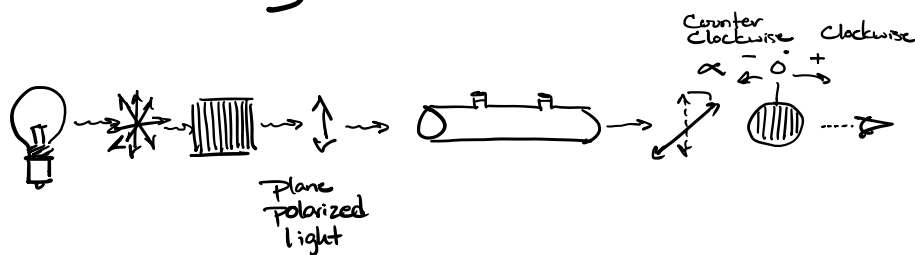


Stereochemistry

Optical Activity



$$\text{Specific Rotation} = [\alpha]_{D, T}^{\lambda} = \frac{\alpha}{c \cdot l}$$

λ ← wavelength
 T ← temp

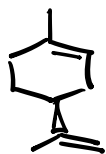
α = observed rotation

c = Concentration of Sample g/mL

l = path length dm

D = Sodium D line = 589 nm

T = °C



(R)-(+)-Limonene

100 mL solution containing 12.3g limonene
20°C

10cm tube = 1 dm

$\alpha = 15.60^\circ$ rotation

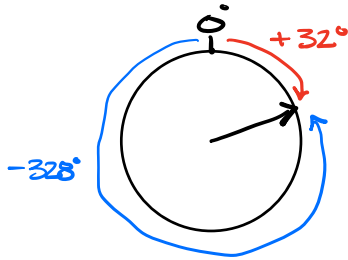
$[\alpha] = ?$

$$[\alpha]_{D}^{20^\circ} = \frac{15.60^\circ}{1 \text{ dm} \times \frac{12.30 \text{ g}}{100 \text{ mL}}} = 126.8^\circ \frac{\text{mL}}{\text{dm g}}$$

$$[\alpha]_{D}^{20^\circ} = 126.8^\circ \quad (c = 0.123; \text{hexane})$$

Solvent

What if a molecule has never been measured,
how do we know if rotation is + or -



New molecule

23.2 g / 100ml MeOH

20°C

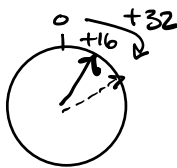
1dm tube

$\alpha = +32^\circ$ or -328° ??

Consider what happens if we cut concentration
in half.

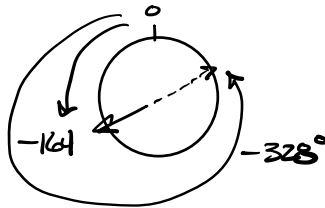
\Rightarrow if $LJ/2$ then $\alpha/2$

if $+32$



New $\alpha @$
 $\frac{1}{2}LJ = +16$

if -328°



New $\alpha @$
 $\frac{1}{2}LJ = -164^\circ$

Mixtures of Enantiomers

Equal amounts of each enantiomer - Racemic

Unequal amounts of each enantiomer - non-Racemic

Enantiomeric excess - the excess of one enantiomer
over the other
%ee

Pure enantiomer -

Single isomer
Enantiomerically pure
Optically pure

%ee = measurement of enantiomeric excess

$$\%ee = |\%R - \%S|$$

Sample 75%R & 25%S

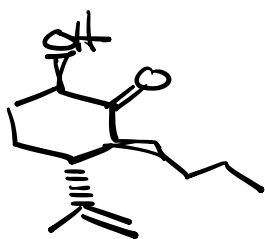
$$|75\%R - 25\%S| = 50\%ee$$

50%ee means I have 50% more of
one enantiomer than of the other

$$\%ee = \frac{|\text{observed } \alpha|}{|\alpha \text{ pure enantiomer}|} \times 100$$

$$\%ee = \frac{|\text{mole}_R - \text{mole}_S|}{\text{mole}_R + \text{mole}_S} \times 10$$

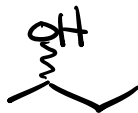
Ways of representing molecules with
Stereogenic Centers



wedge & hash bonds

▷ wedge forward

||||| hash backwards



~ wiggly bond

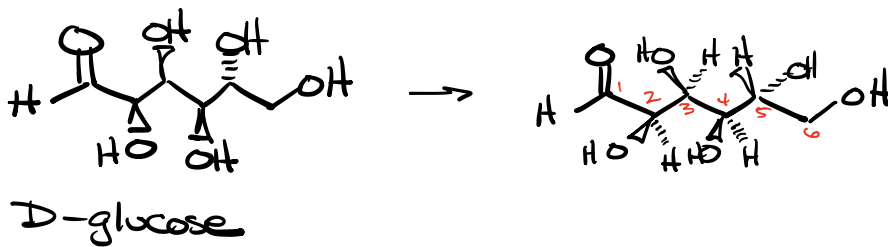
represents something racemic (50/50 mix)

0% ee

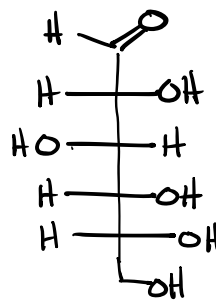
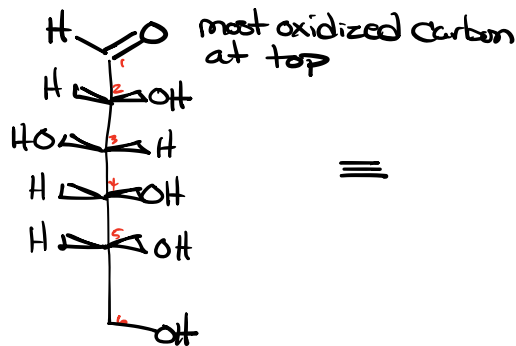
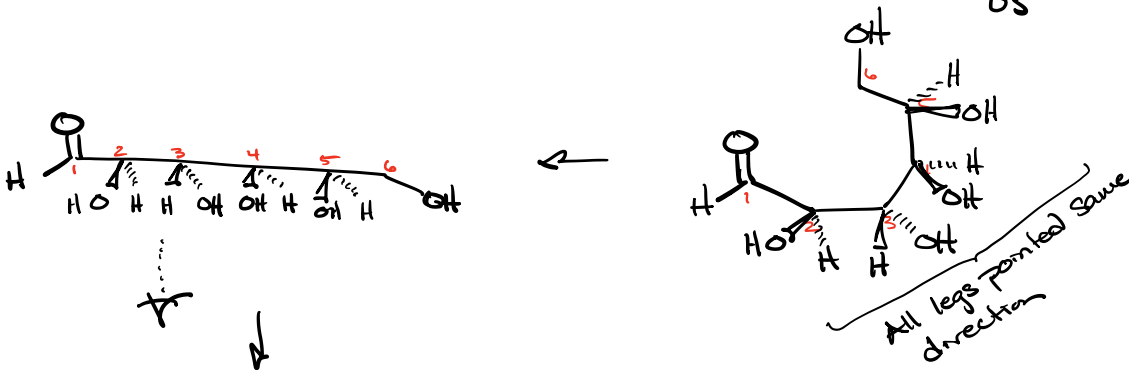


Fischer Projections

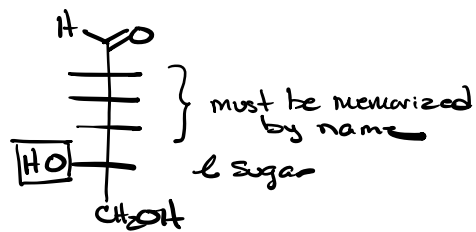
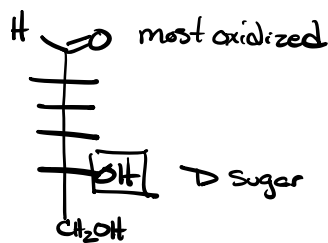
Used for carbohydrates, linear molecules with many stereocenters

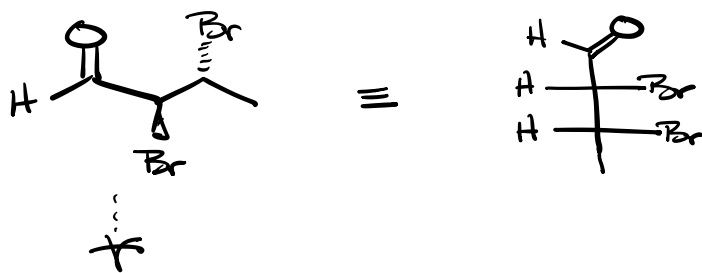


Rotate so that all stereocenters orient towards us

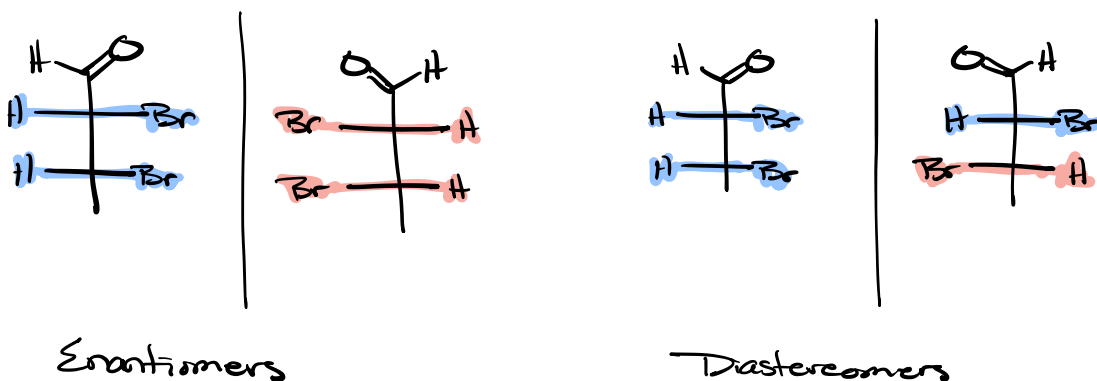


Fischer Projection





Fischer projections not good for Rxn, but good for enantiomers & diastereomer relationships



Resolution of Enantiomers

Enantiomers have same:

BP
MP
polarity
density
⋮

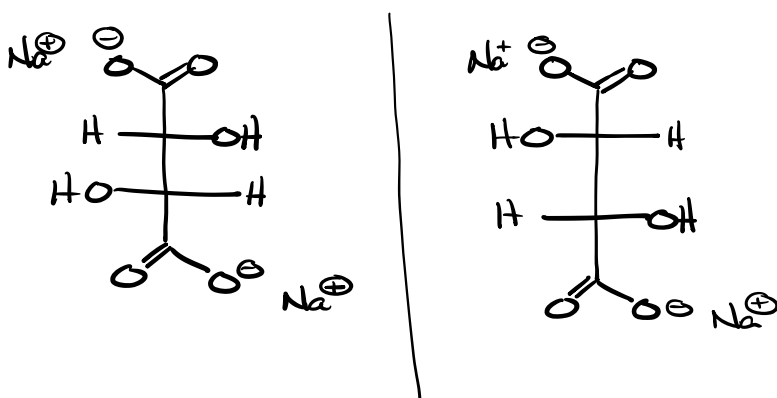
All physical properties except
the rotation of plane polarized light.

⇒ very difficult to separate them

1st time done Pasteur

Crystallized racemic (50/50) tartrate salts

Tartrate

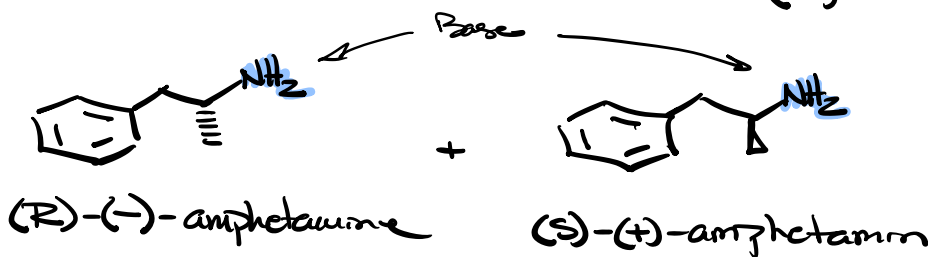
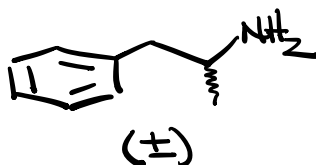


Enantiomers

Crystal structures different & Pasteur separated based on crystal pattern

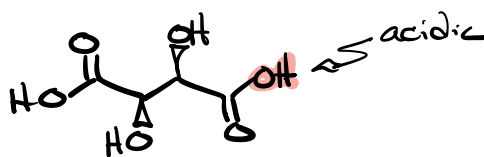
Chiral Resolving Agent

Racemic Amphetamine



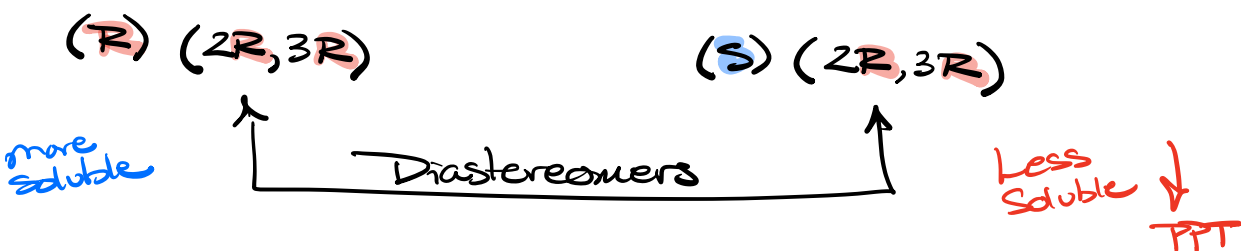
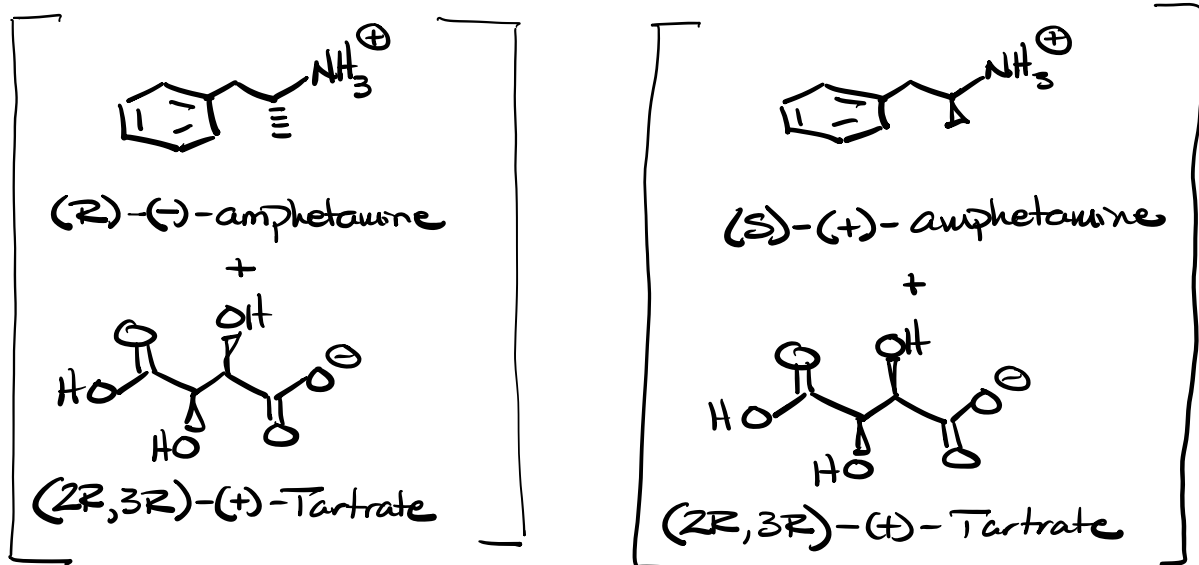
(R)-(-)-amphetamine

(S)-(+)-amphetamine



(2R,3R)-(+)-Tartaric acid
enantiomerically pure

Salts



Diastereomers have all different physical properties

different

BP

MP

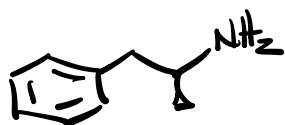
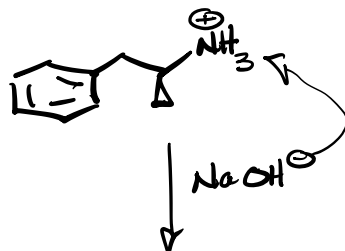
Solubility ←

Dipole moment

⋮

We use solubility to precipitate the less soluble diastereomeric pair

Salt \rightarrow ppt \rightarrow filter \rightarrow free base
 React w/ NaOH



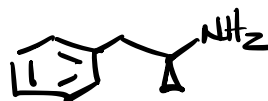
(S)-(+)-amphetamine

100% ee

Single isomer

Resolved

evap
 \leftarrow
 solvent



neutral compound

3rd type \Rightarrow Chiral Chromatography

Notations used

\pm Sign of rotation of light Chiral molecule optical rotation
 Physical property of molecule

d = dextrorotatory = +
 l = levorotatory = - same as \pm

R/S Configuration of a single stereogenic center based on Cahn-Ingold-Prelog rules



D/L Small Cap & Designate the position of highest priority group on last chiral center in Fischer projection

Chiral - molecule that rotates plane polarized light due to having stereogenic centers

achiral - molecule does not rotate plane polarized light. Either no stereogenic centers or meso

Meso - molecule has plane of symmetry and does not rotate plane polarized light

Racemic = 50/50 mix, (\pm)

Enantiomerically Pure = single isomer, 100% ee

Non-Racemic = not 50/50, has $>0\%$ ee