ISOMERS

nonidentical compounds with the same molecular formula

Constitutional Isomers

Structural

isomers with topology (that is, which atoms are bonded to which atoms) can only be interconverted by breaking and forming bonds

Conformational

isomers with the same bonding topology that are interconvertible by free rotation about bonds

Stereoisomers

isomers with the same bonding topology but differ in the spatial arrangements of the atoms and that can be interconverted only by breaking and forming bonds

Enantiomers

stereoisomers that are nonsuperimposable mirror images

Diastereomers

stereoisomers that are nonsuperimposable nonmirror images

Geometric Isomers

diastereomers caused by hindered rotation about a double bond or ring

Enantiomers: stereoisomers of a chiral substance that have mirror-images relationship. Enantiomers must have opposite configurations at all chirality centers

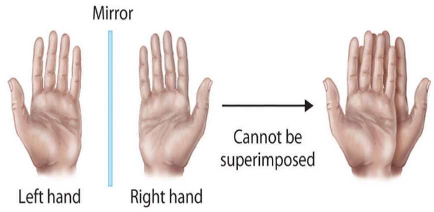
Diastereomers: non-mirror-image steroisomers; diastereomers have the same configuration at one or more chirality centers but differ at other chirality centers

Meso compound: a compound that contains chirality centers but is nevertheless achiral by virtue of a symmetrical plane

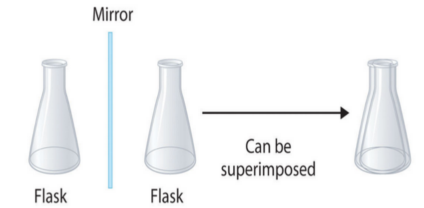
Chirality:

Chiral - has a non-superimposable image

Achiral - has a superimposable image



(a) Chiral objects

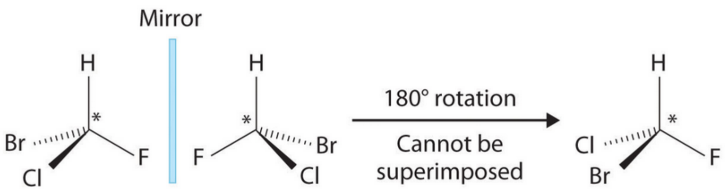


(b) Achiral objects

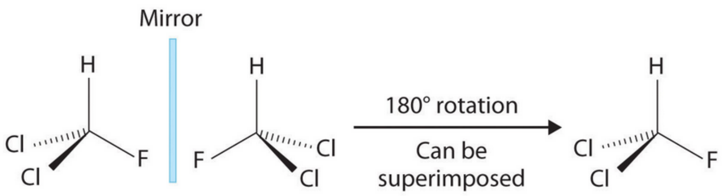
Cause of Chirality: Having an asymmetric center

What is an asymmetric center?

A center atom with 4 bonds to different groups



(a) Bromochlorofluoromethane



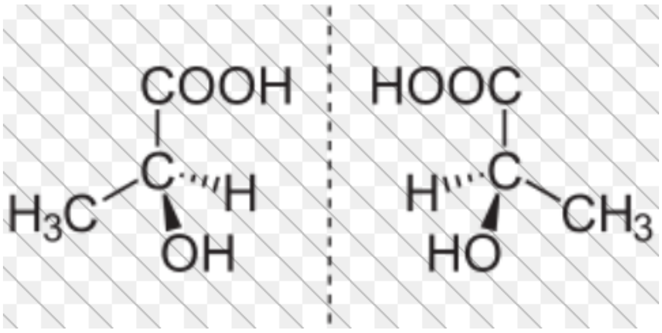
(b) Dichlorofluoromethane

Isomers with 1 asymmetric center:

A) Compound with 1 asymmetric center = 2 stereoisomers

B) Enantiomers - non-superimposable mirror images

(Enantiomers = chiral)



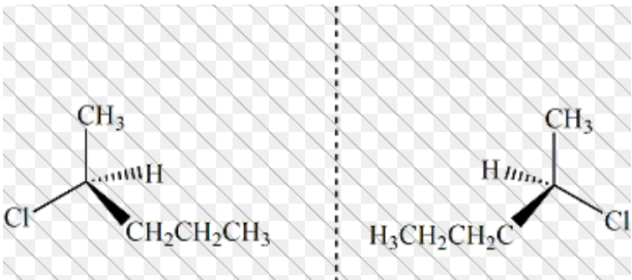
How to Draw and Name Enantiomers:

A) Use perspective (3-D) drawing rules

______ = in plane (2 bonds)

////////// = into page

 = out of page



Which is R and which is S?

Note: ////// and  must be adjcent to each other

B) Draw #1 enantiomer 1st, pretend mirror in between, draw mirror image

C) Naming an enantiomer:

1) When you have a pair of enantiomers, 1 will be R, other will be S

2) How to determine R or S configuration?

a.) # groups (atoms) based on priority (atomic # like in E/Z)

1 = highest priority 4 = lowest priority

b.) Orient molecule so lowest group (#4) is away from you (into paper on the ///// bond)

c.) See which way #1 to #2 goes (but don't actually draw arrows, as they are only for e- movement in rxns)

Right (Clockwise) = R 

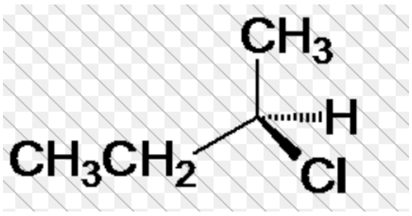
Left (Counterclockwise) = S ("sinister" = left in Latin)

d.) When doing enantiomers on paper only (no models)

1) If you have to rearrange groups so #4 is on the //////

Then when you find R or S, the previous structure before rearrangement was the opposite

Draw the enantiomer of the following, then ID each as R and S:



Chiral compounds are optically active:

A) Enantiomers have many of same properties (ex: BP, MP, solubility)

B) Polarized light interaction with enantiomers differs

C) Polarized light = oscillates in a single plane, Produced by passing through a polarizer

Normal light = (like the sun) consists of rays that oscillate in all directions

D) Molecular symmetry = (+) polarization

1) If polarized light passes through achiral compd = no rotation of light

2) If polarized light passes through chiral compd = change of lights

- If R enantiomer rotated polarized light

Then the S enantiomer will rotate polarized light .

Optically active = chiral compounds (rotates polarized light)

Optically inactive = achiral compounds (does NOT rotate polarized light)

E) Dextrorotary vs. Leuorotatory

Dextrorotary = compd rotates light (+) in name

Leuorotatary = compd rotates light (-) in name

NOTE: R or S don't tell if compound is (+) or (-)

The only way to know is to try it, then the enantiomer will have the opposite (+ or -) value

Measurement of light rotation:

$$[\alpha]^T_\lambda = \frac{\alpha}{l \times c}$$

α = observed rotation

$[\alpha]$ = specific rotation

T = Temp in C

λ = wavelength of the light

l = length of the tube (in dm)

c = concentration of the sample (in g/mL)

Ex: The observed rotation of 2.0 g of a compound in 50 mL of solution in a polarimeter tube 20 cm long is $+13.4^0$. What is the specific rotation of the compound?

Isomers with More Than One Asymmetric Center:

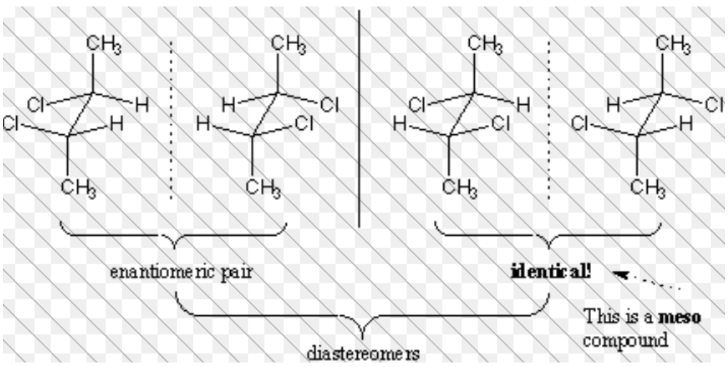
a compound can have a maximum of 2^n stereoisomers, where n equals the number of asymmetric centers

If drawn 2-D it is a Fischer Projection

- by convention, main carbon chain extending from top to bottom (solid line ______)
- vertical lines = represent bonds behind the plane of the paper ()
- horizontal lines = represent bonds that project out of the plane of the paper ()
- permitted to rotate them in the plane of the paper by 180° but by no other angle and can not flip them over (flipping them gives the enantiomer)

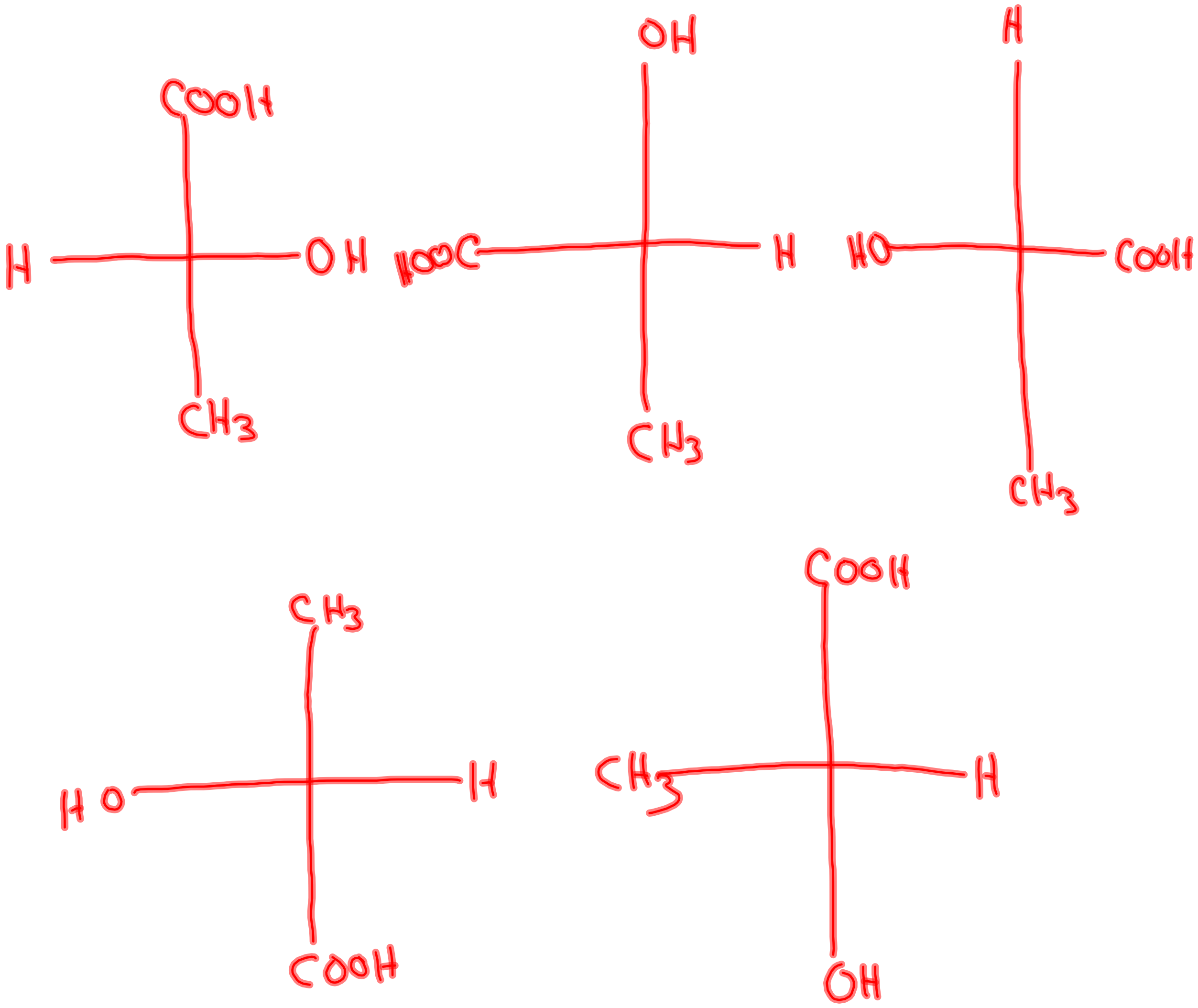
Let's remember what a **diastereoisomer** is?

- Stereoisomers that are not enantiomers (not identical and not mirror images)



Now - what did we say the defintion of a Meso compound was?

Fischer projections:



Draw the forms for:

ex. 2-bromo-3-chlorobutane

Draw the forms for:

ex. 2,3-dibromobutane

Draw the forms for the following:

2-amino-3-hydroxybutanoic acid

tartaric acid: 2,3-dihydroxybutanedioic acid

Facts about enantiomers, dasterioisomers, meso compounds:

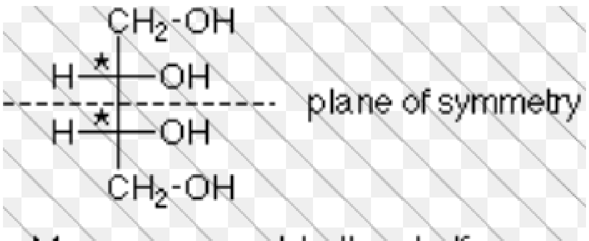
Enantiomers - identical physical and chemical properties except for their interaction with polarized light

Diasterioisomers - have different physical and chemical properties

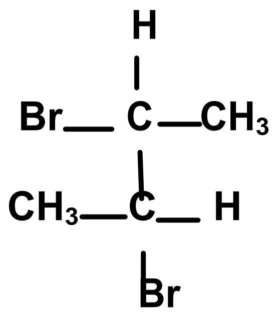
(ex: Diff MP, BP, solubilities and react wih an achiral reagent

Meso compounds - asymmetric centers and are optically inactive

Why are they optically inactive? Look at the following Meso compound and figure out why.



Meso compound, bottom half is mirror image of top half.



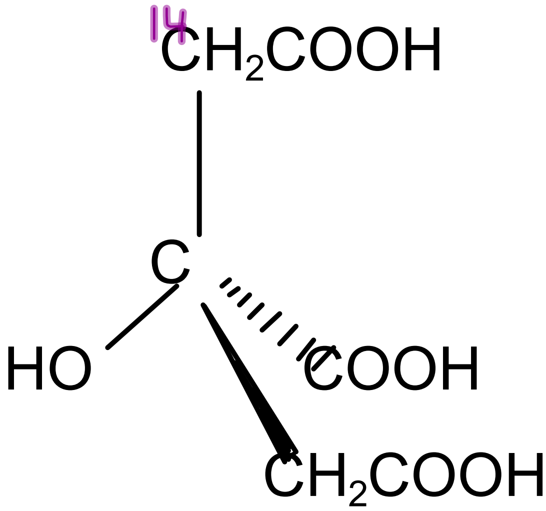
Is this a meso compound?

How can we recognize a meso compound?

How can enantiomers be separated?

1) Crystals rotate polarized light differently (R vs L)
2) Chromatography - prepare column so there is a chiral material in the column that the enantiomers will attract to with different affinities

#49)



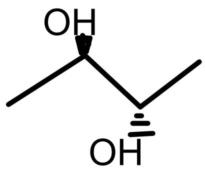
Asymmetric center: an atom that bear 4 different atoms or groups of atoms

Chiral: a compound that is chiral has the ability to rotate plane-polarized light

Achiral: not chiral

Racemic mixture (racemate) -->	d_{form} +	l_{form}
50/ 50 mixture	dextrorotatory	levorotatory
	(+)	(-)
	rotate light to the right	rotate light to the left

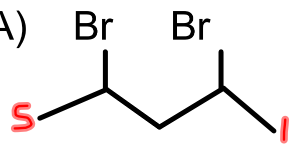
Meso compound: - contains two or more chiral centers
- it is achiral and does not exhibit optical activity
- a meso compound and its mirror image are superimposable and thus are identical structures



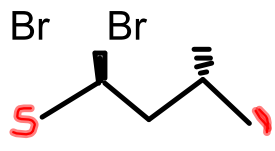
Is this molecule chiral or achiral?

Molecule (B) below is one of the configuration isomers of the structure (A)

(A)



(B)



1) Draw a Fischer Projection for molecule (B)

2) Determine the stereo-configuration of the carbons in molecule (B) (R, S, or none)

C2 ____ C3 _____ C4 _____

Convert the following name to skeletal structure.

(3S, 4S) - 2, 3, 4 - trimethylhexane

Convert the above name and skeletal structure to a Fischer projection with the longest carbon chain vertical and cross points representing C3 and C4

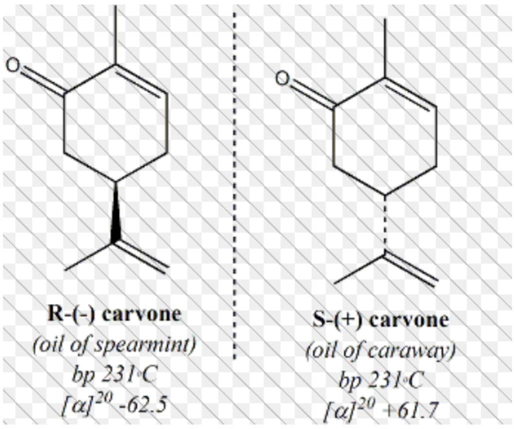
Receptors: Protein that binds a specific molecule

Due to a receptor being chiral, it will only bond the R or S enatiomer

A) Your Smell: molecules bind to reptors, and YES it also differentiates R and S enantiomers

- Your nose can differentiate 10,000 smells

Ex:



B) Drugs in your body - work by "binding" to a cell surface receptor

YES - they also differentiate R and S enantiomers

Example of drugs and receptors:

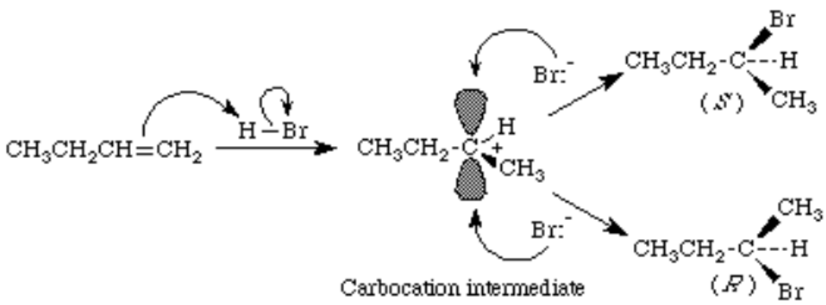
1) 1957 drug for insomnia and morning sickness

- is a dextrorotatory isomer
- commercial drug is a racemic mixture
- levorotatory isomer = damage to fast-growth cells = caused horrible birth defects (DID NOT KNOW ISOMER EXISTED AT TIME)
- it was later found that the isomer could racemize (interconvert) in the body
- Now used as a cancer drug

The stereochemistry of reactions:

A) Only concerned with stereochemistry of the products if the product has an asymmetric center

B) When a reactant with that does NOT have asymmetric center reacts with an achiral reagent and a product with 1 asymmetric center is made, the product will ALWAYS be a racemic mixture



According to this picture, why will it always yield a racemic mixture?

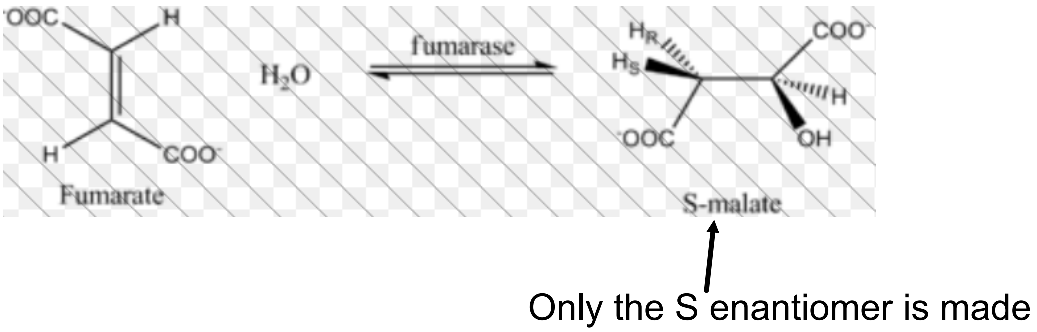
Stereochemistry of enzyme - catalyzed reactions:

Biochemistry - chemistry associated with living organisms and the reactions within them

Enzymes - proteins that catalyze reactions

A) when an enzyme catalyzes a reactant that forms a product with an asymmetric center, only 1 stereoisomer is formed

- WHY?
  - The enzyme is chiral, a chiral binding site restricts its delivery to only 1 side of the reactants functional group



B) An achiral reagent reacts identically to oth enantiomers (like your socks fitting either of your feet)

C) A chiral reagent reacts differently with each enantiomer (sometimes not at all with one of them) - like you putting your left shoe on your right foot

Lesson learned - chiral reactants need specific enzymes, different from their enantiomers needed enzyme