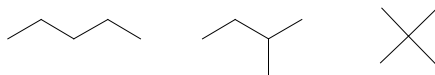


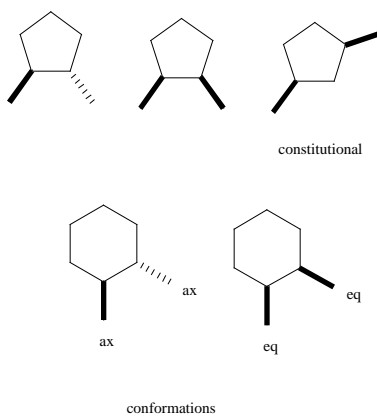
## Chap 5

Stereochemistry-

A) constitutional isomers- different atom-atom connectivity. Have the same molecular formula.  $C_5H_{12}$



B) Stereoisomers- same atom-atom connectivity but different orientation of atoms in space.

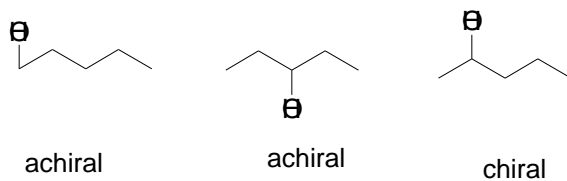


C) Chiral = non-superimposable mirror images.  
achiral = not chiral

Ex. Hands

enantiomers = A pair of non-superimposable mirror images

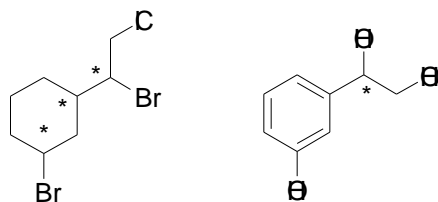
Chiral carbon atoms- usually bound to four different groups.



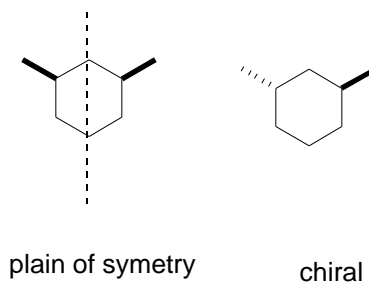
enantiomers-



Label the chiral centers-

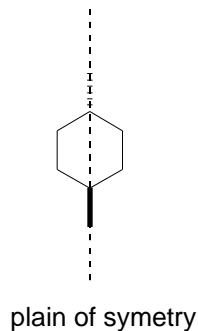


1. One chiral center has an enantiomer.
2. Two chiral centers might be chiral. If it contains two or more chiral centers can have an internal a plain of symmetry.

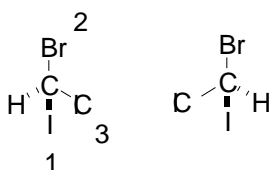


**Ex. 5-1.** Is 1,4-*trans*- dimethyl cyclohexane chiral?

No. Plain of symmetry.



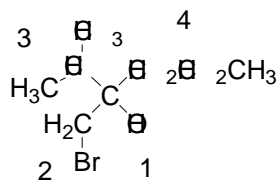
D) R and S designation.



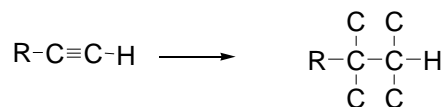
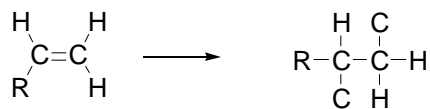
Cahn-Ingold-Prelog convention.

1. Assign priority to each group by the first atom. High atomic numbers are given higher priority.
2. In ties go to the next atom.

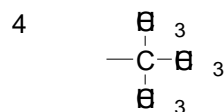
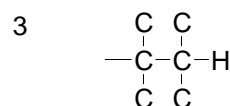
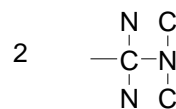
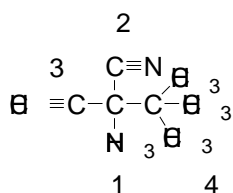
**Ex. 5-2.** Assign priority to the functional groups.



3. Double and triple bonds treat as if attached to separate atoms.



**Ex. 5-3** Assign priority to the following functional groups.

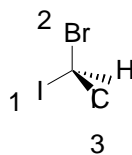


c) Put 4<sup>th</sup> priority group in the back. (dash line)

Look at remaining groups:

If clockwise- assign R

counter clockwise- assign S



**R**

### 3. Optical activity-

Enantiomers have identical physical properties- m.p., b.p., color

But, rotate light in opposite directions.

Have equal but opposite sign in optical rotation.

One enantiomer is optically active. (measure by a polarimeter)

Direction of rotation of light.

d(+) - dextrorotatory (Greek for dexios toward the right)

s(-) - levatory- left

Reported as a specific rotation- concentration dependent.

$$[\alpha]_{\text{temp}}^{\text{D}}$$

D sodium D line

Need to calculate.

$$[\alpha] = \frac{\text{observed}}{c \cdot l} \quad \text{- from polarimeter}$$

c = concentration g/mL

l = length of cell (dm)

### 4. Racemic Mixtures-

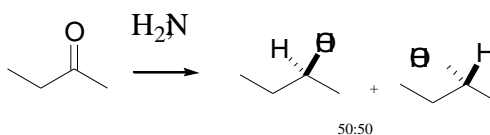
1 enantiomer rotation (+) 23

other (-) 23 net rotation = 0

Has to be 50:50 mixture which is a racemic mixture, optically inactive.

Big rule- optically inactive reactants produce inactive products.

If a chiral center is generated without chiral starting materials or reagents the product will be racemic.



#### 5. Enantiomer Excess (e.e.)- not a racemic mixture

$$\text{e.e.} = \frac{|d - l|}{d + l} \times 100\%$$

**Ex. 5-4.** A mixture of 2-bromobutanes has an e.e. of 50% for (+)-2-bromobutane. What is the ratio of the mixture?

$$d + l = 100\% \quad d = 100 - l$$

$$50\% = \frac{|d - l|}{1.00} \quad 50\% = \frac{|1.00 - l - l|}{1.00}$$

$$1.00 - 2l = 0.50 \quad l = 0.25\% \quad d = 0.75\%$$

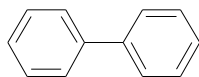
75% = (+)-2-bromobutane

5. Chiral molecules without chiral centers.

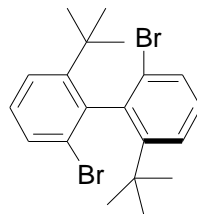
A. Conformational enantiomers.

conformation are in equil. at room temp are not chiral.

Some have such high barriers to rotation one conformation dominates and cannot readily interconvert. Are right or left handed chiral but do not contain a chiral center.

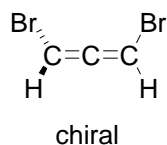
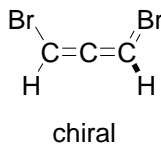
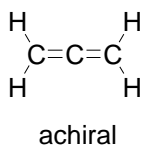


free rotation  
achiral



no rotation  
chiral

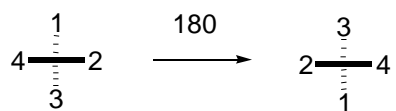
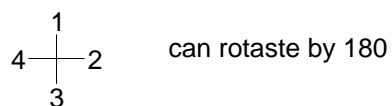
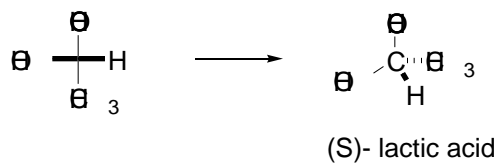
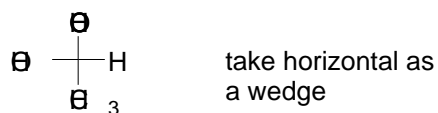
B. Allenes - two linked double bonds- sp hybridized.



Need to add more substituents. Not planar because P orbitals in double bond.

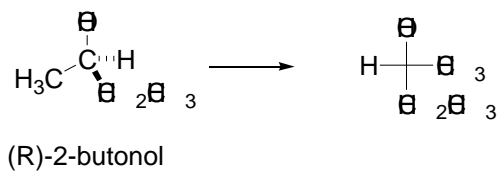
6. Fisher projections-

Draw with a cross.

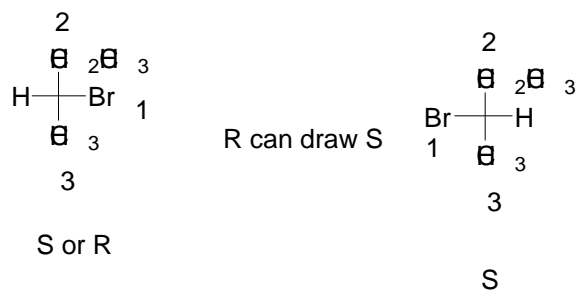


same, do not rotate by any other degree

Put most oxygenated carbon on top.



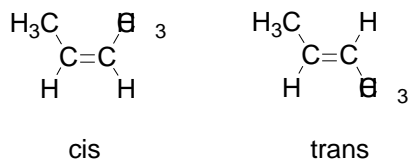
Can draw S by reversing the horizontal



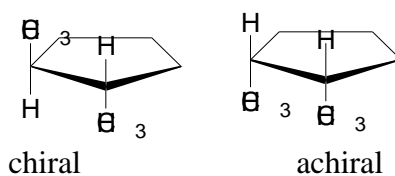
7. Distereomers- stereoisomers that are not mirror images.

A. Cis-, trans- isomers

1) Double bond.

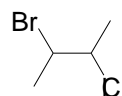


2) cis- trans- on rings

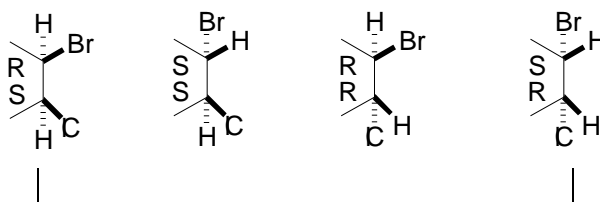


8. Chiral carbons-

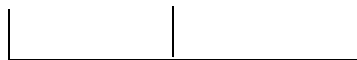
$$2^n = \text{stereoisomers}, \quad n = \text{chiral carbons}$$



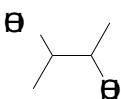
$$2^n = 2^2 = 4 \text{ stereoisomers}$$



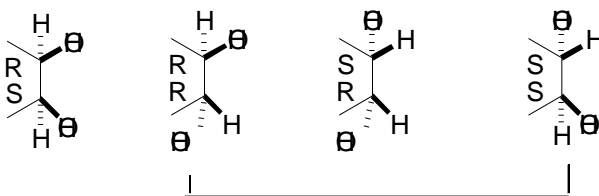
enantiomers



diastereomers



$$2^n = 2^2 = 4 \text{ stereoisomers}$$

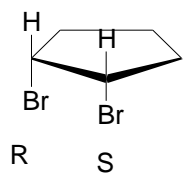


enantiomers



meso compounds, plain of symmetry

Meso achiral but contain chiral centers



meso compound

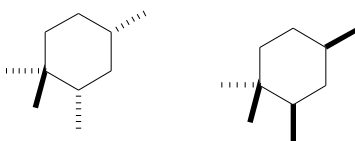
9. Absolute and relative stereochemistry

A. absolute- know R and S designation of each chiral center.

can determine by

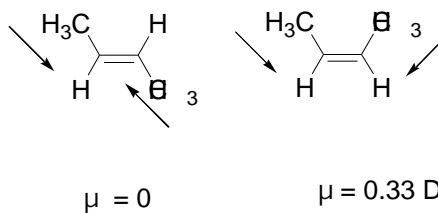
- X-ray.
- Chemical transformation to a known compound with optical rotation data.
- $^1\text{H}$ - NMR, certain restrictions apply.

B. Relative configuration- know cis- or trans but not R or S designation.



10. Separation of enantiomers and distereoisomers.

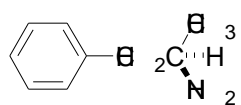
A. Distereomers have different physical properties. Polarity, B.P.



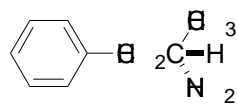
Physical properties different can separate by standard methods, chromatography, distillation, re-crystallization

B. Enantiomers cannot be resolved by the above methods, same physical properties.

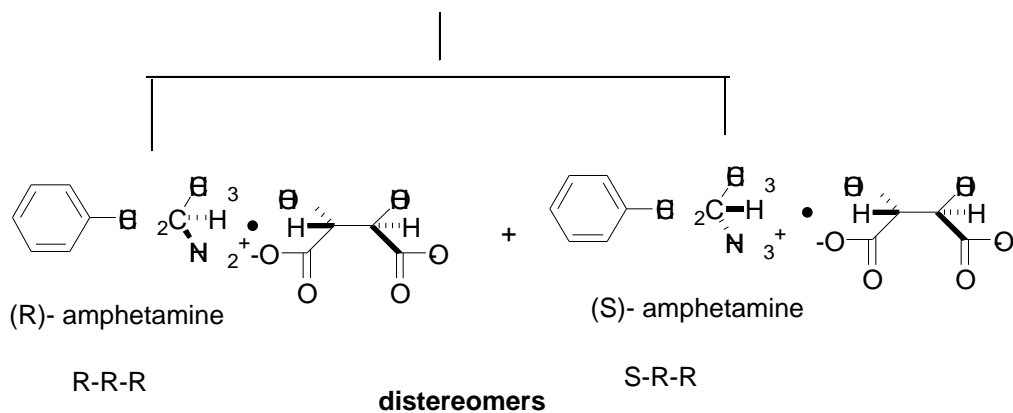
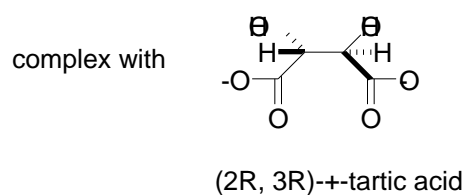
1. Convert enantiomer to a distereomer.



(R)- amphetamine



(S)- amphetamine



2. Chromatographic resolution using a chiral column.

