BHARATHIDASAN UNIVERSITY

Tiruchirappalli-620024

Tamil Nadu, India

Programme: M.Sc. Chemistry

Course title: Organic Chemistry-I

Course Code: CHE611CC

UNIT-II

Stereochemistry and Conformation Analysis

Dr. K. Srinivasan

Professor, School of Chemistry

Chirality

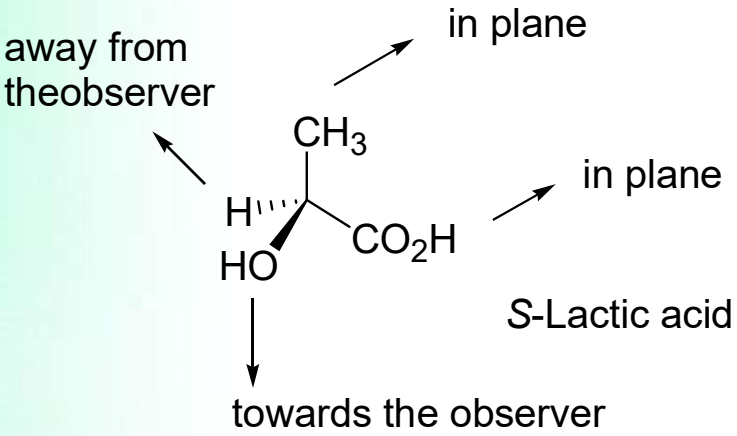
The property of a molecule being non-superimposable on its mirror image (enantiomerism) (σ, i or simply S_n should be absent).

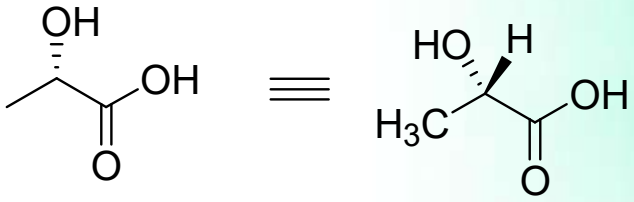
Configuration and Conformation

Configuration: Three dimensional arrangement of atoms or groups of a stereoisomer (*D, L, R, S, E, Z, meso, dl, erythro, threo, P, M*)

Conformations: Various structures of a stereoisomer arising from rotation about a carbon-carbon single bond (or other changes) (eclipsed, staggered, chair, boat, twist-boat, half-chair, envelope)

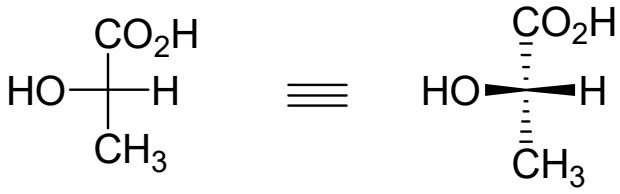
How to write molecules in three dimension?



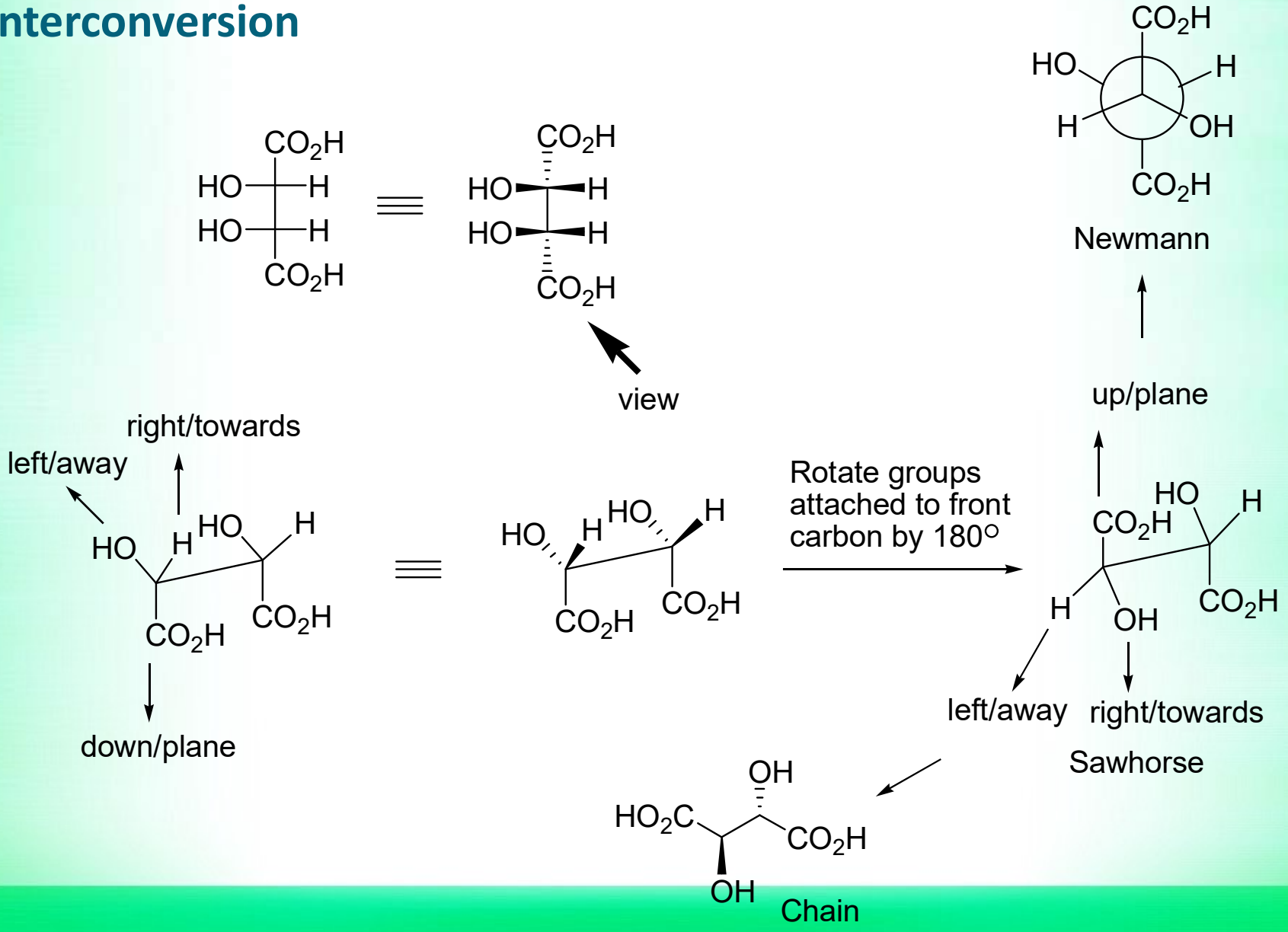


Representing 3D structures in 2D: Projection formulas

Fischer:



Fischer, Sawhorse, Newmann and Chain formulas & their interconversion



Assigning configuration to stereocenters:

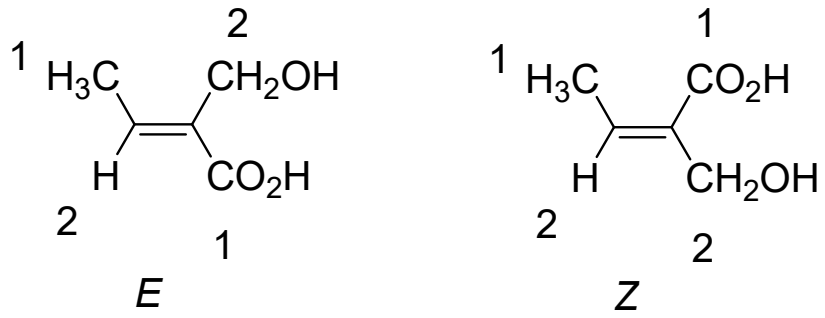
CIP rules:

1) An atom with higher atomic number gets higher priority (in case of isotopes, an atom with higher mass number gets higher priority).

2) If there is a tie, the atomic numbers of successive atoms are considered until a difference is found.

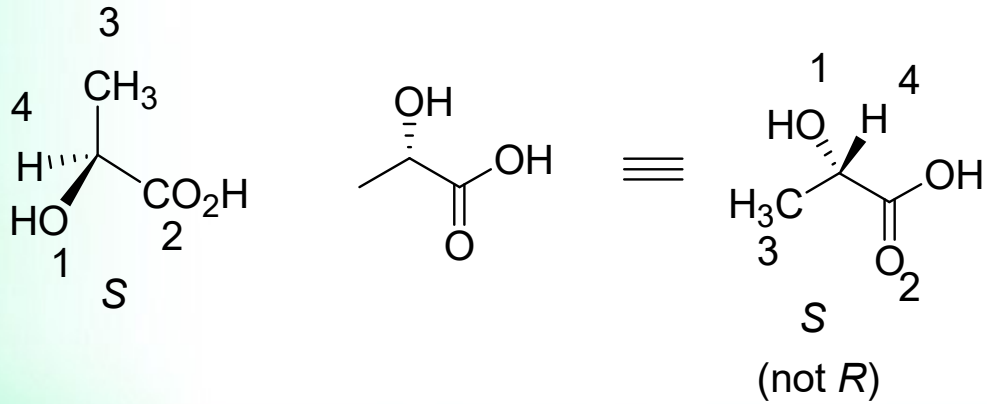
3) An atom attached to double/triple bond is counted as two/three atoms.

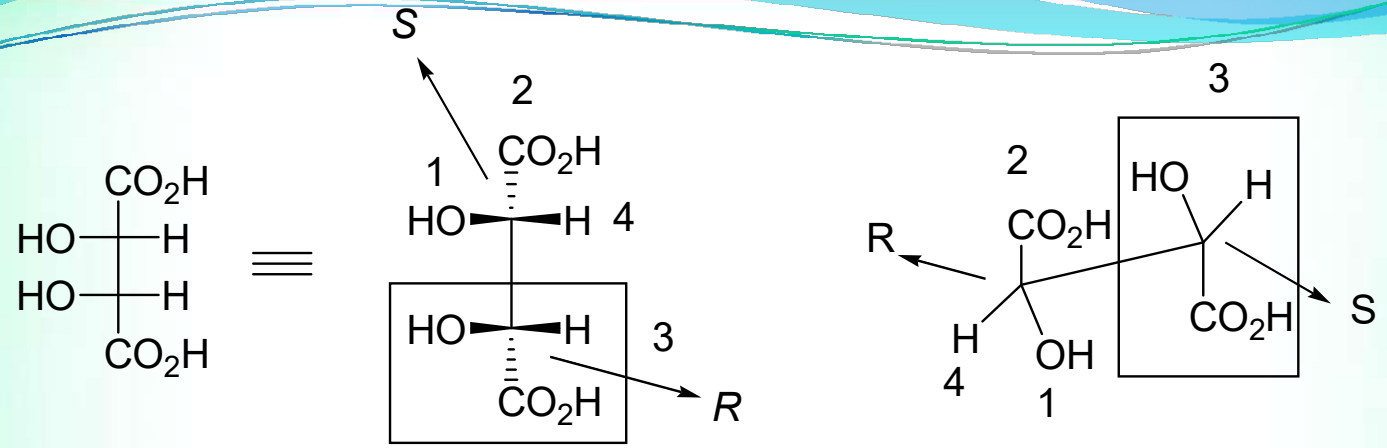
E/Z: (for alkenes) (old: *cis/trans*)



R/S: (old: *D/L, Ref: D-glyceraldehyde*)

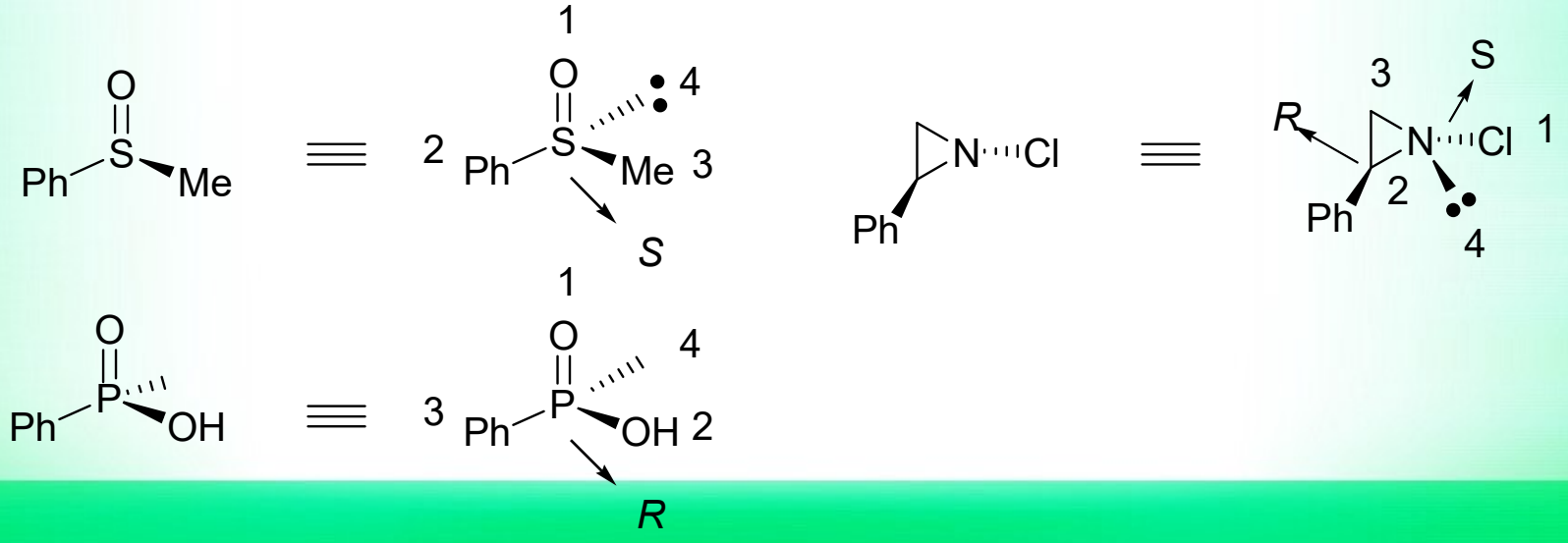
(The lowest priority group should be pointing away from us)



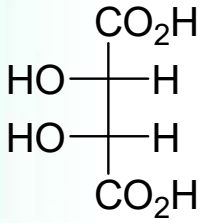


Note: A Newmann formula may be converted into sawhorse formula before assigning configuration.

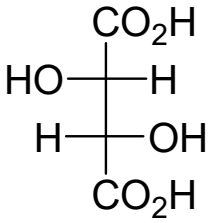
Non-carbon stereocenters:



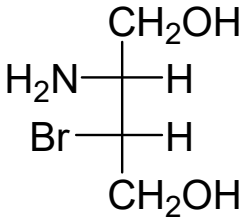
Meso/dl/erythro/threo:



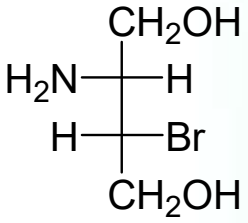
meso



dl

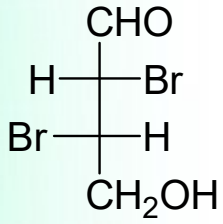


erythro

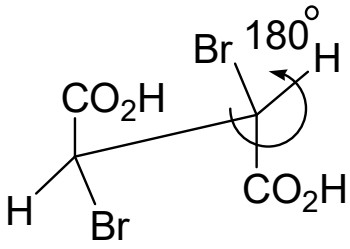


threo

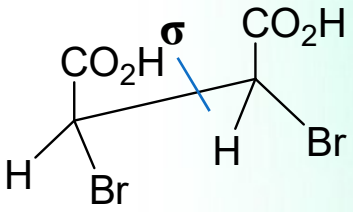
Examples:



threo

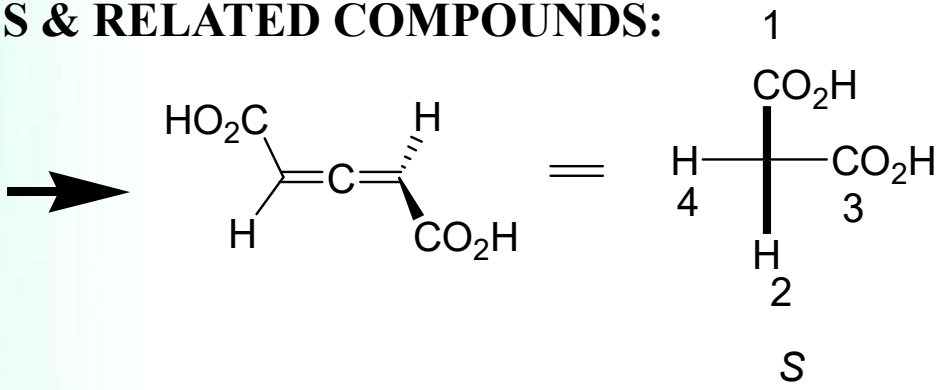


meso



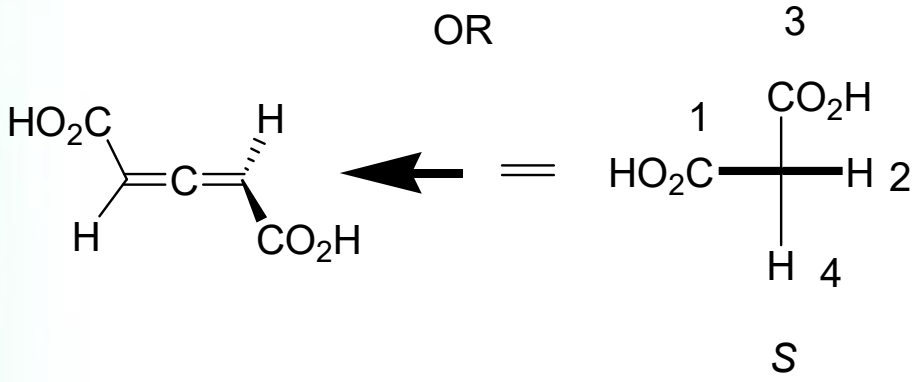
For compounds devoid of stereocenters:

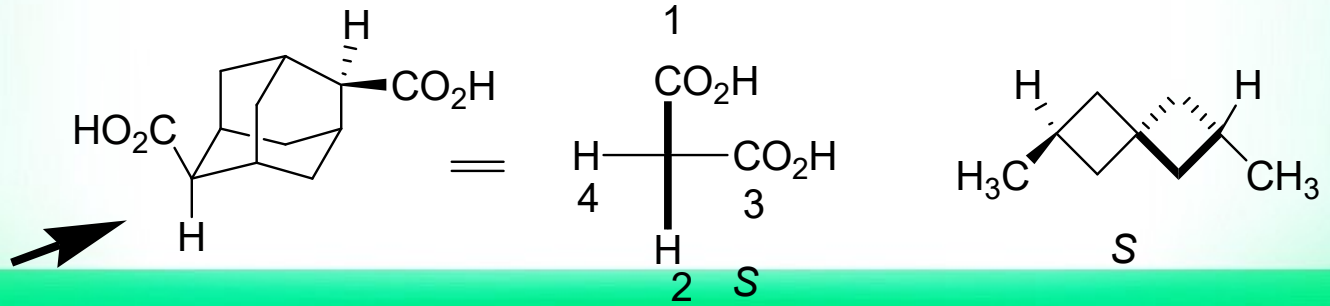
ALLENES & RELATED COMPOUNDS:



Allenes = elongated tetrahedron
Point group: D_2d
possess less symmetry
Axial chirality

OR

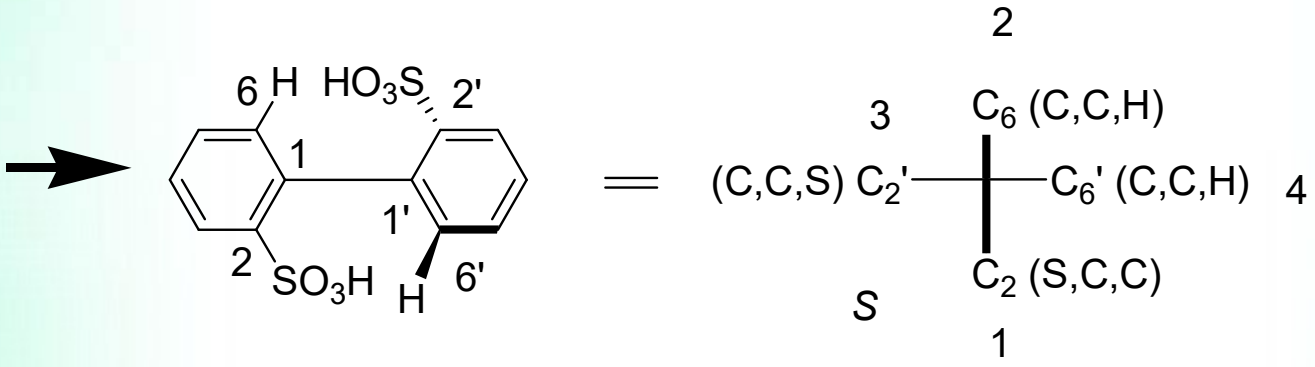


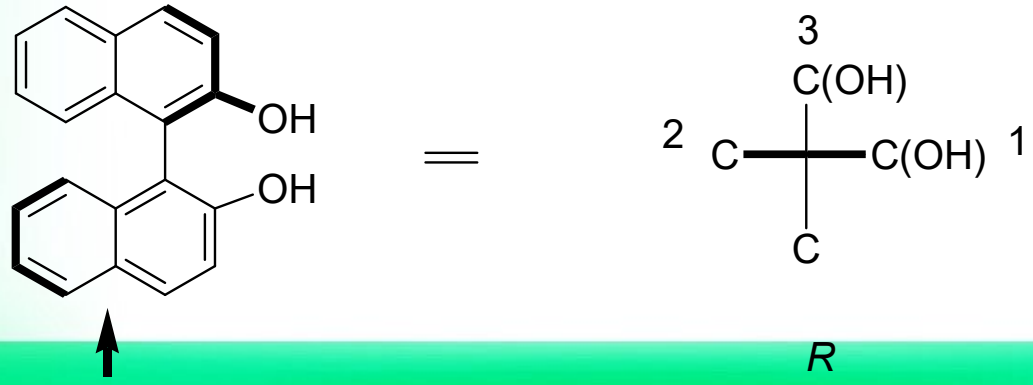


BIPHENYLS:

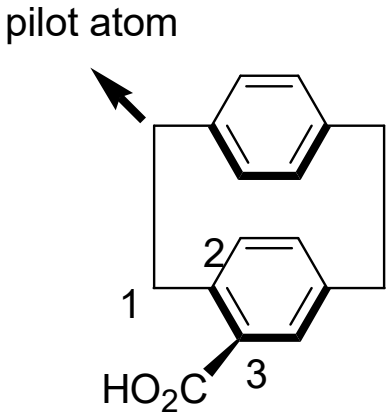
To be chiral, *o*-substituents should be bulky enough (sum of van der Waals radii of *o*-substituents > 0.29 nm)

Atropisomerism; axial chirality





Planar chirality:

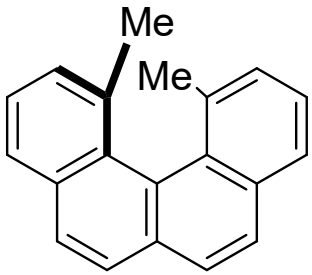


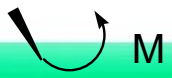
cyclophane

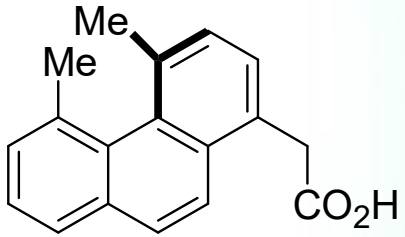
trans-cyclooctene

E

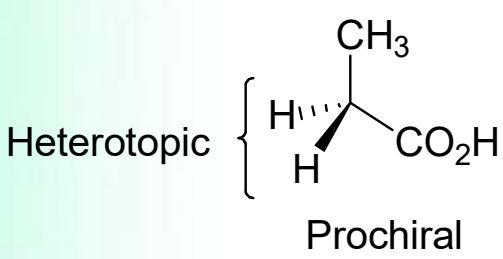
Helical chirality (a kind of axial chirality):

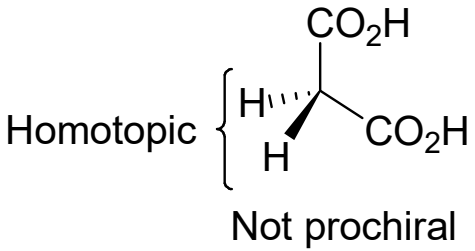


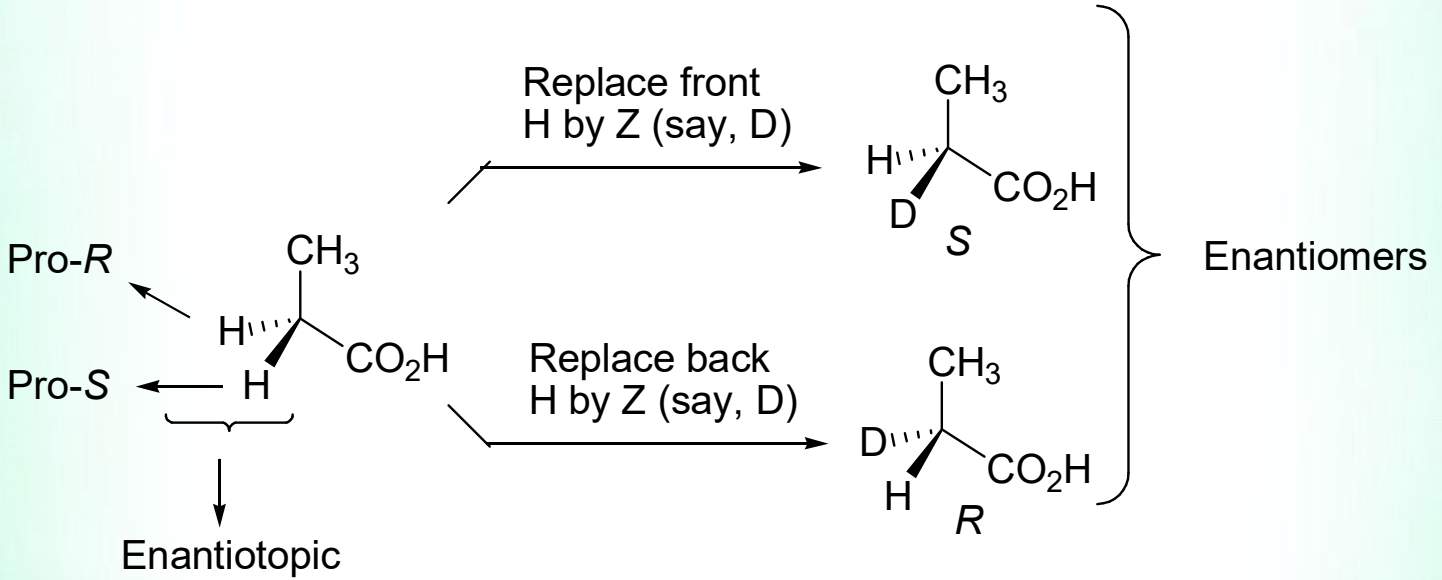


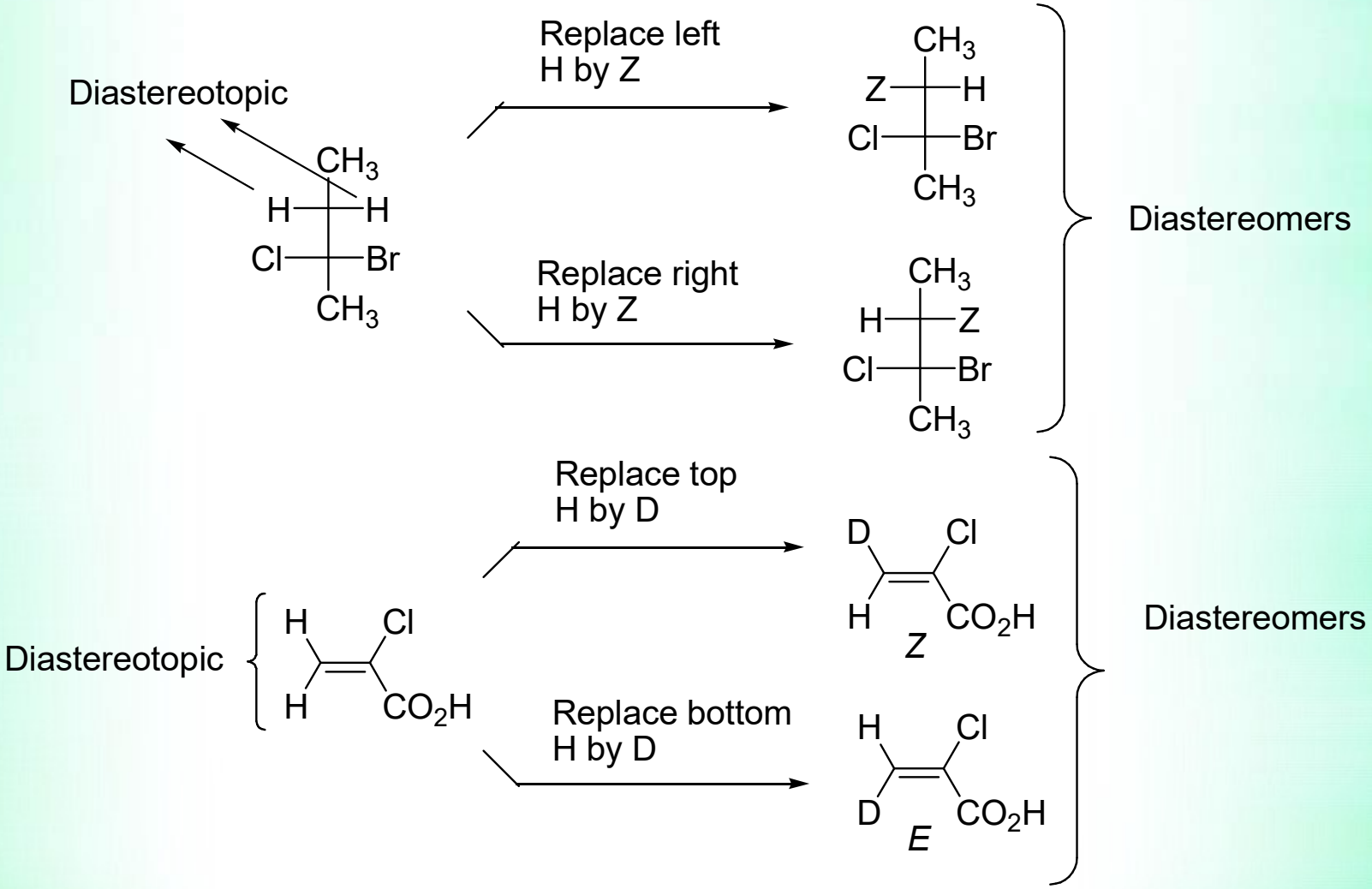


Prochirality and Topicity:

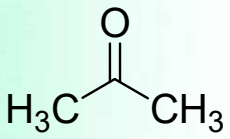




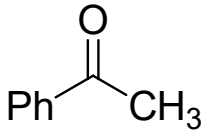



Diastereotopic
CH3
H
H
Cl
Br
CH3
Replace left
H by Z
Replace right
H by Z
CH3
Z
H
Cl
Br
CH3
CH3
H
Z
Cl
Br
CH3
Diastereomers
Diastereotopic
H
Cl
H
CO2H
Replace top
H by D
Replace bottom
H by D
D
Cl
H
CO2H
Z
H
Cl
D
CO2H
E
Diastereomers

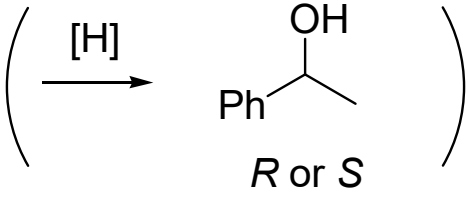
Faces (sp^2 carbons):



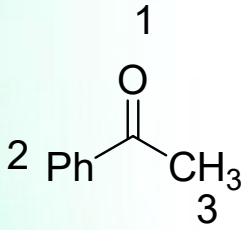
Not prochiral



prochiral



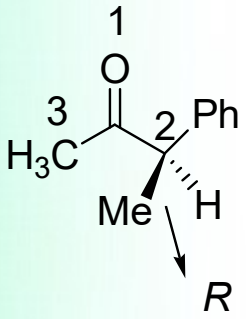
Enantiomers



Front face: *Si* face

Back face: *Re* face

} Enantitopic face

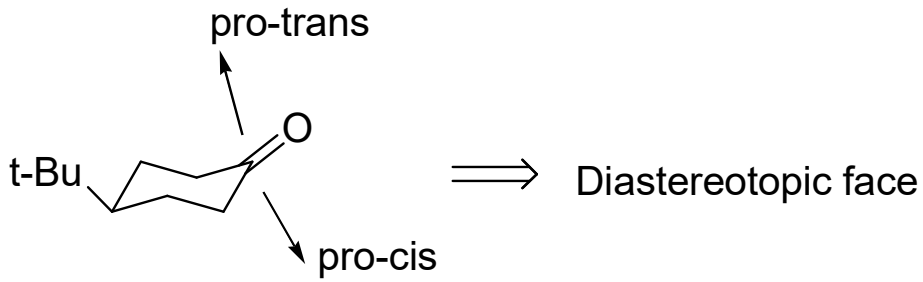


Front face: *ReR* face

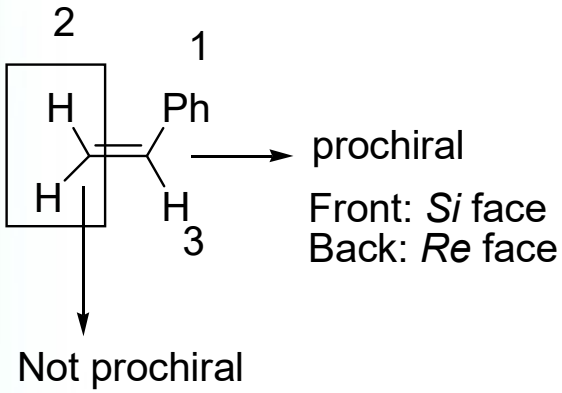
Back face: *SiS* face

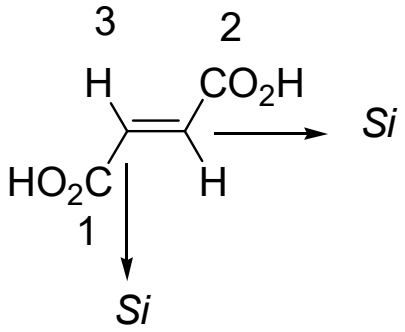
} Diastereotopic face

(Reduction would give diastereomers)



Alkenes:





Front: *Si*-*Si* face or simply *Si* face


THANK YOU