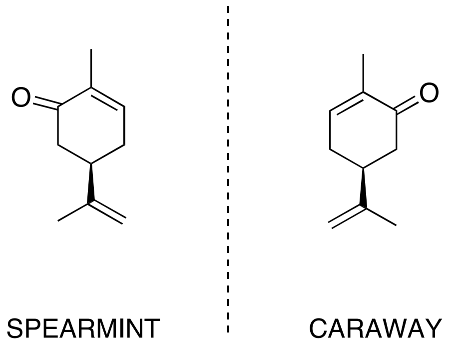
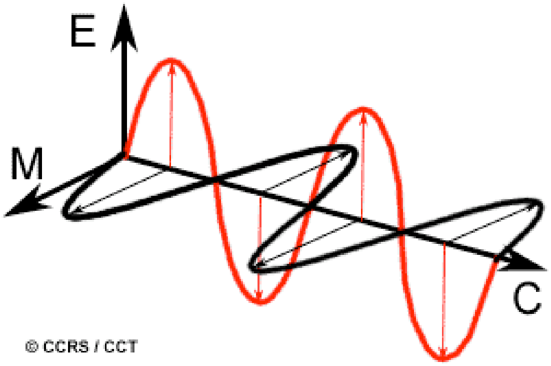
CARVONE



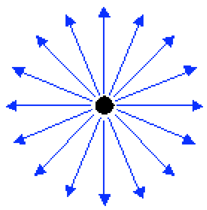
Light: Electromagnetic radiation

$$\text{Light} \rightarrow E = h\upsilon = \frac{hc}{\lambda}$$

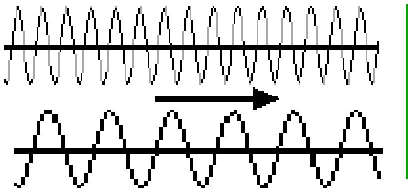
υ = frequency E = energy h = Planck's constant λ = wavelength
c = speed of light



Light has oscillating Electric field (red) combined with magnetic field (black)



End on view of vector components of normal light



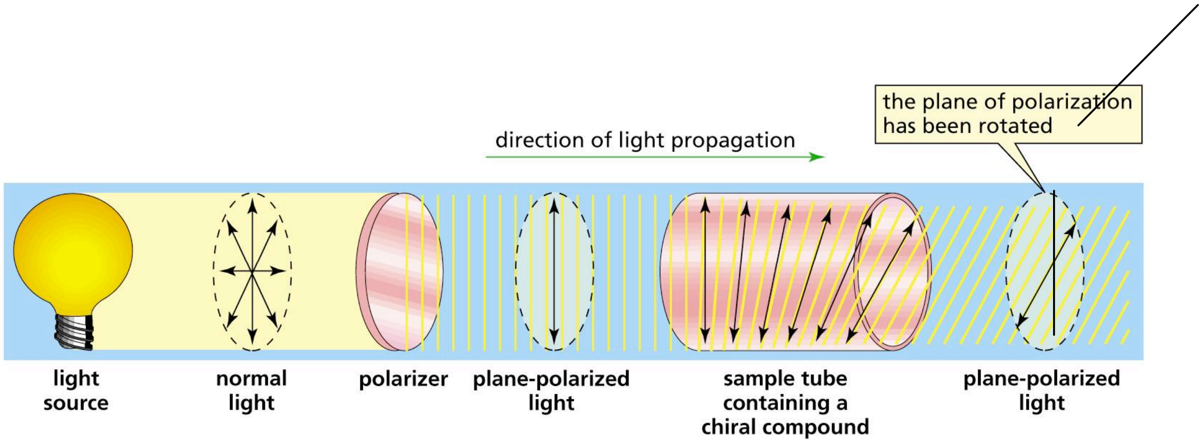
short wavelength = high frequency

long wavelength = short frequency

High energy

Low energy

The plane has been rotated by α degree
to get the maximum transmission

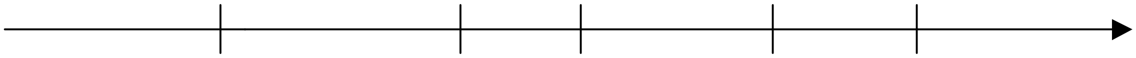


$$[\alpha]_D = \frac{\alpha}{c \bullet l}$$

α = measured rotation c = concentration (mol/L) l = path length (cm)

D = D-line of sodium light [α] = absolute rotation

X – Ray UV visible IR Microwave Radio



High Energy

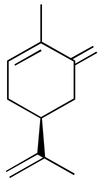
λ = 4000 – 8000 Å
visible

Low Energy

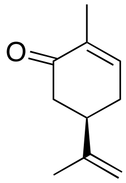
Optical Rotation

$[\alpha]_D$ = Absolute Rotation

Pure enantiomers rotate in equal but opposite direction



$[\alpha]_D = +100$
Dextrorotatory
d



$[\alpha]_D = -100$
Levorotatory
l

Optical Purity = enantiomeric excess
↑ ↑
Measured Reality

- excess of one enantiomer over the other
-

Eg.Assume pure enantiomer has 100^{o} rotation (pure R isomer = -100^{o} ; S isomer = $+100^{o}$)

R	S	Rotation (^{o})	Optical purity
100%	0%	-100	100%
75%	25%	-50	50%
50%	50%	0	0%
25%	75%	+50	50%
0%	100%	+100	100%

Racemic Mixture = Racemate

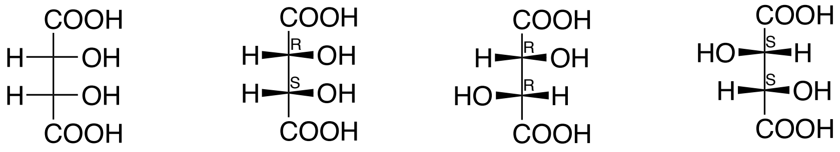
50 : 50 mixture of enantiomers $[\alpha]_D = 0$

$$\text{Optical purity} = \frac{[\alpha]_{observed}}{[\alpha]_{pure-enantiomer}} \times 100\%$$

Resolution: Separation of enantiomers.

- Always need chiral agents
- Physical separation (crystallization of specific enantiomer)
- "reaction" with chiral substance to get 2 diastereomers, which can be separated.

Ex) Tartaric Acid – mixture of meso, RR, and SS



Fisher projection:
Horizontal groups toward you
and vertical groups back

Meso
Achiral

R,R

S,S

Resolution by reaction to diasteromers (these can be separated by conventional means)

RACEMATE

Acid_{RR} + Acid_{SS} 50/50 mix

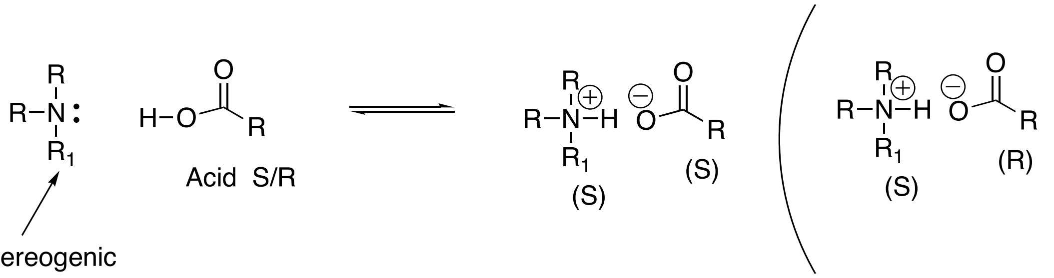
↓ reaction (S-enatiomer ← optically pure
reactant)

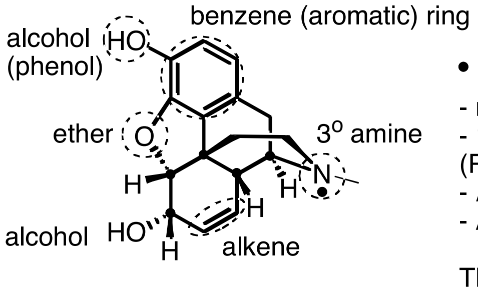
Reactant(S) -Acid_{RR} Reactant(S)- Acid_{SS}

S R R S S S

diastereomers

Formation of Diastereomer Salts





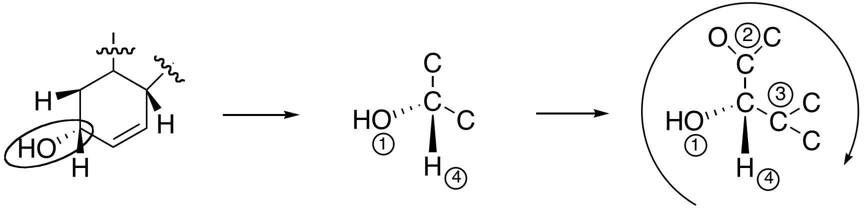
morphine

- ● stereogenic centers (6)

- morphine from Morpheus (god of sleep)
- 10% opium is morphine, from opium poppy (Papaver somniferum).
- **Alkaloid:** N-containing substance, from plants
- Analgesic and addictive

Theriac - ← Therapeutics
Mithridates - king of Pontus

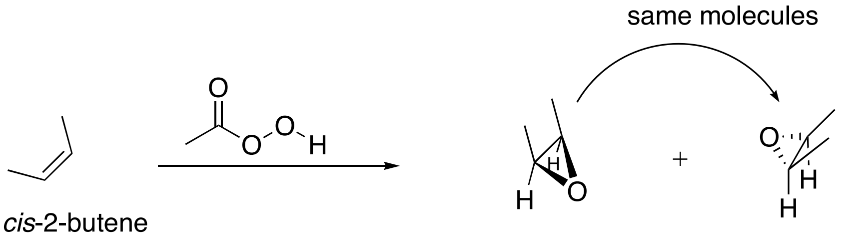
Assign R/S stereochemistry to stereogenic centre



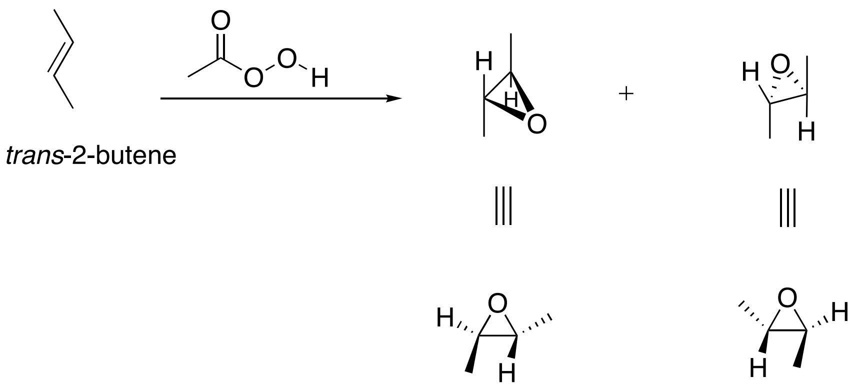
CW rotation (but H is up) = S-configuration

Stereospecific addition reaction: (see reactions of alkenes)

Eg. Epoxidation:



achiral - meso compounds
(plane of symmetry)



(R, R) (S, S)

- both starting materials are achiral (not chiral), but each of the products can be chiral
- however they are formed as a 1:1 mixture of enantiomers – racemic mixture

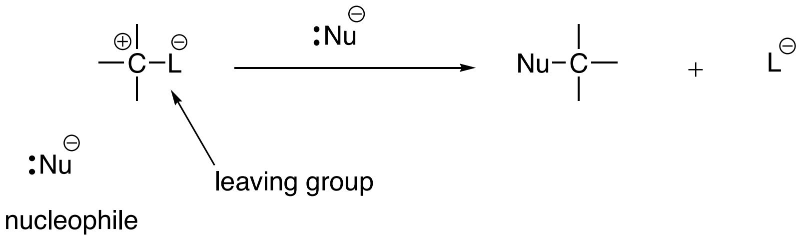
Generally get pure (or partially pure) chiral products only if one of the reagents is chiral

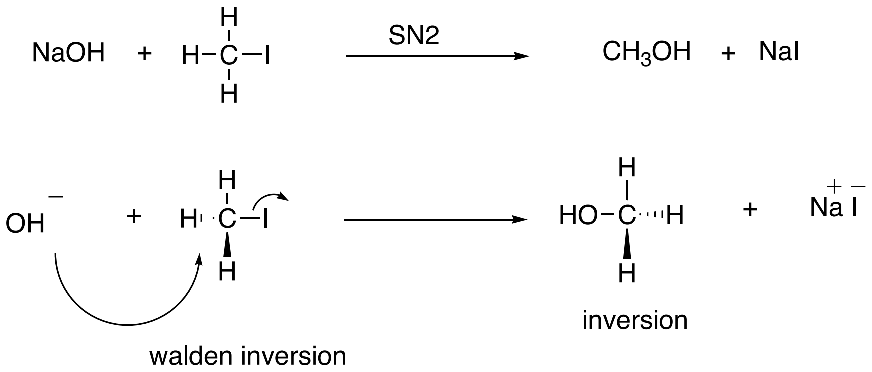
Substitution Reactions:

S_N2 reaction:

S = Substitution
N = nucleophilic
2 = bimolecular reaction (rate of reaction depends on 2 reagents)

- stereospecific reaction
- inversion of configuration
- concerted reaction
- rate depends on two reagent concentration
- favored for primary 1° carbons




NaOH
+
H
H–C–I
H
SN2
CH3OH
+
NaI
OH⁻
+
H
H–C–I
H
walden inversion
H
HO–C–H
H
inversion
+
Na⁺ I⁻