CHAPTER 7

STEREOCHEMISTRY II

Contents

Chiral Molecules

7.1 Chiral Molecules

-another type of stereoisomer when Compound having carbon (chiral carbon) with 4 different groups attached

-has nonsuperimposable mirror image

ex) 2-chlorobutane

Then 2-chlorobutane is chiral.

A pair of nonsuperimposable mirror images (stereoisomers) are called enantionmers.

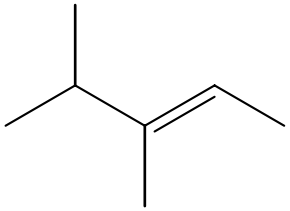
Chirality = handedness

Chiral object; feet, glove, golf club, screw,

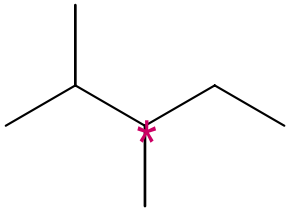
A chiral object; pencil, paper, baseball bat,

7.2 Recognizing Chiral Molecules

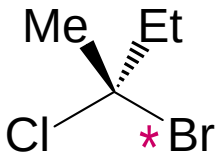
- any molecule with chiral center (carbon with four different groups is chiral).
- any molecule with a carbone with two identical groups are not chiral (achiral).



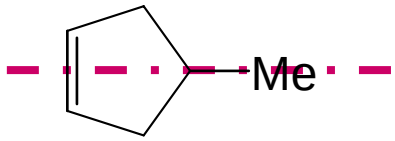
achiral



chiral



chiral



achiral

See Fig 7.2 in p.223

7.3 Designating Configuration of Enantiomers

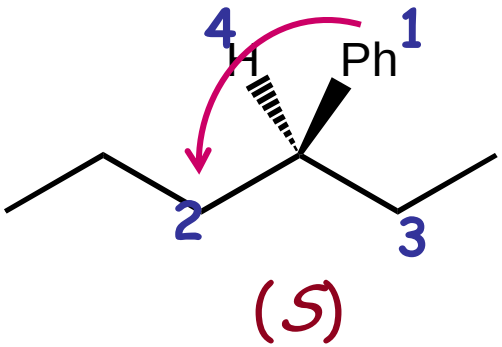
1. **Find the chiral carbon.**

2. **Assign priority of the groups (1, 2 , 3, 4) using Cahn-Ingold-Prelog rules (used in Z- & E-)**

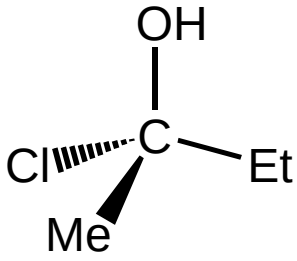
3. **View from chiral carbon to group 4.**

4. **Determine the direction from group 1 to 2; Clockwise -(*R*) and Counterclockwise (*S*)**

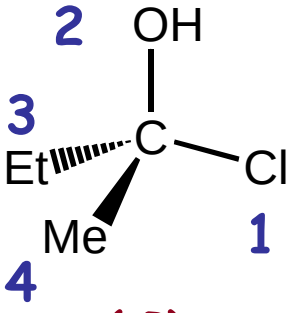
examples



(S)

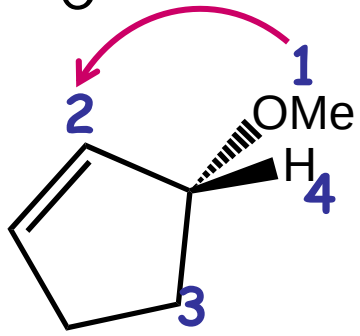


(S)



(R)

(S)–2–chlorobutane



(R)

- Configuration; need to break bond(s)

  therefore stereoisomers have different configurations

- Conformation; need not to break bond (rotation about the axis)

- Absolute and relative configurations
  - absolute configuration – *R or S*
  - relative configuration -- same or different according to the rxn

7.4 Properties of enantiomers

Enantiomers are different when they are in a chiral environment, otherwise they are identical

Ex) think of your two hands (glove, shaking……)

-mp, bp, $\Delta H_{combustion}$, and solubility to achiral solvent are identical

-properties measured in chiral environment are different

- solubility to chiral solvent
- reactivity with one enantiomer of a chiral comp'd
- Odor (nose is chiral!)
- optical rotation

Optical activity

When plane-polarized light is passed through one enantiomer of a chiral compound, the plane of polarization of the light is rotated.

Sodium D line of 589 nm wavelength

-Optical rotation by optical activity of the sample

clockwise rotation -- dextrorotatory; (*d*); (+)

counterclockwise rotation -- levorotatory; (*l*); (-)

no rotation -- not optically active (achiral)

⇒racemate (racemic mixture); equal mixture of (*d*) and (*l*)

-Specific rotation $[\alpha]_D$ is a constant value for a chiral compound like a mp or bp of a organic compound.

-There is no relationship between the absolute configuration (R or S) and the direction of rotation (+ or -)

⇒ Observed rotation indicates only chirality and excess of one enantiomer.

7.5 Molecules with multiple chiral centers; Diastereomer

Diastereomers are not morror images and have different properties in all environment

Molecule with *n* chiral centers has 2^n stereoisomers (max).

Ex)

2^8 stereoisomers are possible.

Nature produces only one (cholesterol)

Ex) 2-(methylamono)-1-phenyl-1-propanol

Meso-stereoisomer

= Compounds contain chiral centers but not chiral

7.6 Stereoisomers and Cyclic Compounds

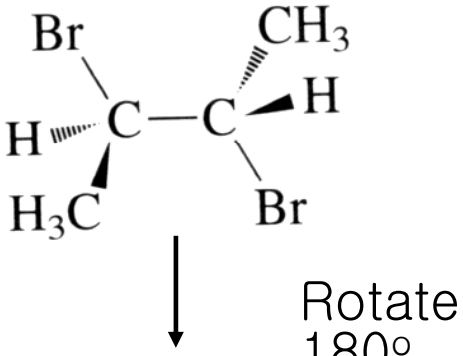
Ex) 1,2-dimethylecyclohexane

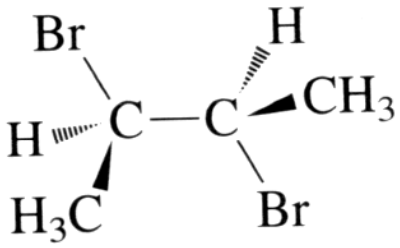
Ex) 3,4-dimethylehexane

Meso-stereoisomer

1. Contains (multiple) chiral centers, but achiral.
2. Has plane of symmetry.
3. Has internal mirror plane.
4. Makes a compound have less than 2^n stereoisomers.

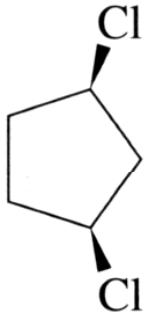
Examples





chiral

chiral



Meso

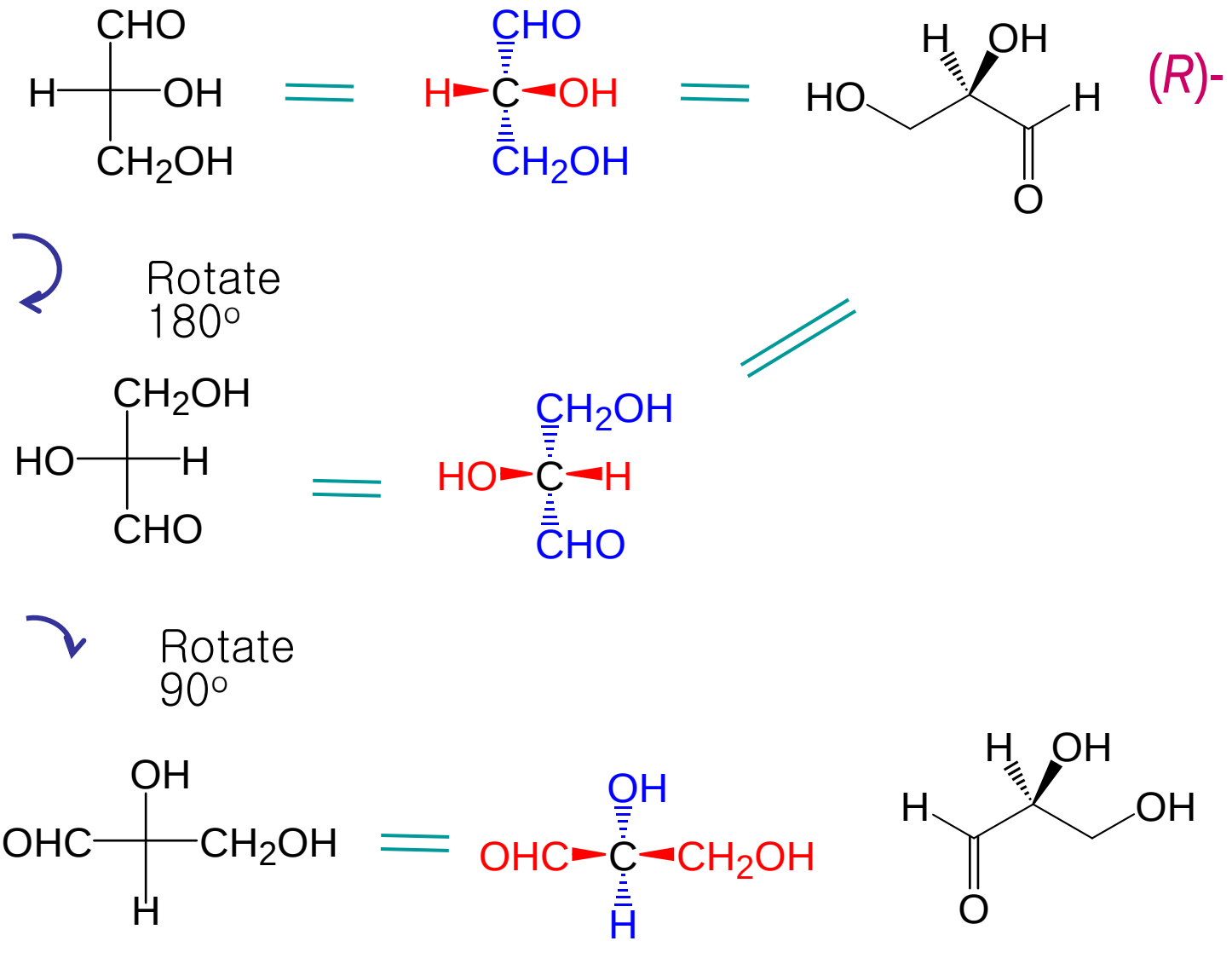
7.7 Resolution: Separating Enantiomers

1. To react a racemic mixture with one enantiomer of some other chiral compound to produce diastereomers. Then as the diastereomers have different properties, they can be separated.
2. The selective reaction of one enantiomer with one enantiomer of a chiral compound, for example enzyme. Then the unreacted compound or reacted compound can be separated.
3. Using chromatography using a chiral stationary phase.

7.8 Fischer projection

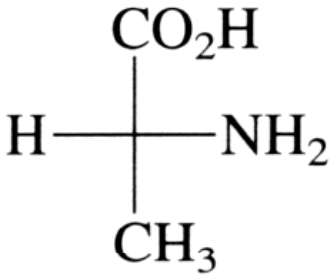
⇒Horizontal bonds project above the paper; vertical bonds project behind the paper.

180 ^{o} rotation in the plane is allowed, while 90 ^{o} and 270 rotation is not allowed

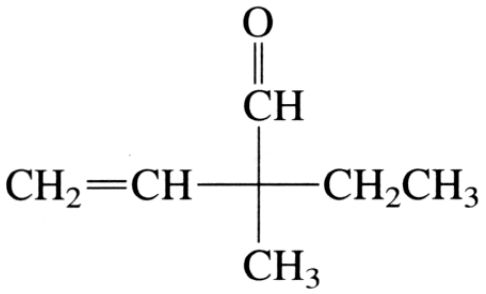

CHO
H
OH
CH2OH
CHO
H
C
OH
CH2OH
H
OH
HO
H
O
(R)-
Rotate
180°
CH2OH
HO
H
CHO
CH2OH
HO
C
H
CHO
Rotate
90°
OH
OHC
CH2OH
H
OH
OHC
C
CH2OH
H
H
OH
H
OH
O
(S)-

Application of Fischer projection; Useful for comp’ds with multiple chiral centers

R or *S*



R



S

7.9 Reactions that produce enantiomers

Racemate
Racemic mixture

- Producing one or another enantiomer is desirable.
- If chirality is not provided, racemate is produced.

7.10 Other Chiral Compounds

- Other Tetrahedral Atoms (N, Si, …)

- Pyramidal Atoms

Activation barrier; 5 kcal/mol (Room Temp. E; 20 Kcal/mol)

$\Rightarrow$ Inversion occurs 10^{11} times per second

Activation barrier;30 kcal/mol for the P compound, 35 kcal/mol for the P compound

$\Rightarrow$ Can be resolved !

- Substituted Allenes

- Biphenyls

Do not interconvert at RT

At 118 ^{o}C Half-life for racemization is 78 min

- Helical Molecules