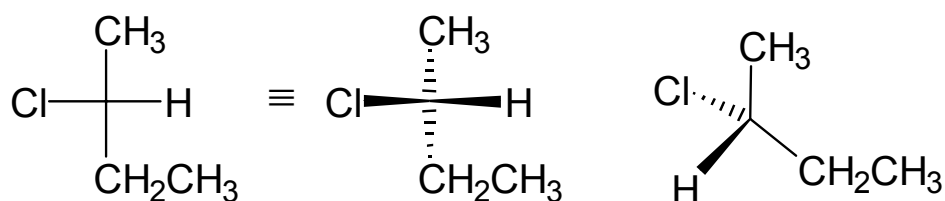
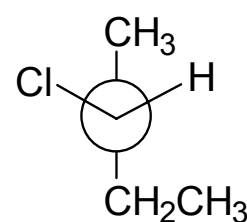


Chap. 2 Stereochemistry

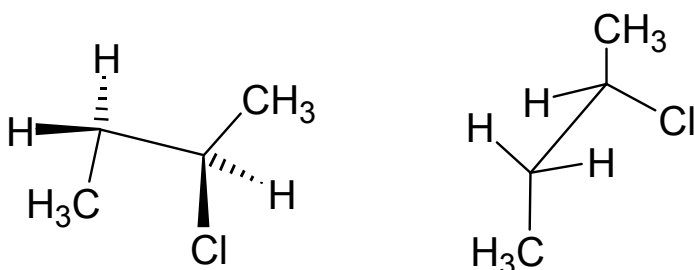
§ Structural representations that convey 3-D information



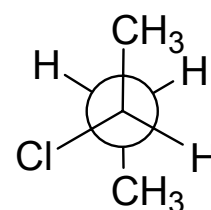
Fischer projection.



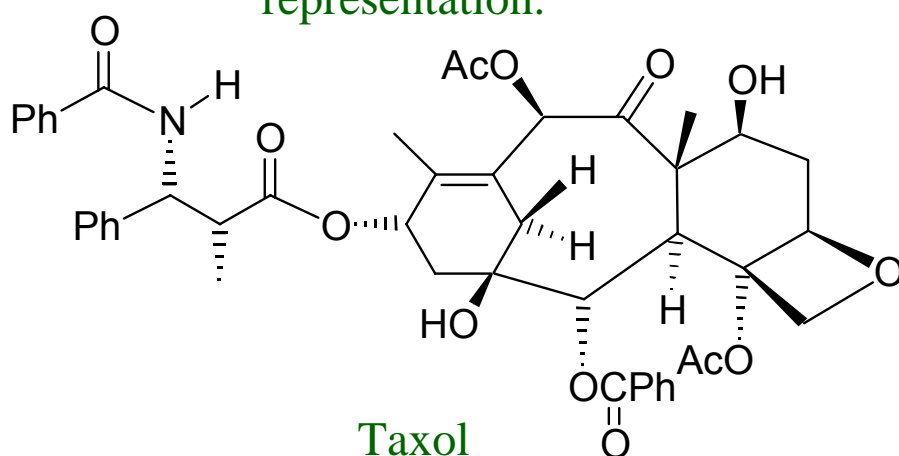
Ball & Stick



Sawhorse representation.



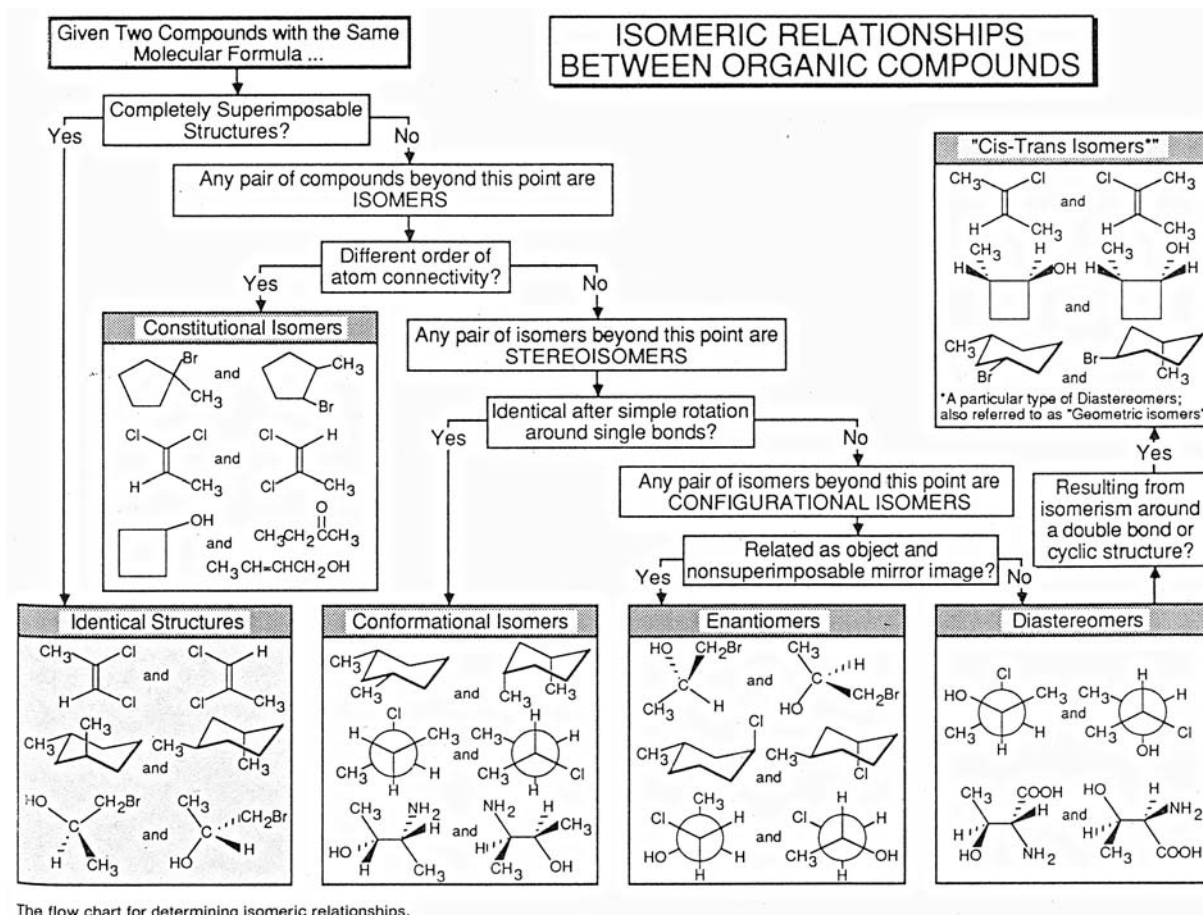
Newman projection



Taxol

§ Isomerism

Isomers : Different compounds that have the same molecular formula.



Conformational Isomer : Stereoisomers that are superimposable by rotation around a single bond.

Enantiomer : Isomers that are non-superimposable mirror images to each other. → chiral

Diastereomer : Isomers that are non-superimposable, not mirror images.

- Cis-trans isomer (geometric isomer)
configurational isomers differ around a double bond or cyclic structure.

§ Symmetric, Asymmetric, Dissymmetric and Nondissymmetric molecules.

— Symmetry operation

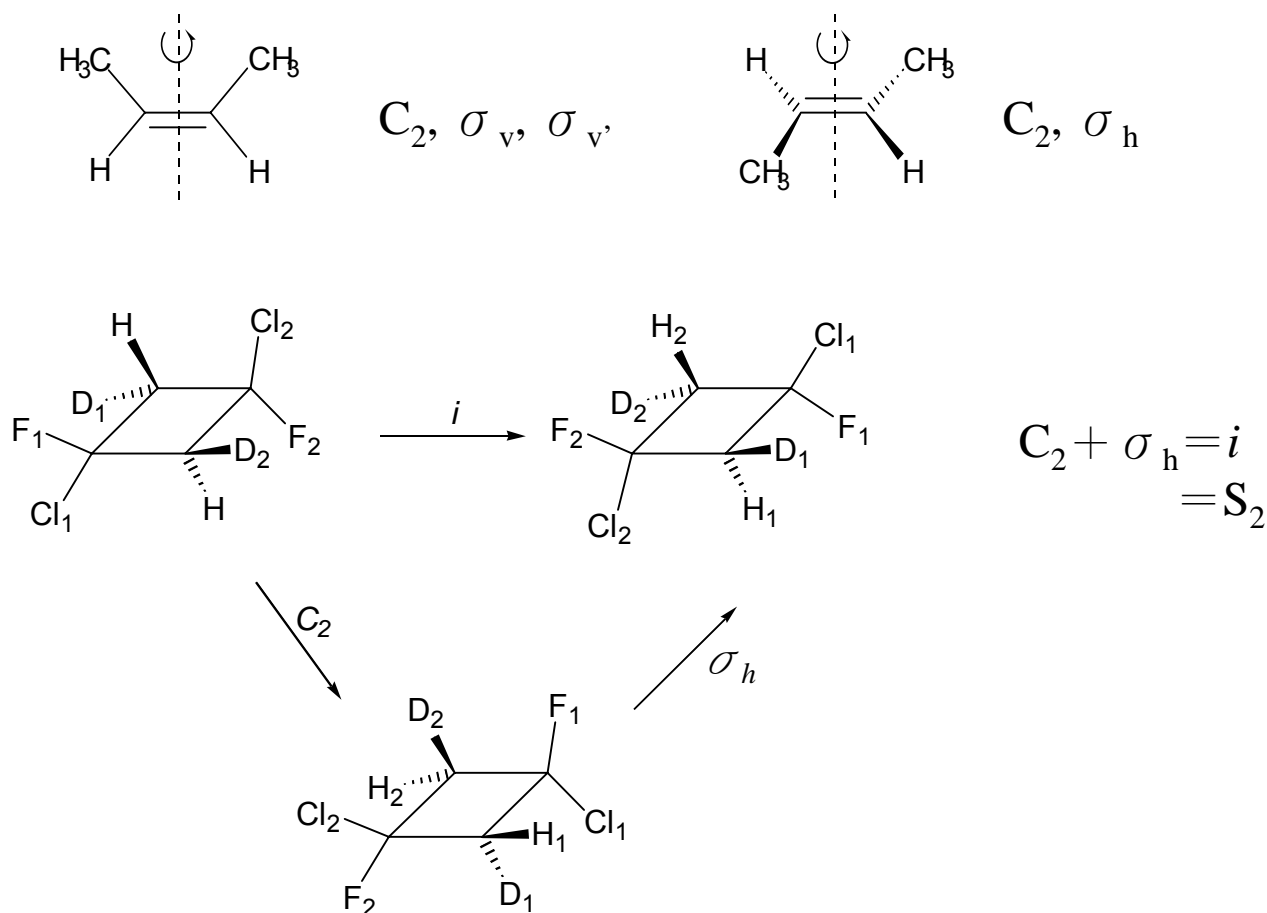
reflection in a plane (對稱面) : σ

inversion through a center (對稱中心) : i

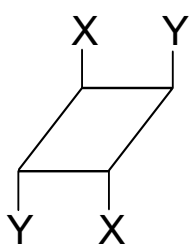
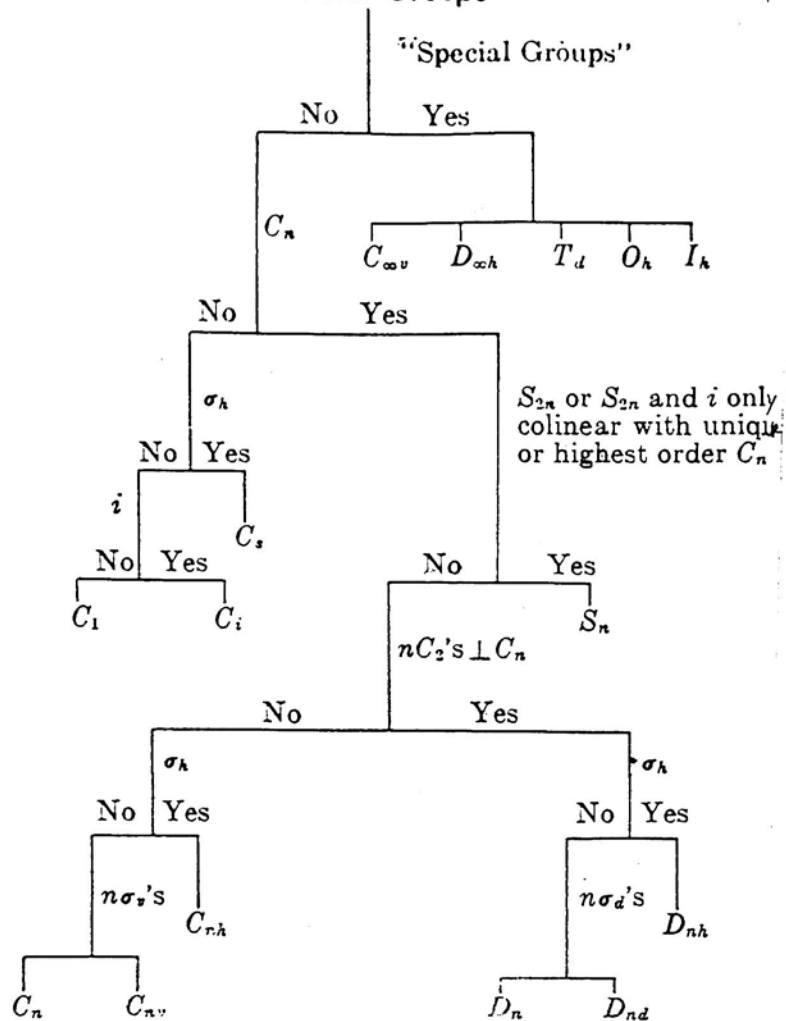
rotation about a proper axis (對稱軸) : C_n , for $360^\circ/n$

rotation about an improper axis (更迭對稱軸) : S_n

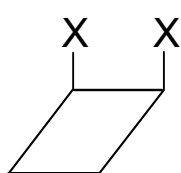
(= rotation about an axis, followed by reflection through a plane perpendicular to the axis)



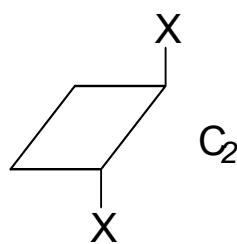
A Flow Chart for Classifying Molecular Symmetry I Point Groups



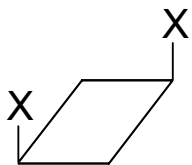
C_i



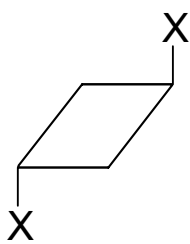
C_s



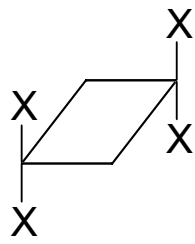
C_2



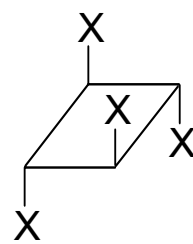
C_{2v}



C_{2h}



D_{2h}



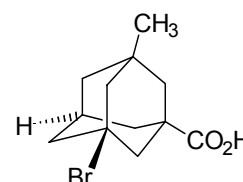
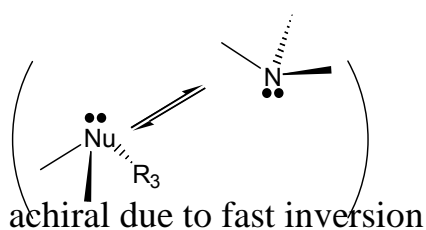
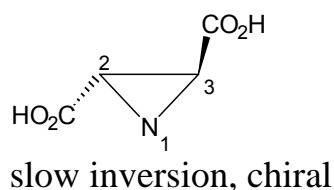
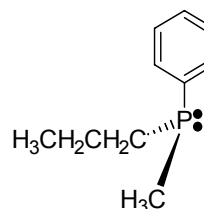
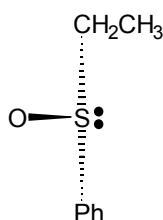
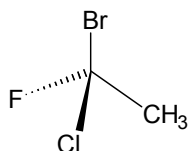
D_{2d}

Chirality : Molecules that are not superimposable with their mirror image \Rightarrow chiral. (enantiomeric)

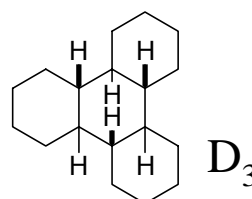
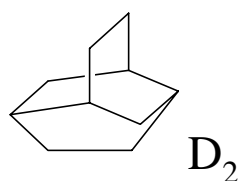
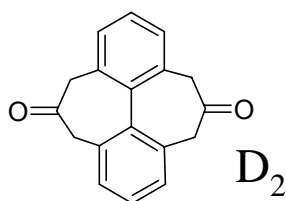
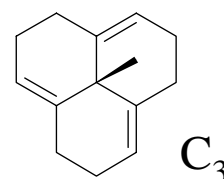
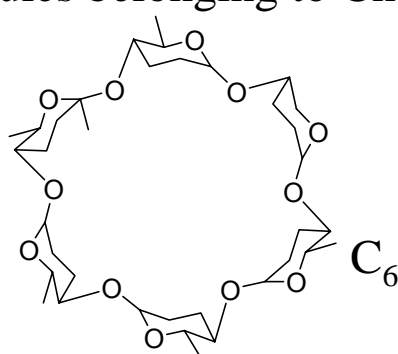
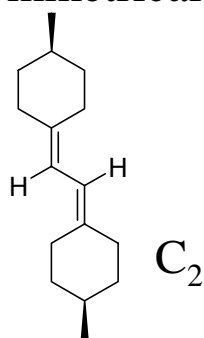
\rightarrow dissymmetric molecules : molecules without S_n axis (including $n=1$). Dissymmetric molecules are chiral, chiral molecules are dissymmetric.

Dissymmetrical with a chiral center (asymmetric):

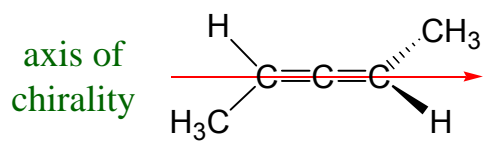
\rightarrow asymmetric molecules : molecules without any symmetry element, except C_1 .



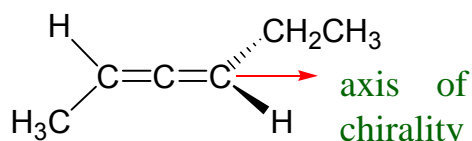
Dissymmetrical molecules belonging to C_n or D_n group



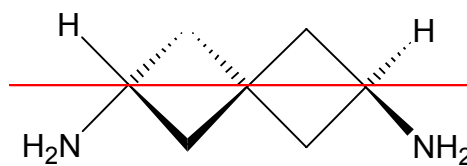
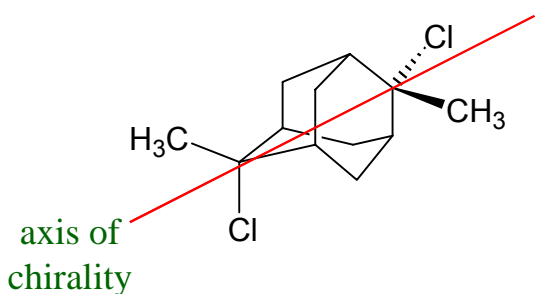
chirality along an axis



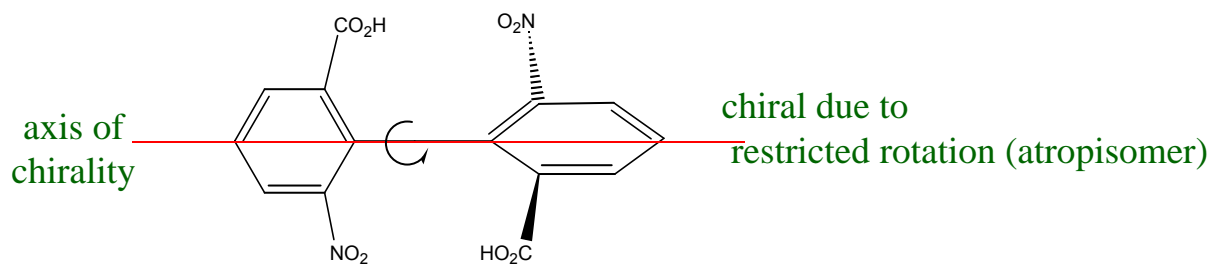
has C_2 , chiral, dissymmetric



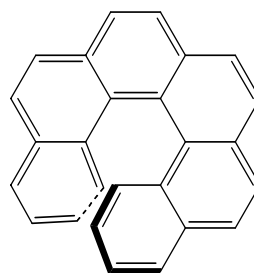
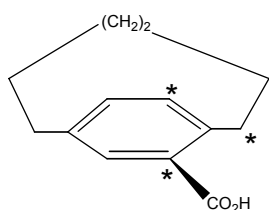
C_1



chiral

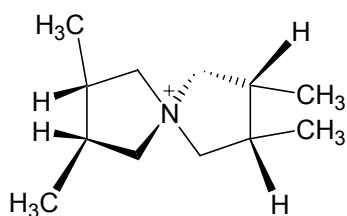


chirality about a plane

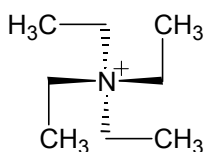


Non-dissymmetric molecules : having C_i , C_s , C_{nv} , C_{nh} , D_{nh} , D_{nd} , T_d , O_h or S_n symmetry.

($S_1 = \sigma$, $S_2 = i$)



achiral



with S_4 symmetry, achiral

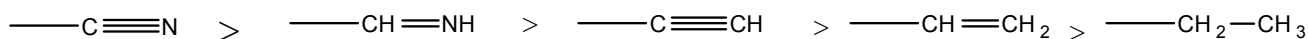
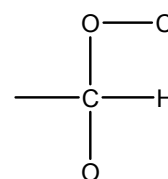
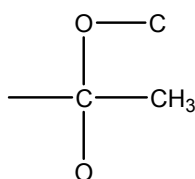
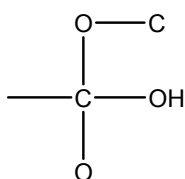
§ Designation of Molecular Configuration (Cahn-Ingold-Prelog convention)

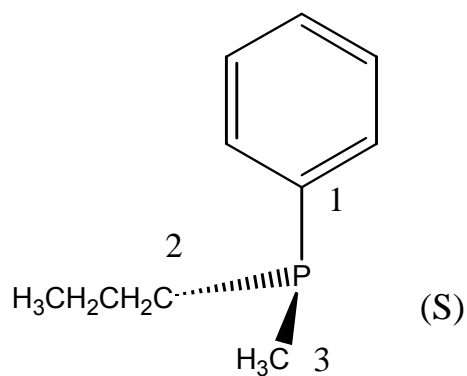
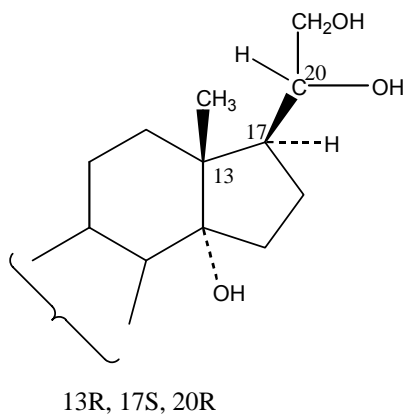
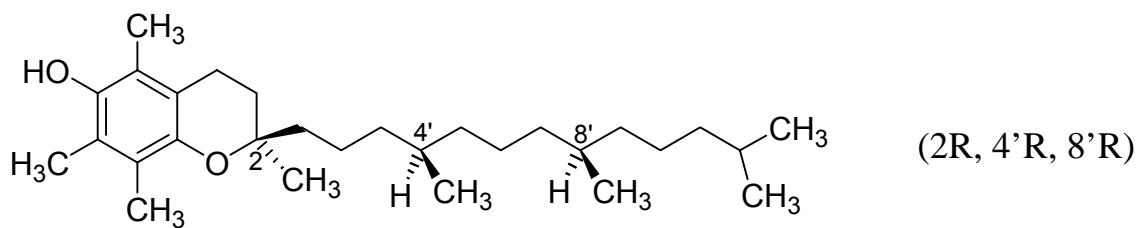
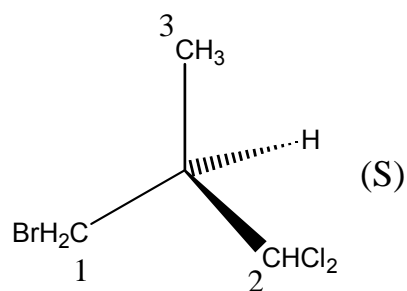
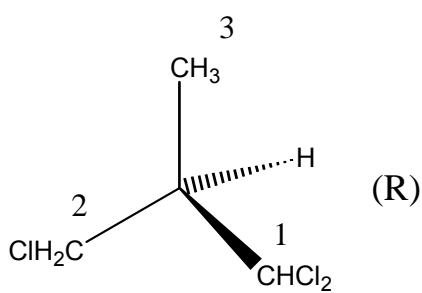
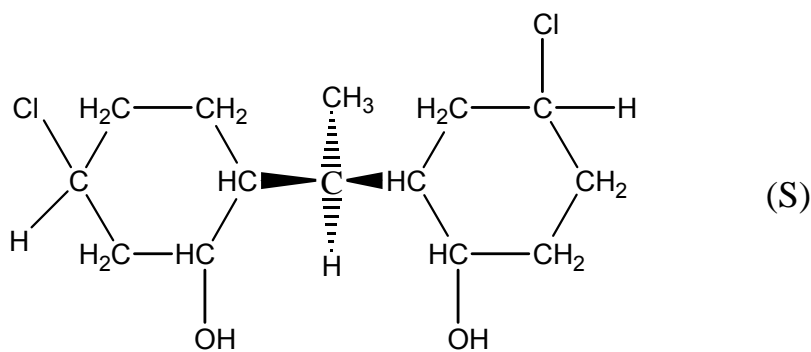
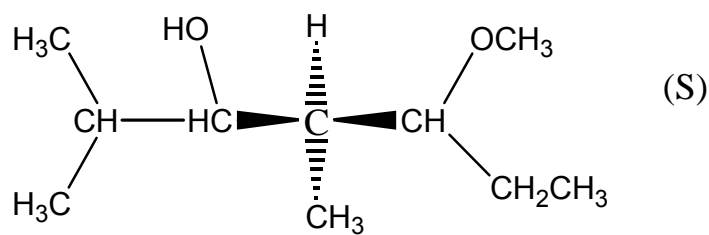
Chirality about a point

1. Determine the priority of four groups.
2. With least priority group pointing away, determine the direction of 1→2→3 priority, clockwise →R, counterclockwise →S

Criteria for priority

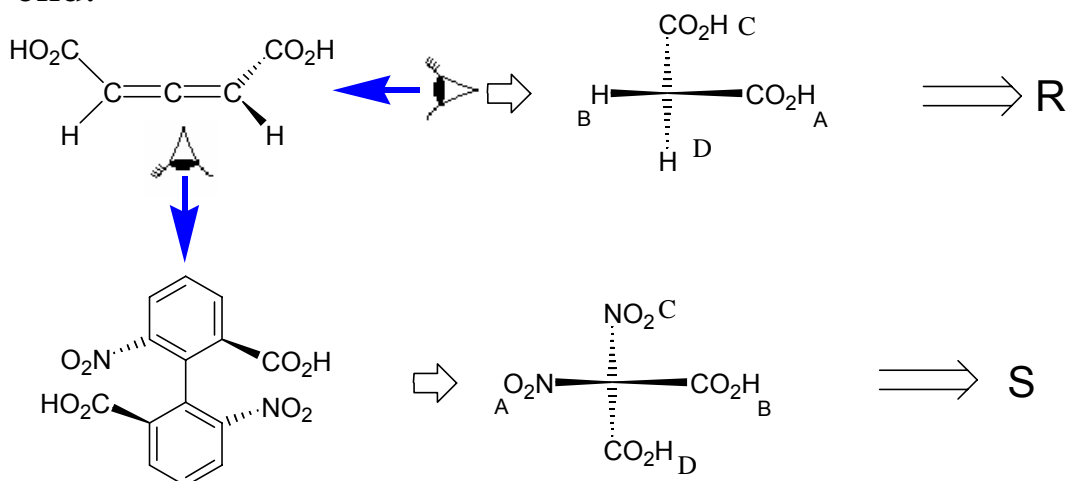
1. higher atomic number ⇒ higher priority
Br > Cl > C > H ...
2. if the two have same atomic number, count substituent next to it.
3. double bond counted twice, triple bond counted three times for both ends
4. tricoordinate : a group of atomic number of "0" assigned for the long pair



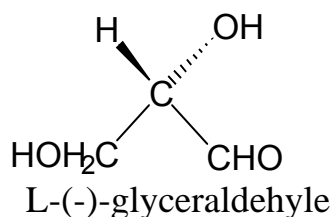
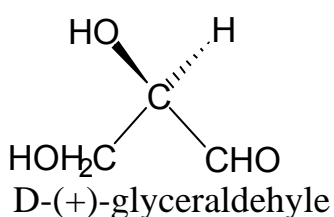


Chirality about an axis

Start from the near end to determine the priority, then to the far end.

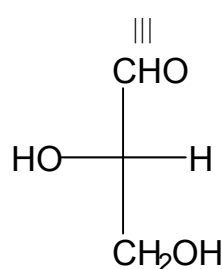
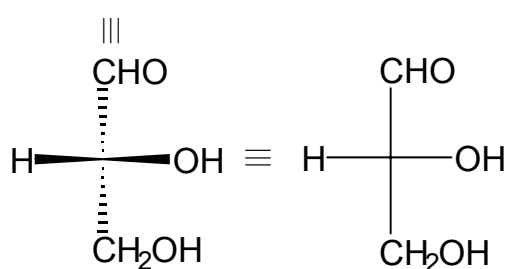


Fischer Projection, popular in sugar chemistry, relate the config. at an assym. center to that of (+)glyceraldehyde, the standard

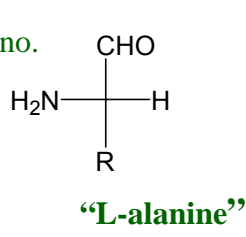
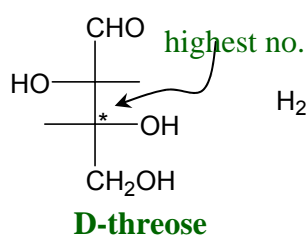
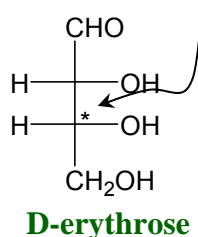


Rules :

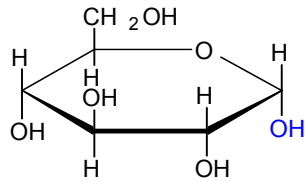
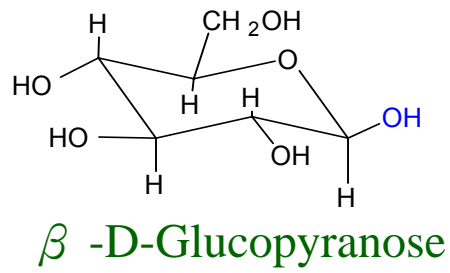
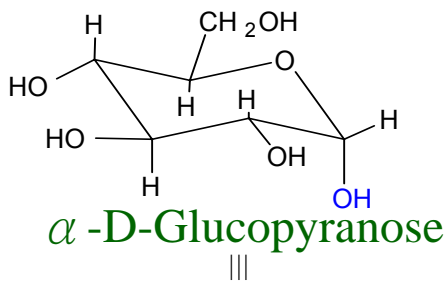
1. most highly oxidized carbon on top.
2. vertical bonds point backward
3. horizontal bonds point forward



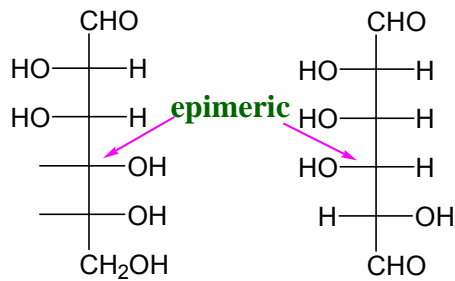
Compare the configuration around an asymm. center, and assign D · L



There is no direct correlation between R · S and D · L, configuration

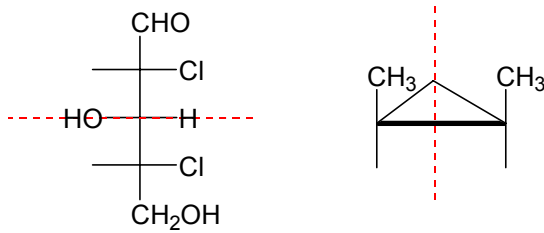


epi



epimers

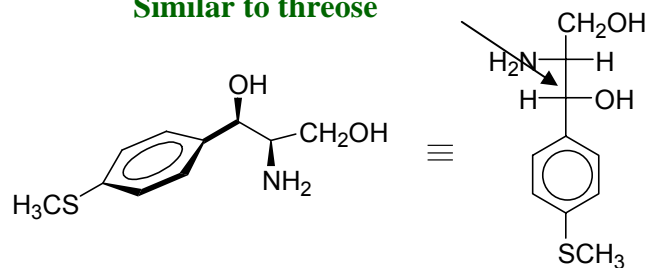
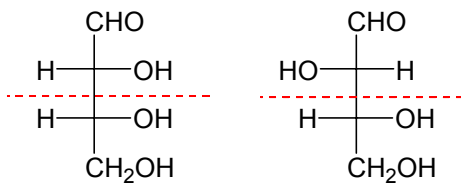
meso



erythro-

threo-

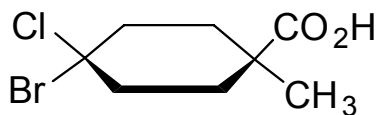
Similar to threose



D-Erythrose D-Threose

Threo-(1R,2R)-2-amino-

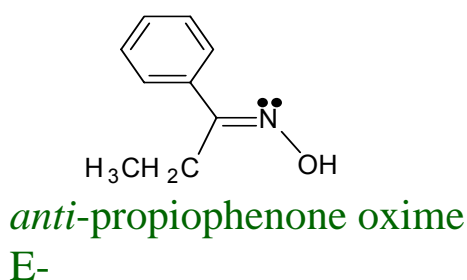
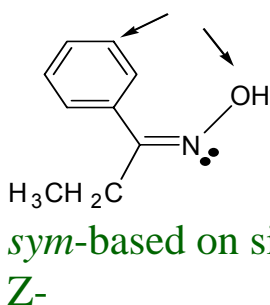
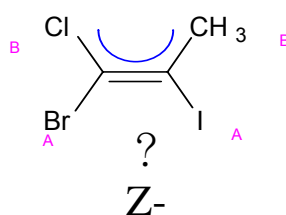
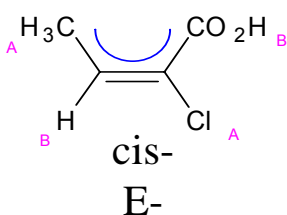
Other Stereochemical Nomenclature



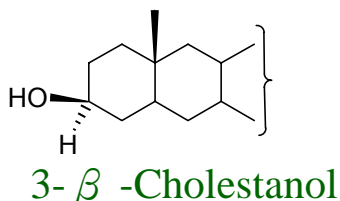
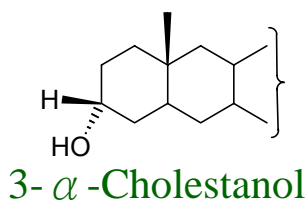
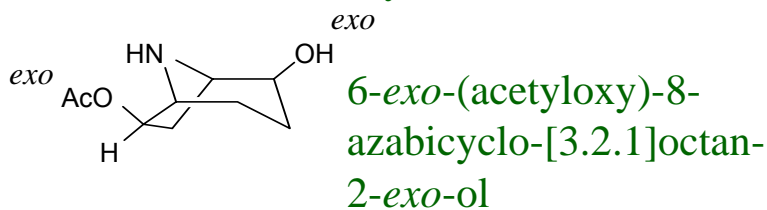
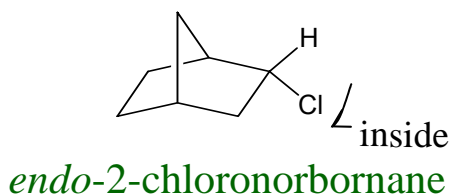
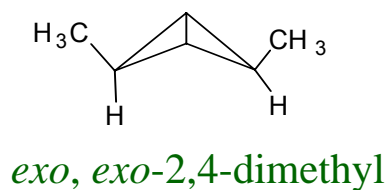
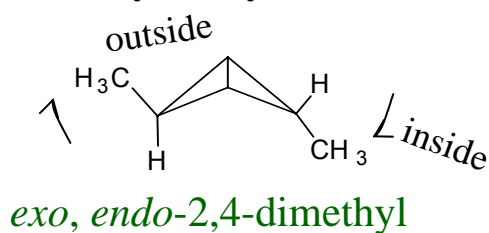
close a reference

t-4-bromo-*c*-4-chloro-1-methyl-*r*-cyclohexanecarboxylic acid

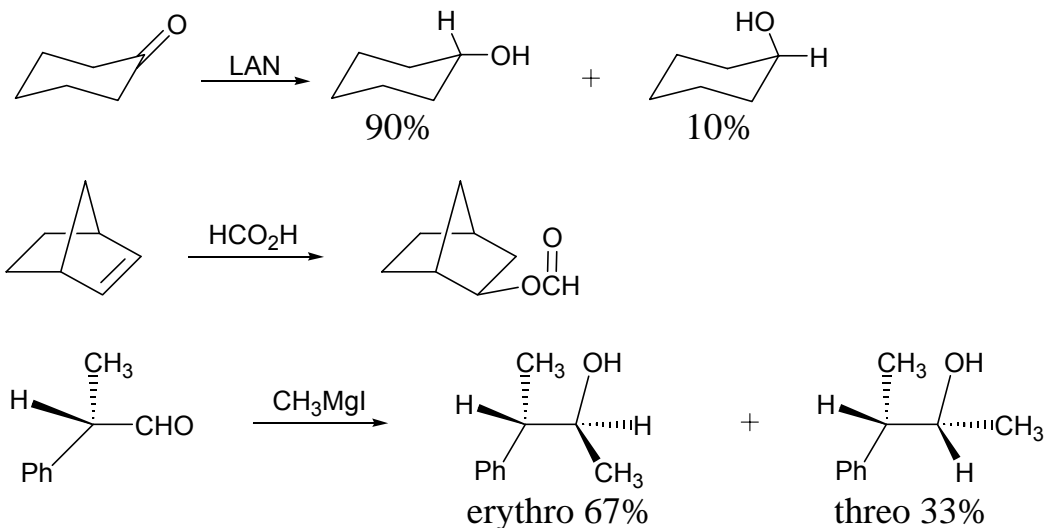
Alkene cis,trans based on the shape of the molecules E, Z based on priority rule used for R,S.



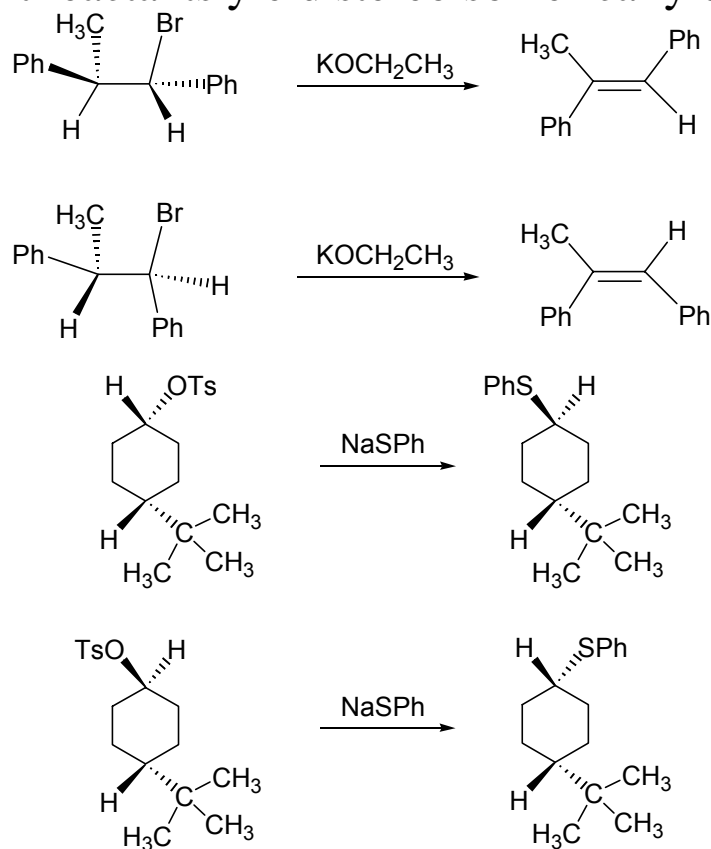
For bicyclo systems : *exo*-, *endo*-,



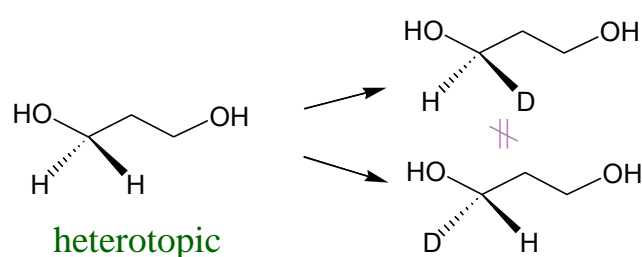
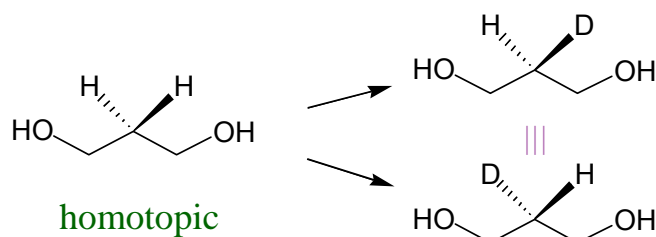
Stereoselective Reaction : A reaction in which one stereoisomer (or pair of enantiomer) is formed or destroyed at greater rate or to a greater extent than other possible stereoisomer.



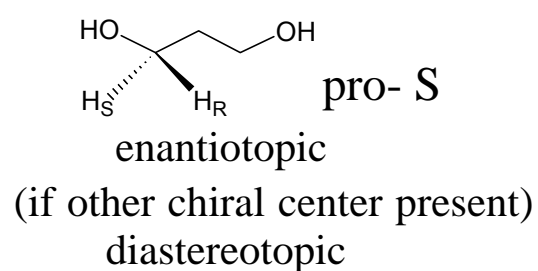
Stereospecific Reaction : A reaction in which stereoisomerically different reactants yield stereoisomerically different products.



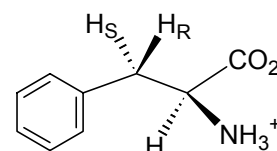
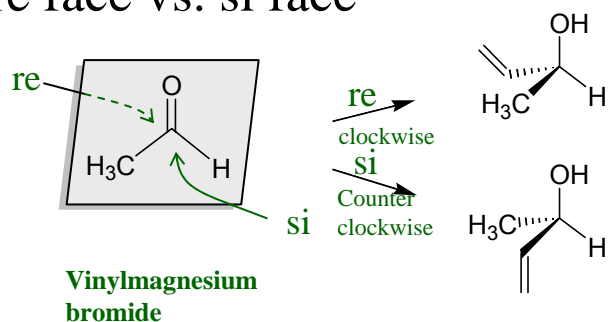
homotopic vs. heterotopic



prochiral center pro-R



re face vs. si face



Optical Activity

Enantiomers can exhibit optical activity—rotation of plane polarized light.

The two enantiomers rotate light to opposite direction, but to the same magnitude. rotation clockwise $\rightarrow +$ (d)

counterclockwise $\rightarrow -$ (l)

for pure (+)-glyceraldehyde, specific rot. $+14^\circ$

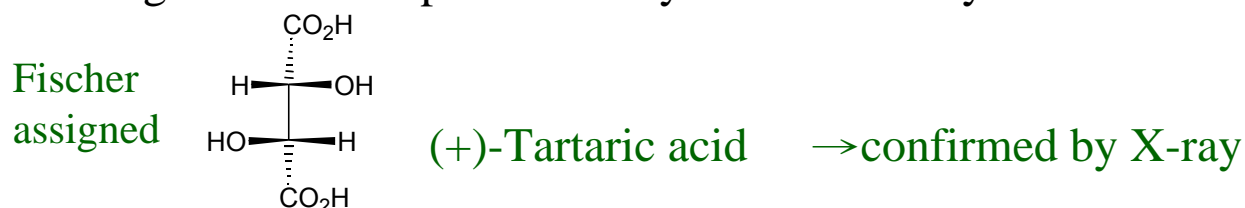
for a mixture of enantiomeric glyceraldehyde giving $+12.6^\circ$,
the excess is $\frac{12.6}{14} = 90\% \rightarrow 95\%$ (+) -and 5% (-) -cpd.

Configuration and Optical Activity

R,S, D,L,- erythro- threo- are artificial molecular notation, based on arbitrary rules.

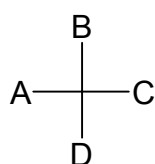
+ , - are molecular property, obtained by expt'l observation.

Configuration and optical activity are not directly related.



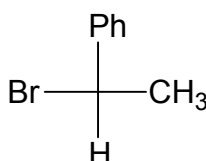
To relate absolute config. and configuration

⇒ Prediction of optical activity :

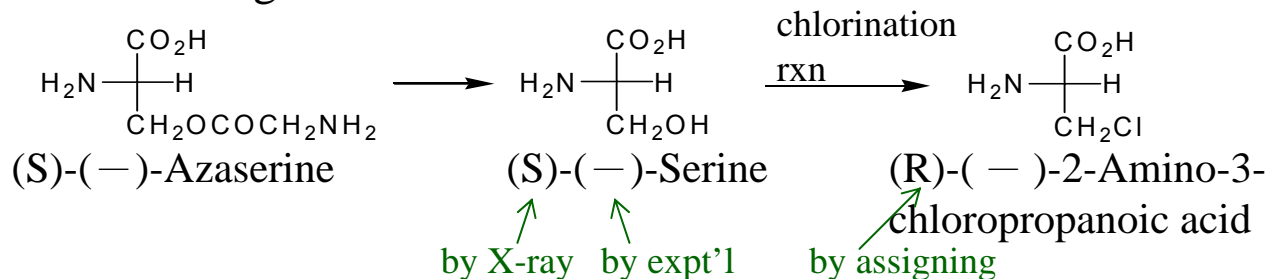


if polarizability is $A > B > C > D$

⇒ Dextrorotatory, +,



⇒ correlating



the bonds connected to chiral center are not broken the abs. configuration remains.

