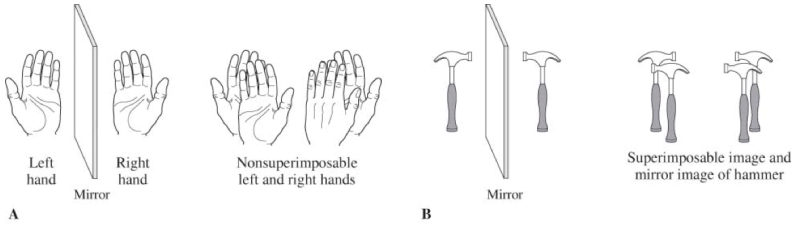
chirality

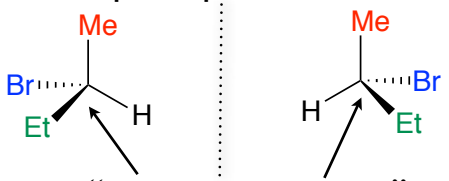
enantiomers: non superimposible mirror images

Another type of stereoisomerism is called mirror-image stereoisomerism. Mirror-image related stereoisomers are said to be left-handed and right-handed and occur when a molecule and its mirror image are non-superimposable.



enantiomers
have same mp, bp, NMR, IR, etc

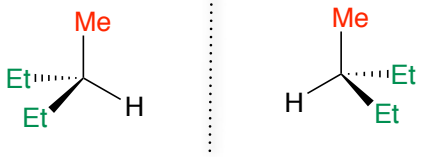
enantiomers: non superimposible mirror images



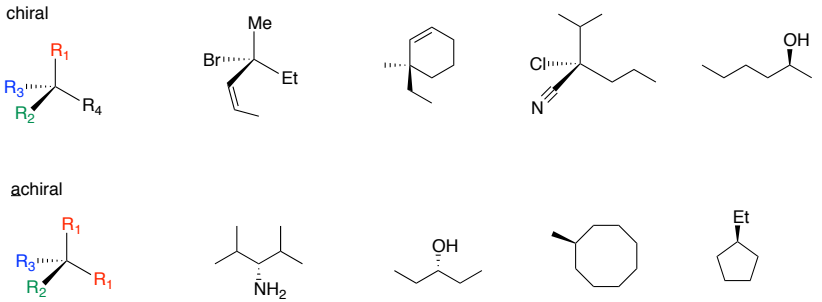
"stereogenic center"

formalism:
wedge (forward)
dashed (back)

Not all mirror images are chiral. These are the same (not chiral)



How to tell if molecules are chiral? Clue: many (but not all*) chiral carbons have 4 different things attached

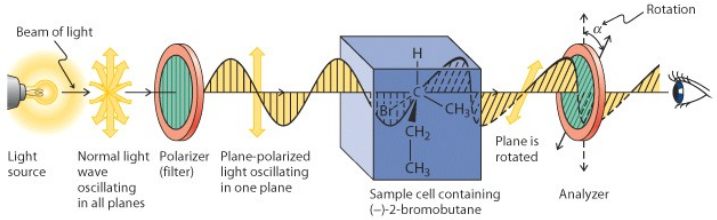


* exceptions to be discussed

When plane-polarized light interacts with a chiral molecule, the plane of polarization of the light is rotated to the left or right.

This effect is called optical rotation and the molecule is said to be optically active.

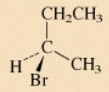
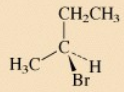
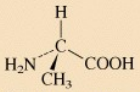
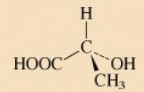
Optical activity is measured using a polarimeter. This device contains a light source, a polarizer to produce the plane-polarized light, a sample cell, and an analyzer to determine the amount of rotation.



The measured rotation (in degrees) is the observed optical rotation, α, of the sample.

Specific rotation is a physical constant for a substance, as is melting point, boiling point, density, etc.

TABLE 5-1 Specific Rotations of Various Chiral Compounds $[\alpha]_D^{25^\circ C}$

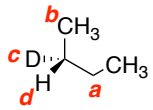
 (−)-2-Bromobutane	−23.1	 (+)-2-Bromobutane	+23.1
 (+)-2-Aminopropanoic acid [(+)-Alanine]	+8.5	 (−)-2-Hydroxypropanoic acid [(−)-Lactic acid]	−3.8

Note: Pure liquid for the haloalkane; in aqueous solution for the acids.

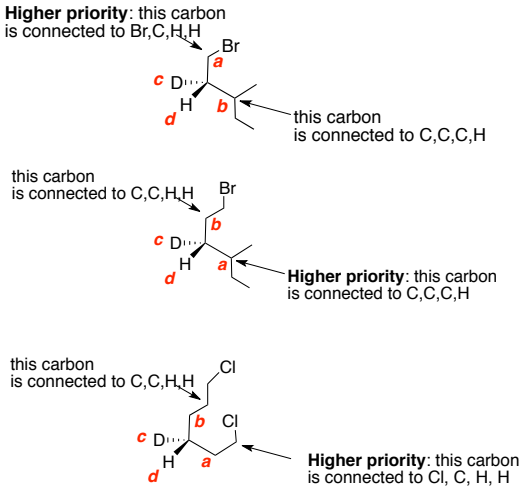
Cahn Ingold Prelog rules

prioritize by:

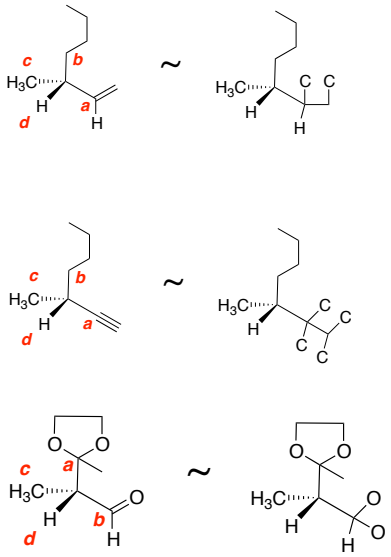
1) Highest atomic #
2) then by isotope atomic weight
3) then by substituents, one atom at a time



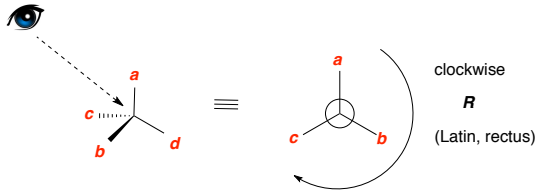
4) if atoms are equal, go to <u>first point of difference</u>



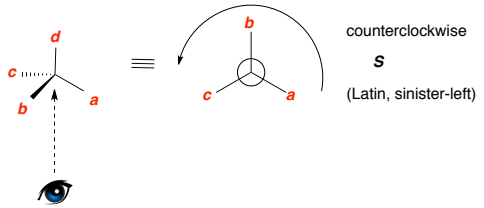
5) multiple bonds

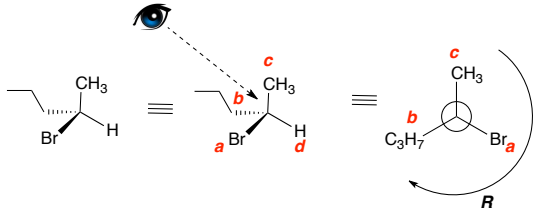


View the molecule with the lowest priority group in the back

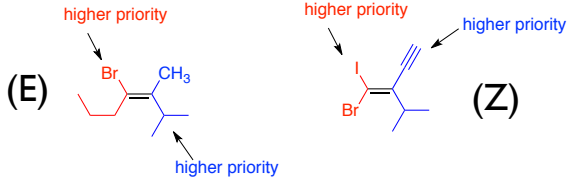


opposite enantiomer:





same rules for alkenes



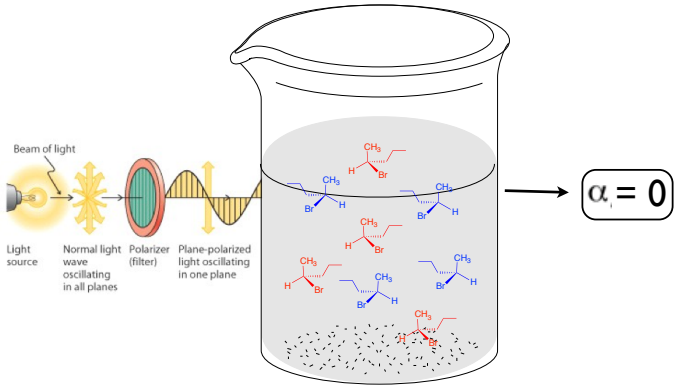
Chiral molecules are not necessarily optically active

Pile of Latvian Mittens (50% Left, 50% Right)

The Latvians are knitting 4,500 mittens for the participants of the NATO summit there (2006)!

See here: www.rigasummit.lv/en/?id=newsin&nid=115

Racemates are not optically active



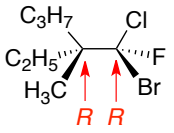
What happens if an enantiomer interacts with another element of chirality?

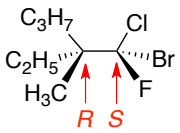
L + R

L + L

diastereomers

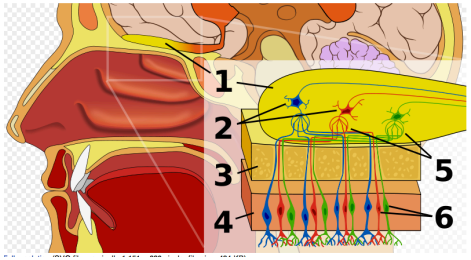
What happens if an enantiomer interacts with another element of chirality?

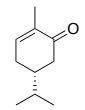




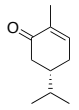
diastereomers
have different mp, bp, NMR, IR, etc

diastereomeric pairs up the nose





R-carvone
spearment



S-carvone
caraway

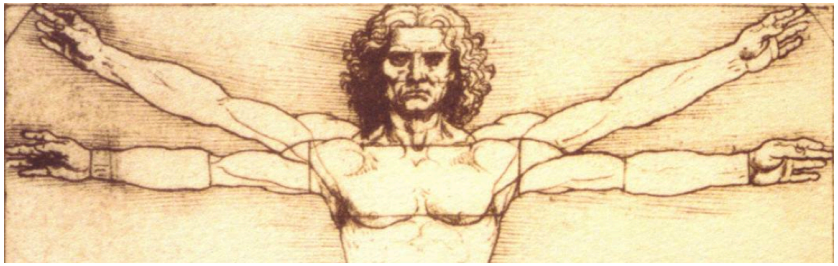
diastereomers

easy to see in ring compounds

easy to see in acyclic compounds if we are consistent in our drawings

meso compounds

Meso compounds contain an internal mirror plane (or center of symmetry) which divides the two halves of the molecule which are mirror images of each other. NOT OPTICALLY ACTIVE!

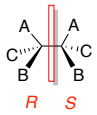


Vitruvian man = meso man. He has symmetrically substituted elements of chirality, equal and opposite

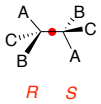
meso compounds

recognizing planes and centers of symmetry

plane of symmetry



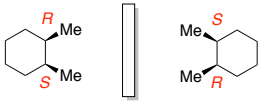
center of symmetry



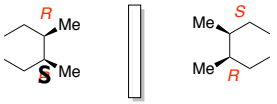
in general, look for R & S stereocenters in the same molecule attached to exactly the same thing

meso compounds

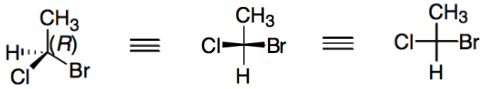
easy to see in ring compounds



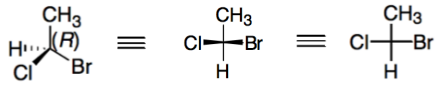
easy to see in acyclic compounds if we are consistent in our drawings



Fischer Projections



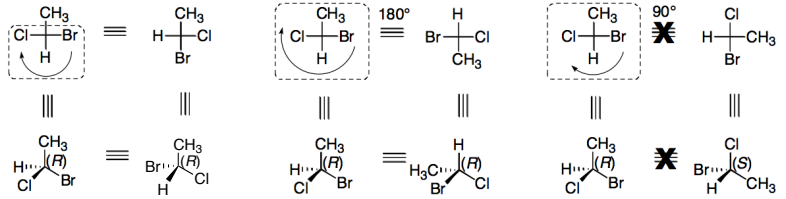
Fischer Projections revisited



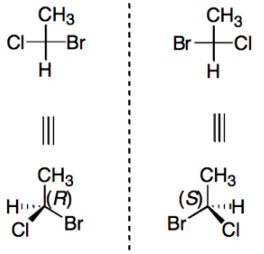
Remember that 3 group rotations are always allowed

180° rotations of entire molecule are allowed

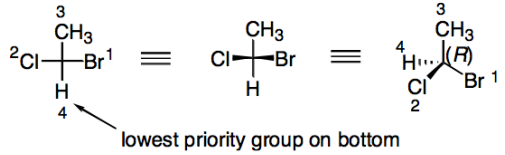
90° rotations of entire molecule are NOT allowed

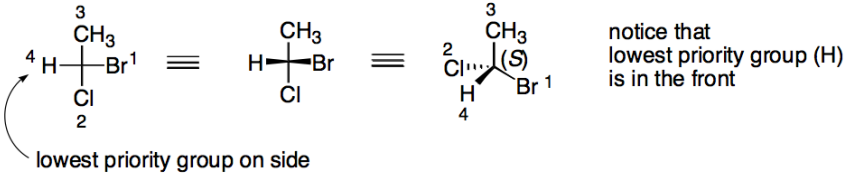


mirror images are enantiomers



a Helpful way to assign stereochemistry





identification of meso compounds by a horizontal mirror plane