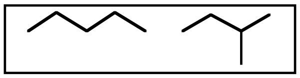
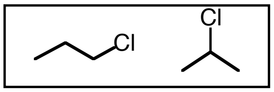
Chem 350 Chapter 5 Stereochemical Terminology Summary
Terms and Definitions

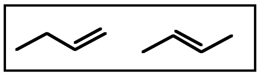
Classification of Isomers

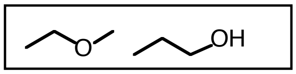
isomers-different compounds with the same molecular formula.

structural isomers (or constitutional isomers)-isomers that have their atoms connected in a different order.



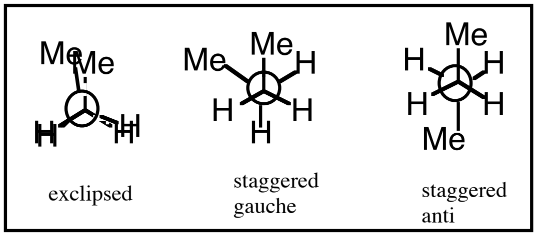


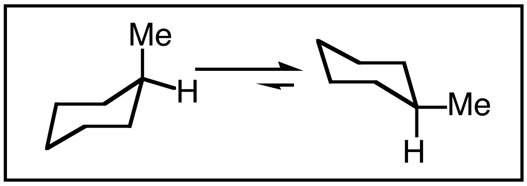




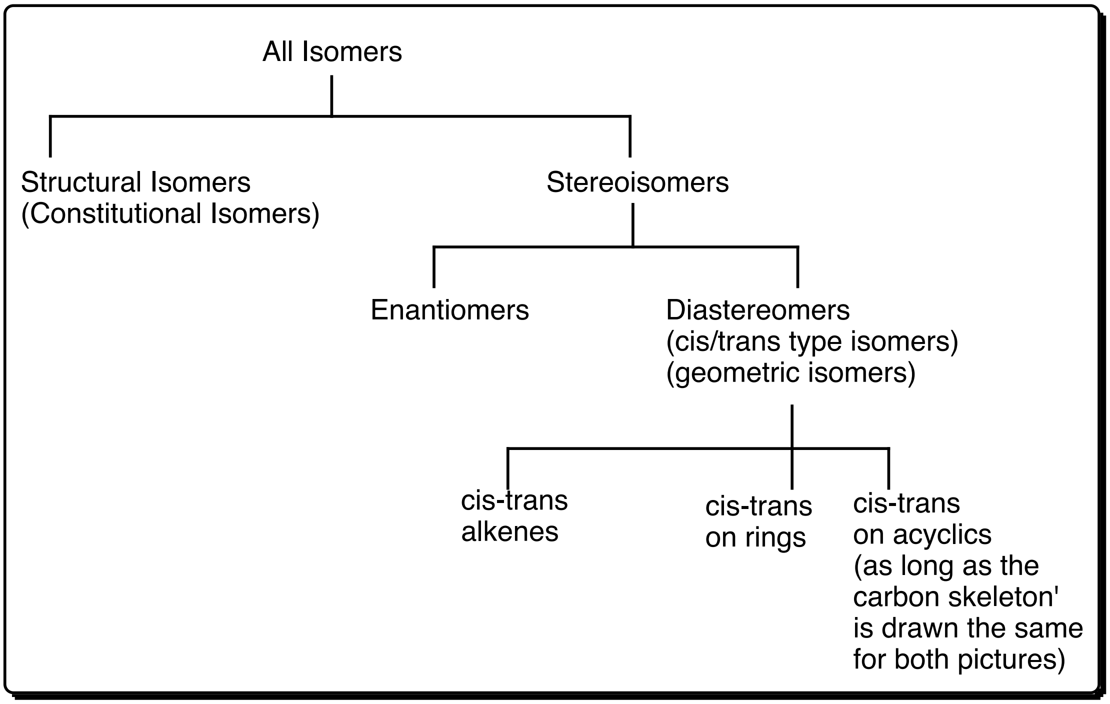
stereoisomers (or configurational isomers)-isomers in which atoms are joined in the same order but differ in the way their atoms are arranged in space. Stereoisomers are subdivided into two categories: **enantiomers** and **diastereomers**.

conformations-easily interconverted by σ-bond rotation or cyclohexane chair flips. In butane, for example, the gauche, eclipsed, and staggered forms are considered to be different **conformations**; in cyclohexanes, the two chairs are conformations. Different conformations are not considered stereoisomers.



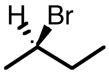


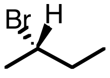
Summary: Types of Isomers



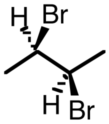
Classification of Stereoisomers

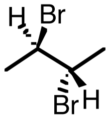
enantiomers-stereoisomers that are not superposable on their mirror reflections. Ex. (R)-2-bromobutane and (S)-2-bromobutane. Separate enantiomers rotate polarized light and are said to be optically active.





diastereomers-stereoisomers that are not enantiomers, that is, not mirror images of each other. Ex. cis- and trans-2-butene; cis- and trans-1,3-dimethylcyclopentane; (2R)-(3R)-2-bromo-3-chlorobutane and (2R)-(3S)-2-bromo-3-chlorobutane. Diastereomers are cis/trans-type isomers, although isomers such as those drawn below are sometimes called syn/anti instead. If the carbon skeletons are drawn analogously, two molecules whose hash/wedge attachments have a cis-trans type relationship will be diastereomers.





Miscellaneous Stereochemical Terms

chiral-equivalent to "handed". A molecule is chiral if it is not superimposable on its mirror image; an achiral molecule is superimposable on its mirror image.

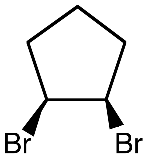
chiral carbon (or stereocenter or asymmetric carbon atom)-an atom bearing groups such that interchange of 2 of the groups produces a stereoisomer. Any tetrahedral atom that has four different attached groups is a chiral carbon.

- Most molecules containing tetrahedral stereocenters are chiral (the exception being "meso compounds".) The configuration of a tetrahedral stereocenter can be designated as (R) or (S).

configuration-the particular arrangement of atoms in space that is characteristic of a given stereoisomer. The configuration of each stereocenter can be designated as (R) or (S).

racemic mixture-a 50/50 mixture of two enantiomers that will not rotate light.

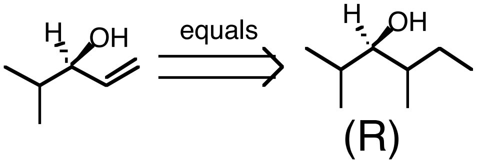
meso compound-an achiral, optically inactive molecule that contains tetrahedral stereocenters (usually two). Both of the Br-bearing carbons in cis-1,2-dibromocyclopentane are stereocenters, but the molecule itself has a plane of symmetry and is achiral.

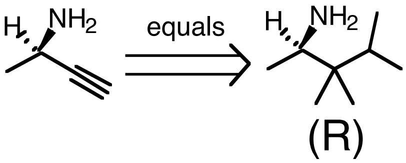


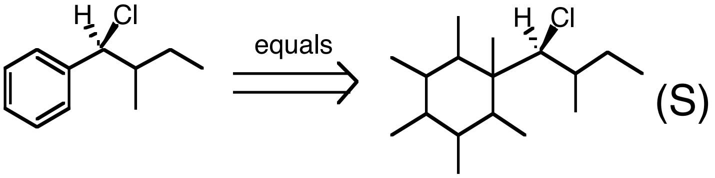
meso, has stereocenters but is
achiral due to plane of symmetry

R/S Classification for Chiral Carbons

1. Assign Priority of Atoms/Groups attached to a tetrahedral stereocenter (1 highest, 4 lowest)
    a. For different elements, higher atomic number takes priority
        - Halogen > Oxygen > Nitrogen > Carbon > Hydrogen
    b. In case of carbon versus carbon ties: Differentiate at nearest point of difference
        1. A carbon with a heteroatom attached beats one without
        2. For carbons with no heteroatoms, one with more H's loses to one with less
            - 3º carbon > 2º carbon > 1º carbon > CH_3
    c. Handling double bonds and triple bonds
        - A carbon with more H's again loses to one with fewer
        - Double or triple bonds are treated as if each of the bonds has extra C's attached







2. If the low priority group 4 (normally H) is in the back (hashed), trace a path from 1→ 2 → 3.
    d. If the path goes clockwise, the stereocenter is (R)
    e. If the path goes counterclockwise, the stereocenter is (S)

3. If the low priority group 4 (normally H) is in front (wedged), then the situation is reversed.
    f. If the path goes clockwise, the stereocenter is (S)
    g. If the path goes counterclockwise, the stereocenter is (R)

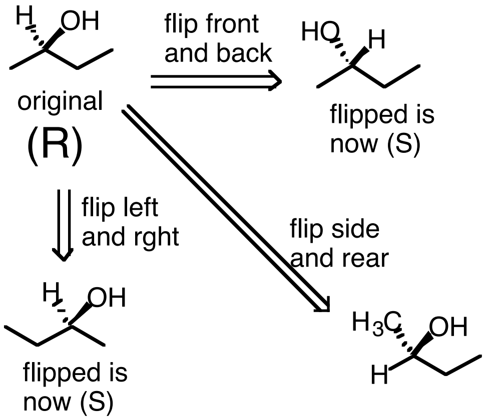
4. If the low priority group 4 (normally H) is to the left or to the right, exchange it with the group in the back (hashed), and trace the path on the resulting figure.
    h. If the path goes clockwise, the stereocenter is (S)
    i. If the path goes counterclockwise, the stereocenter is (R)

5. In Fisher projections, since H is always in front, clockwise is (S) and counterclockwise is (R)

Drawing Mirrors/Enantiomers: Exchange of any two attachments inverts the stereochemistry and produces a mirror image of the original:

1. front and back (hashes and wedges)
2. left and right (while keeping your hashed and wedged attachments unchanged)
3. flipping something on a side (could be the left side or the right side) with the hashed position in back

Flipping any two attachments inverts the stereochemistry



Recognizing Chiral Molecules: Key is to look for chiral carbons/stereocenters

1. If **zero** chiral carbons → molecule is **achiral**
2. If **one** chiral carbons → molecule is **chiral**
3. If **two** (or more) chiral carbons → molecule may be **chiral or achiral**
    e. if it has no plane of symmetry under any conditions, it is chiral.
    f. If it has a plane of symmetry (in one conformation or drawing perspective), then it is achiral
    g. if a molecule has ≥2 chiral carbons but is achiral with a plane of symmetry, it is called a **meso** compound
    h. to recognize whether a molecule with ≥2 chiral carbons is achiral or chiral, try to draw it in a way such that the carbons are maximally symmetrical, so that it will be easiest to see whether or not a plane of symmetry exists. This may sometimes involve using a sawhorse rather than a zig-zag picture to maximize the ease of seeing potential symmetry.

Terminology Related to Enantiomeric Purity

enantiomeric excess (ee) = [(mole fraction major enantiomer)-(mole fraction minor enantiomer)] x 100

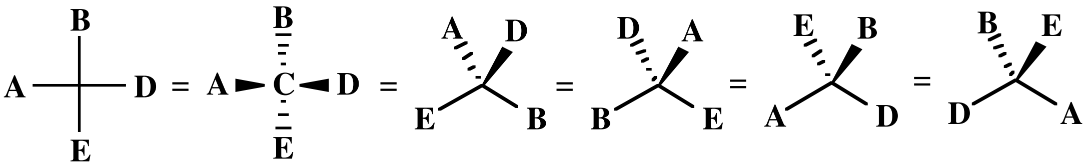
optical purity = [observed rotation/rotation of pure enantiomer] x 100

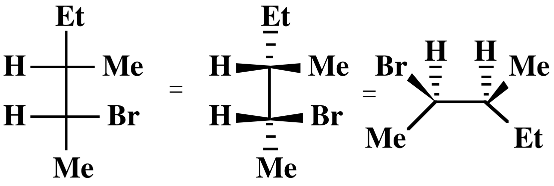
Note: Enantiomeric excess and optical purity values are exactly the same, but are used depending on the experimental method of measurement. Enantiomeric excess is used when you determine the mole/mole ratio of enantiomers by NMR or some other method; optical purity is used when you use optical rotation to characterize a solution containing a mixture of enantiomers.

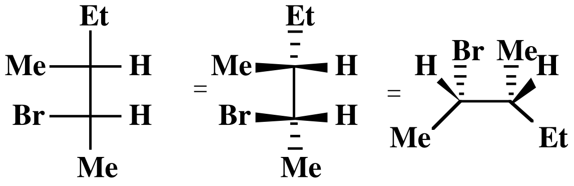
racemic mixture-an equimolar mixture of enantiomers. A racemic mixture will not rotate light.

Fischer Projections

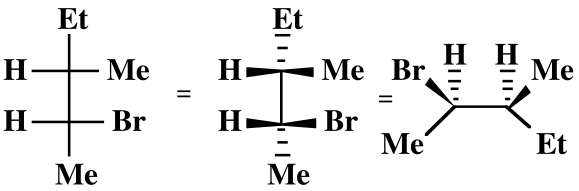
In Fischer projections, atoms attached to horizontal lines are viewed as being in front of the plane (wedged), and atoms attached to vertical lines are viewed as being behind the plane (wedged). In the following pictures, Et=ethyl, Me=methyl.

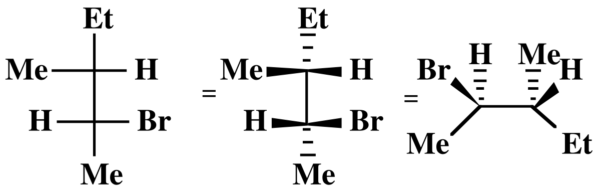




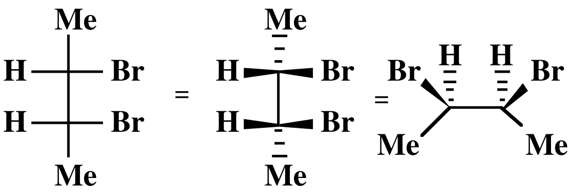


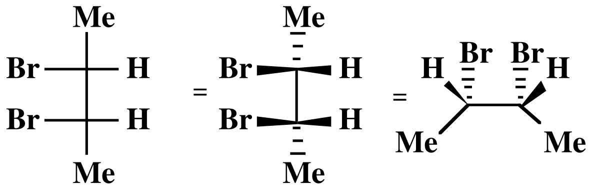
The two structures shown above are enantiomers





The two shown here are diastereomers.





The two shown here are not stereoisomers; they are "meso compounds", because there is a plane of symmetry.