Chapter 7 Stereochemistry II

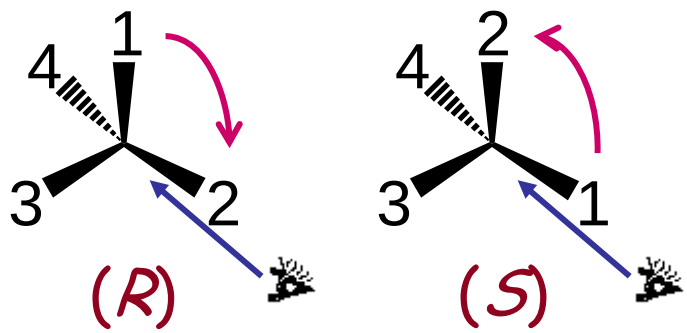
- What to master
  - Identifying Chiral Compounds and Chiral Centers
  - Locating Symmetry Planes
  - Designating the Configuration of Chirality Centers
  - Recognizing When Enantiomers Are Different
  - Understanding Optical Activity
  - Recognizing Meso Strereoisomers
  - Using Fischer Projections
  - Understanding How to Separate Enantiomers
  - Identifying Other Types of Chiral Molecules

Chiral Molecules

- Enantiomers: 4 different substituents; 📖 220
  - non-superimposable mirror images: stereoisomers
  - chirality/chiral: handedness (in Greek, *kheir*)
    - hands (screws) are chiral vs mittens (nails) are achiral
- conditions for chiral molecules: no plane of symmetry
  - chirality center: 📖 221 bottom & 📖 222 top
    - stereogenic/asymmetric center (chiral carbon atom)
  - *practice*: 📖 224 Problem 7.3 & 📖 222 Problem 7.2

Configuration of Chirality Centers

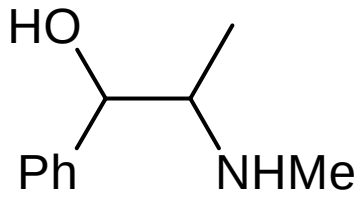
- the (Cahn-Ingold-Prelog) sequence rule: 📖 224
  1. assign priorities to substituents
  2. view the molecule away from the lowest number 4
  3. rotate from 1 to 2 to 3: 'absolute configuration'
     - clockwise: *R* (*rectus*), counterclockwise: *S* (*sinister*)
- *practice*: 📖 225 Practice 7.2, 📖 226 Problem 7.4 & 7.5



Properties of Enantiomers

- Enantiomers: all the same physical properties except
- Optical rotation: polarimeter, 📖 229 Figure 7.4
  - optically active/optical activity: $[\alpha]_D^{temp}$; 📖 229 middle
  - (+) / *d*, (-) / *l*, (±) / *dl* [racemate or racemic mixture]
    - no relationship: absolute configuration and optical rotation
  - ee [e.e.]: enantiomeric excess (%) = |*R* (%) - *S* (%)|
    - $[\alpha]_D$ of 80% ee of (*S*)-2-butanol? [(*R*)-2-butanol: -13.9°]
- Different rate of reaction with another chiral reagent
  - smell: 📖 228 top; *practice*: 📖 230 Problem 7.6

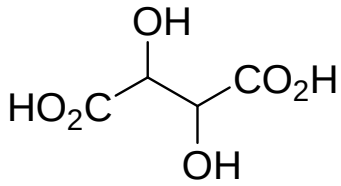
Molecules with Multiple Chirality Centers (I)

How many stereoisomers with 

?

- diastereomers: non-mirror image stereoisomers
  - maximum stereoisomers: 2^n (n: No. of chiral centers)
    - different physical & chemical properties: mp, $[\alpha]_D$, etc.
  - absolute vs relative configuration: (*R*/*S*) vs (*RS*/*SS*)
  - *practice*: 📖 232 top: cholesterol, 📖 232 Problem 7.8

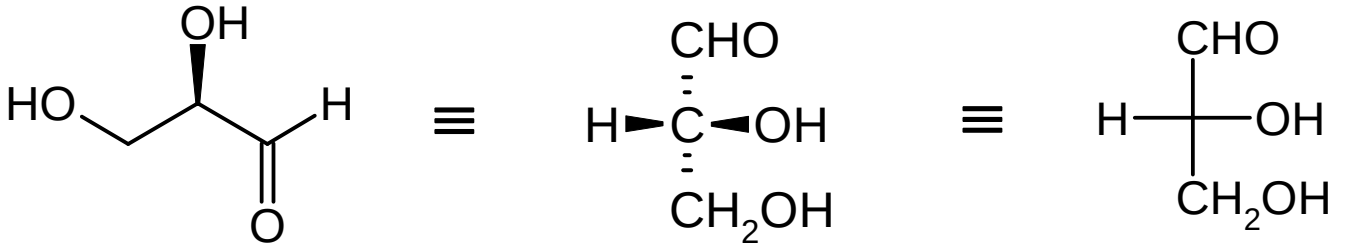
Molecules with Multiple Chiral Centers (II)

How many stereoisomers with  ?

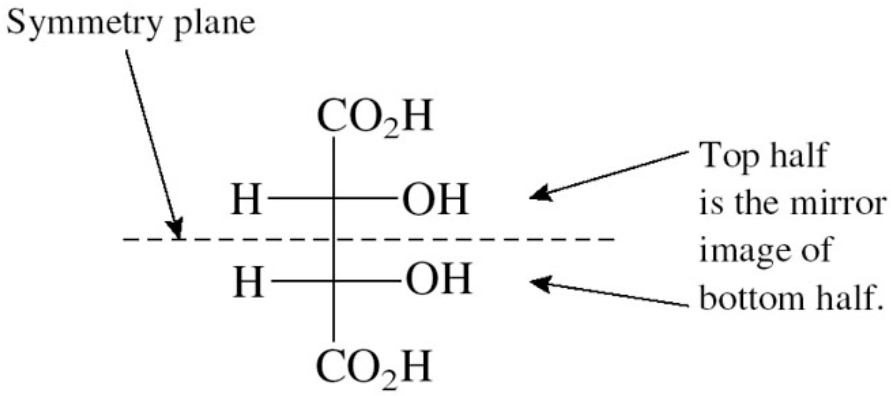
- *meso*-isomer: achiral (plane of symmetry), 📖 233
  - 1,2-dimethylcyclohexane: 📖 234 bottom
  - 3,4-dimethylhexane: 📖 235 top
  - *practice*: 📖 234 Problem 7.9 & 📖 234 Problem 7.11

Fischer Projections

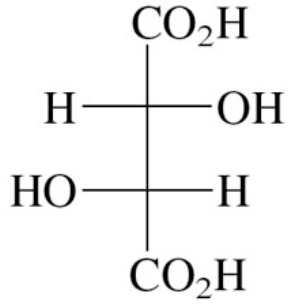
- How to draw: from 3-D into 2-D; 📖 237-8
  - vertical skeleton with the most oxidized group on the top
    - vertical: behind the plane, horizontal: above the plane
  - allowed 180° rotation & two interchange: 📖 240 middle
  - *practice*: 📖 240 Problem 7.4, 📖 239/242 Problem 7.12/7.13
- D/L: amino acids, α-hydroxyacids, carbohydrates
  - stereochemical descriptors: the bottommost chirality center in a Fischer projection; D (right NH_2/OH), L (left NH_2/OH)



D-glyceraldehyde



meso-Tartaric acid

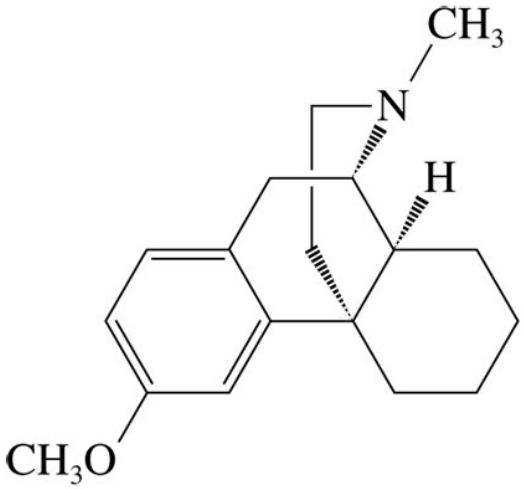


(+)-Tartaric acid
(2*R*,3*R*)-stereoisomer

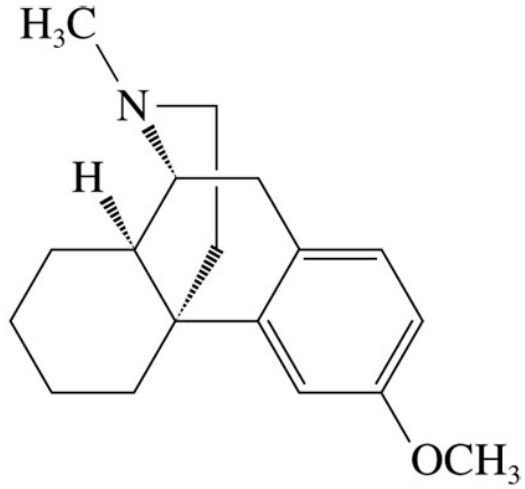
L-tartaric acid

Enantiomerically Pure Products

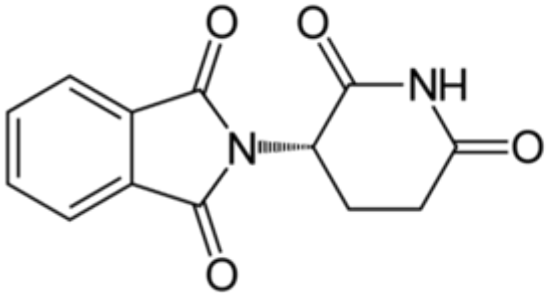
- Enantiomers: different activity; 📖 243 Focus On
  - asymmetric synthesis: prochiral molecules; 📖 242 middle
- Resolution: separation of enantiomers, 📖 237 Fig. 7.5
  - diastereomeric salts with a chiral base: solubility difference
  - resolving agents: enzyme, chiral reagent, chiral column
- other chiral molecules: 📖 244-7
  - other sp^3 atoms, allenes, biphenyls, helical molecules



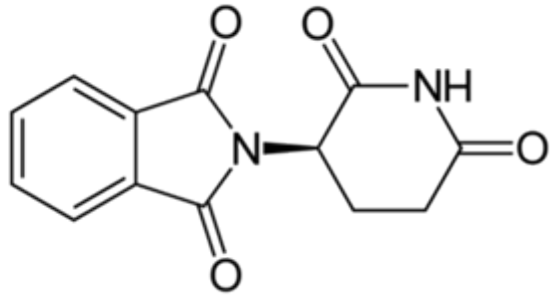
Dextromethorphan
(cough suppressant)



Levomethorphan
(narcotic)

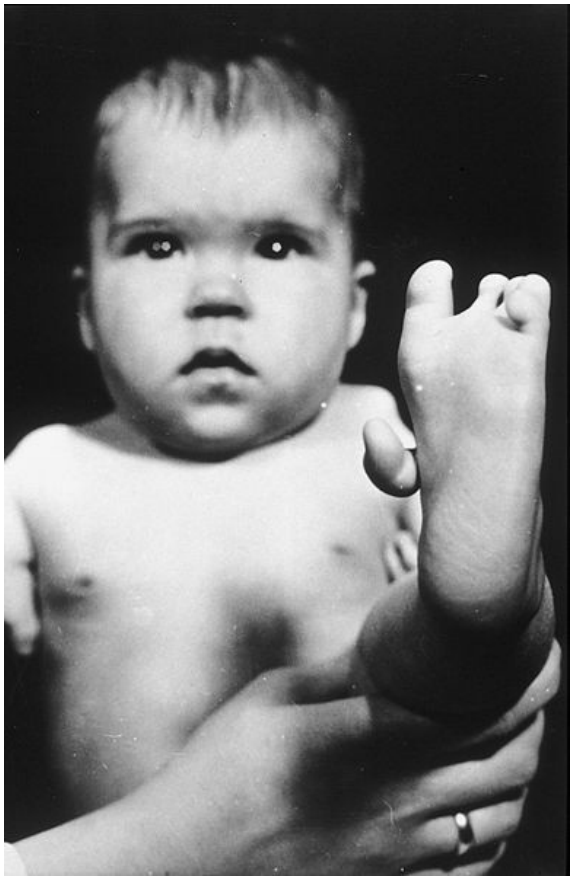


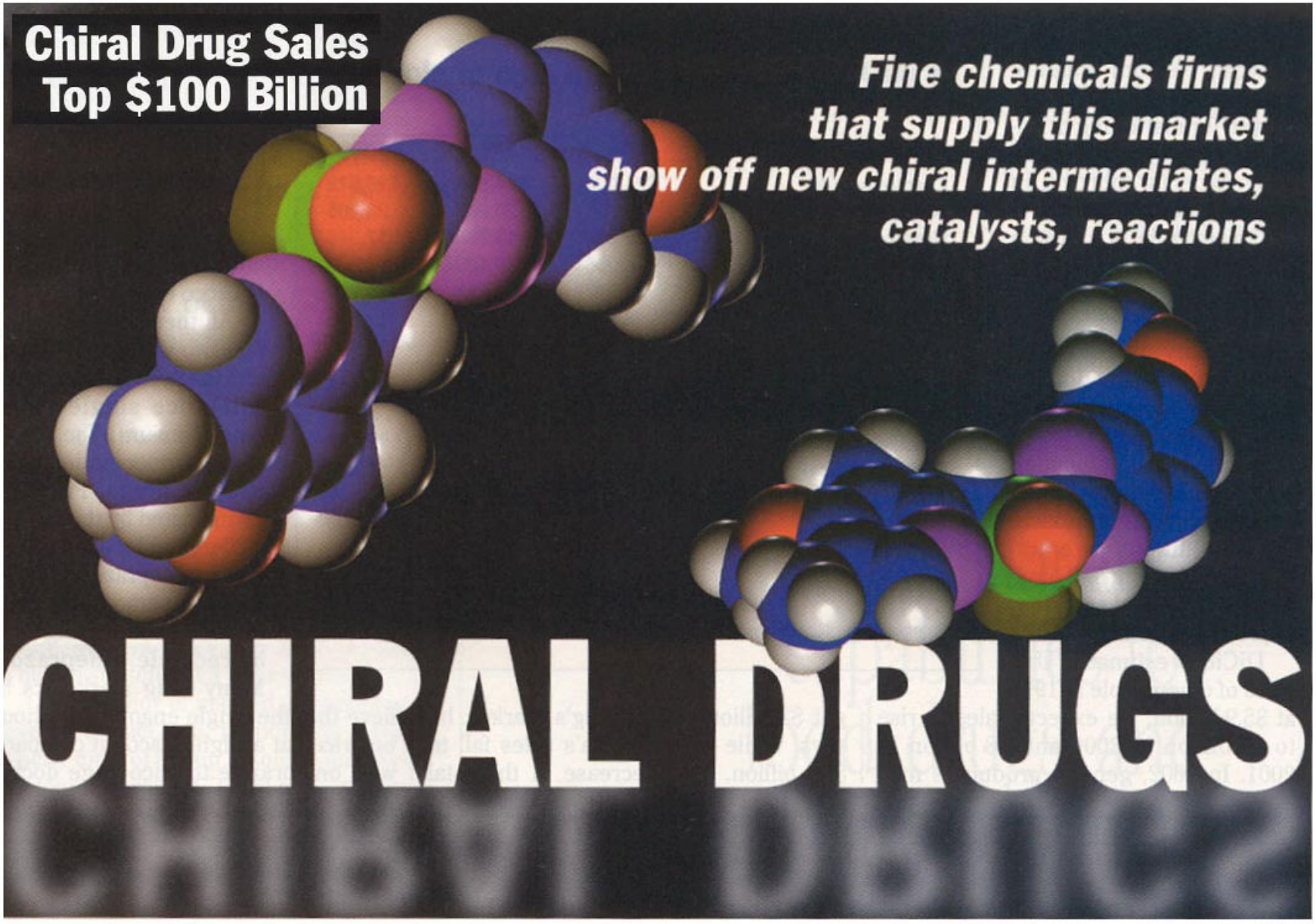
(*S*)-thalidomide: teratogenic

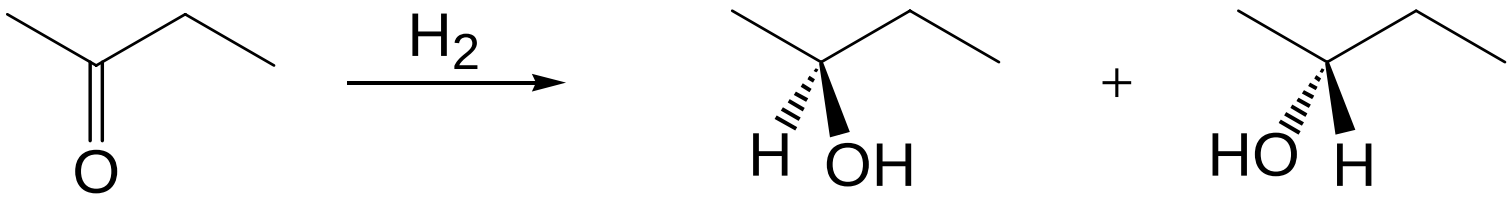


(*R*)-thalidomide: sedative

Thalidomide Tragedy




Chiral Drug Sales
Top $100 Billion
Fine chemicals firms
that supply this market
show off new chiral intermediates,
catalysts, reactions
CHIRAL DRUGS



achiral (prochiral) (*S*)-2-butanol (*R*)-2-butanol

racemate

공부하는 방법

"그저 익숙하도록 읽는 것뿐이다. 글을 읽는 사람이, 비록 글의 뜻은 알았으나, 만약 익숙하지 못하면 읽자마자 곧 잊어버리게 되어, 마음에 간직할 수 없을 것은 틀림없다.

이미 읽고 난 뒤에, 또 거기에 자세하고 익숙해질 공부를 더한 뒤라야 비로소 마음에 간직할 수 있으며, 또 흐뭇한 맛도 있을 것이다." - 퇴계 이황 (금장태 著)