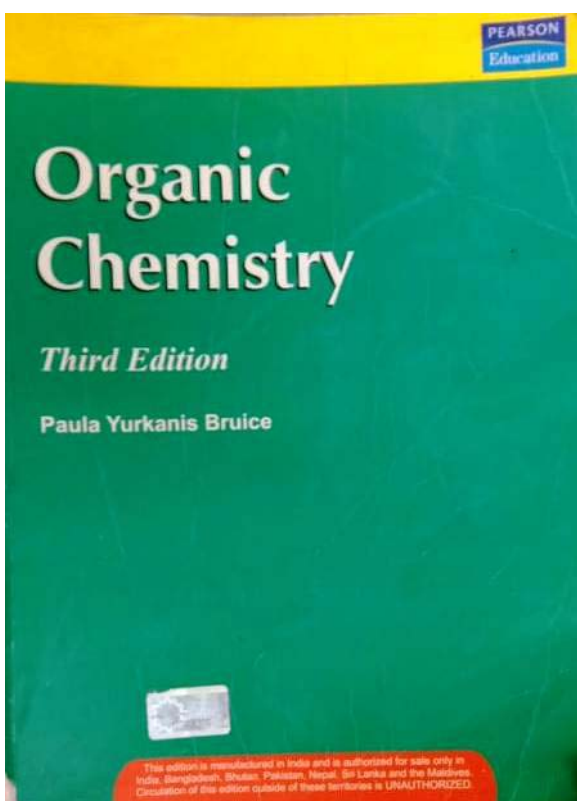
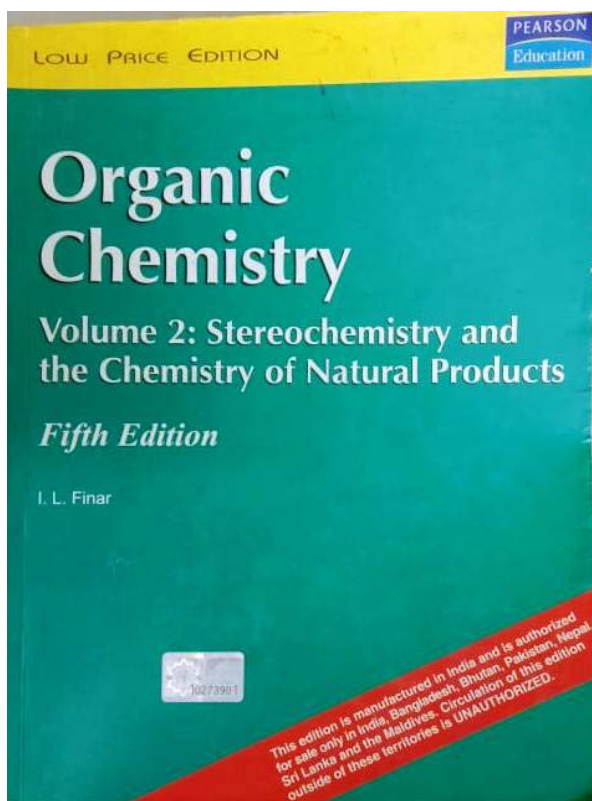
↕ ring flip



No 1, 3 - diaxial
interaction
more stable

R - tertiary butyl group
is so large that exists almost
entirely as equatorial position.

REFERENCES:



Recommended further study:

Comprehensive Stereochemistry by Sonia Ratnani, Shrinivas Gurjar and Abha Kathuria