

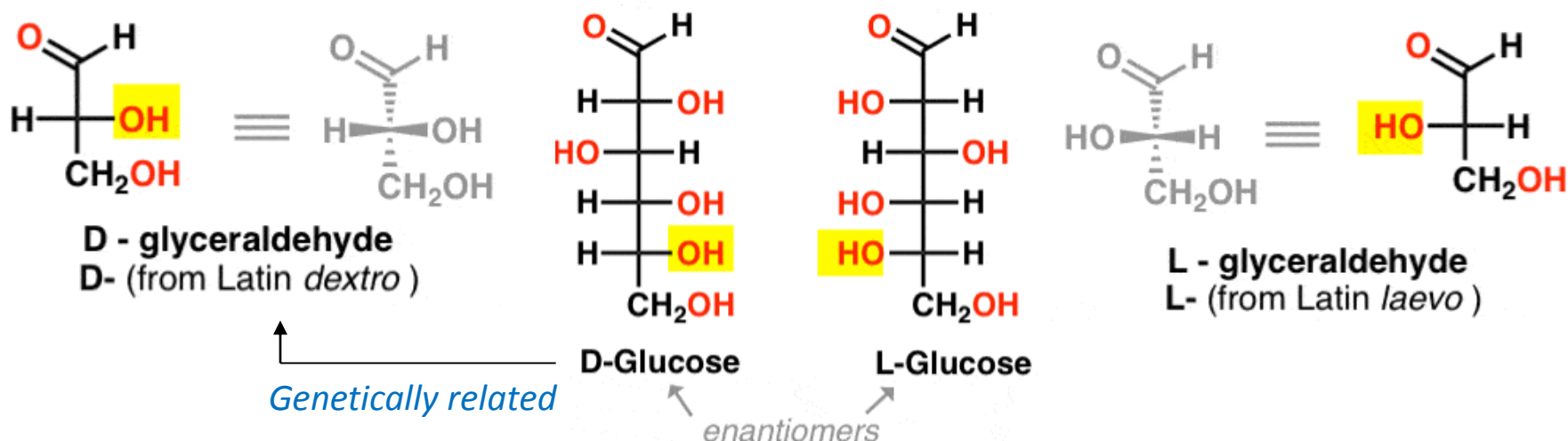
CYI101
Common CHEMISTRY(Organic)

Stereochemistry: Nomenclature
R/S, D/L and E/Z

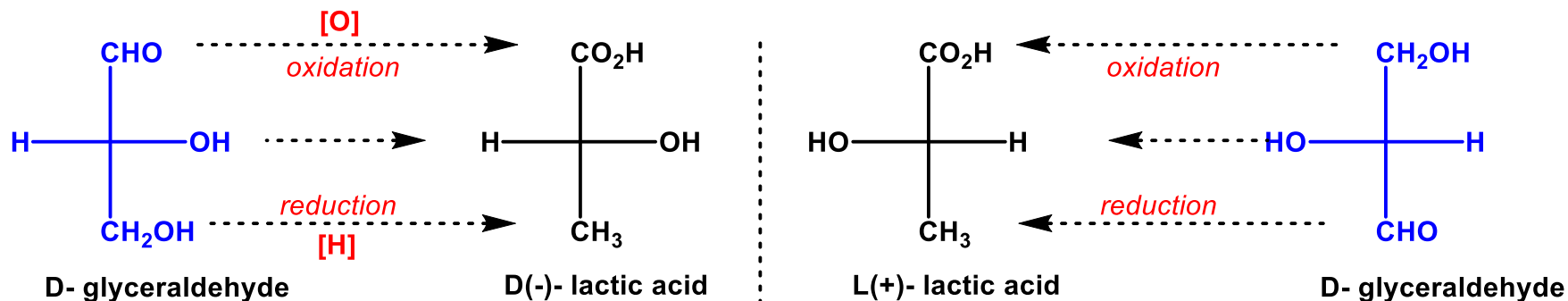
Configurational Nomenclature

- 1890, Emil Fisher while working in the Sugar and Amino acid chemistry

Fischer's D/L nomenclature



This genetic nomenclature, however, did not work since in many cases, both the enantiomers of a compounds may be chemically correlated to the same glyceraldehyde.

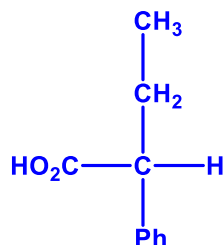


Fisher D/L-nomenclature turns out CONFUSION!

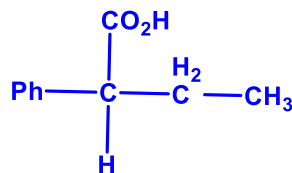
Configurational Nomenclature

- 1906, To circumvent the difficulty, **Rosanoff** modified the system and suggested a projection nomenclature according to the following conventions:
 - As in Fischer's system, the molecule is written with the longest carbon chain placed vertically.
 - The most highly oxidised end of the chain is placed at the top.
 - If in the projected structure, the OH group (or any negative group) at the bottom-most chiral centre (C-5 in glucose) is on the right hand side, the molecule is given D-configuration and if is on left, the molecule is given L configuration. The fisher-Rosanoff system does not refer to the origin of the compound (non-generic.)

Problem: 1-phenylbutyric acid:



1- phenylbutyric acid

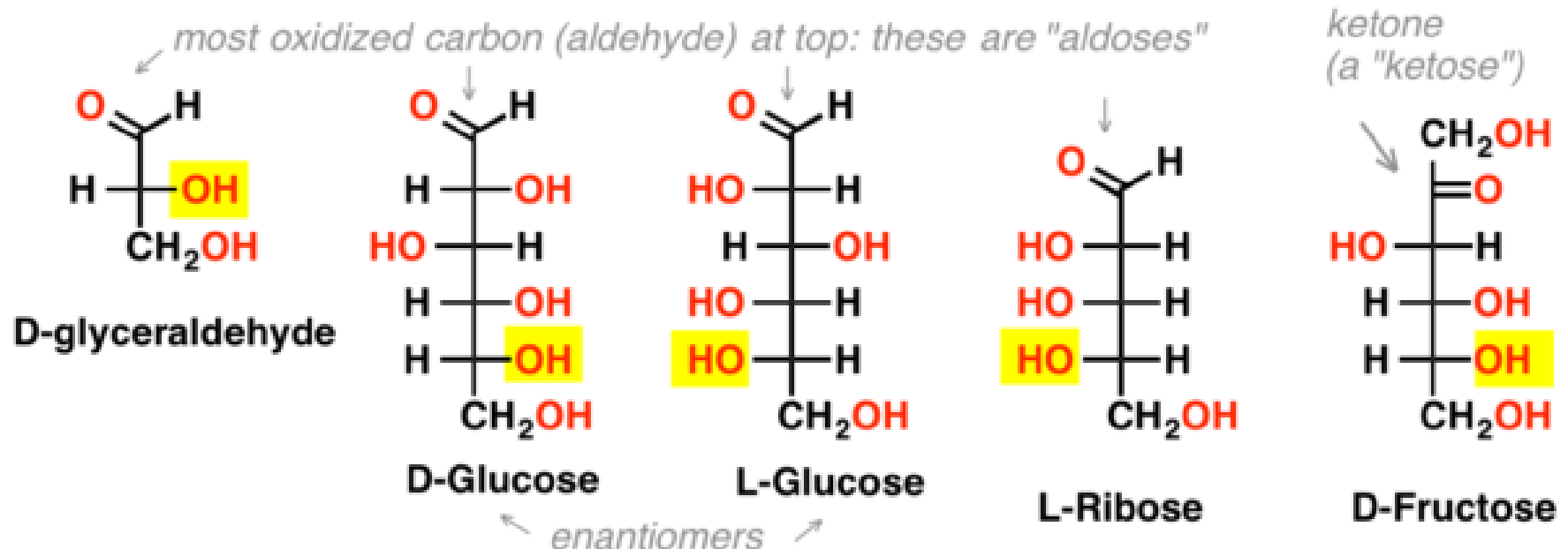


1- phenylbutyric acid

D- and L- Sugars

For a sugar drawn in the Fischer projection with the most oxidized carbon at the top:

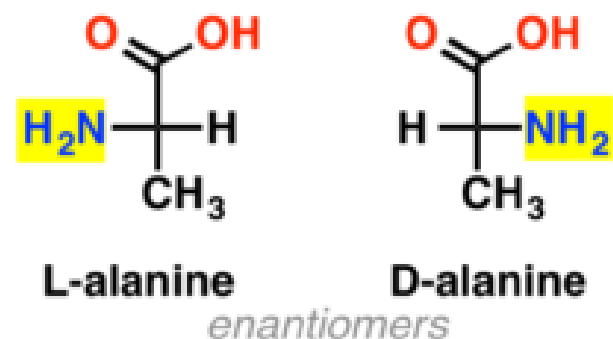
- If the OH on the bottom chiral center points to the **right**, the sugar is **D**
- If the OH on the bottom chiral center points to the **left**, the sugar is **L**



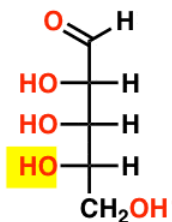
L- and D- is a means of describing the **absolute configuration** of a molecule that pre-dates *R* and *S* but is still used for some biological molecules (sugars, amino acids). It's a quick way of denoting enantiomers: e.g. L-glucose and D-glucose are enantiomers.

L- and D- have no relation to the optical rotation of a molecule.

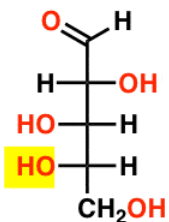
The D- L- system can also be applied to other chiral molecules, e.g. amino acids:



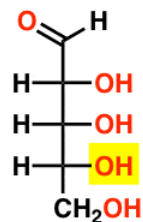
Five carbon aldehyde sugars (aldopentoses)



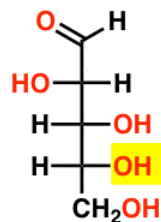
L-Ribose



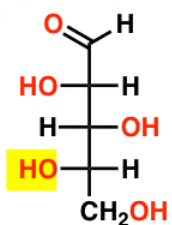
L-Arabinose



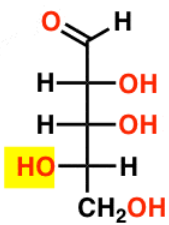
D-Ribose



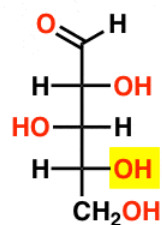
D-Arabinose



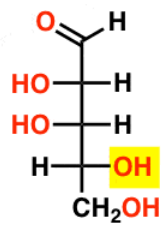
L-Xylose



L-Lyxose

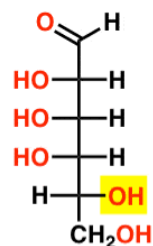


D-Xylose

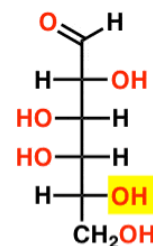


D-Lyxose

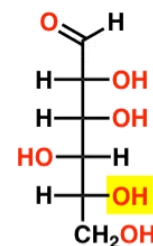
Six carbon sugars (hexoses) D-sugars



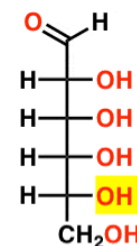
D-Talose



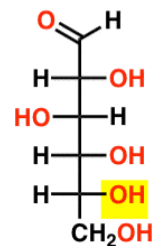
D-Galactose



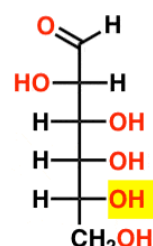
D-Gulose



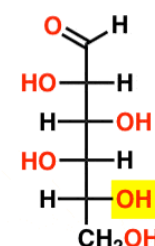
D-Allose



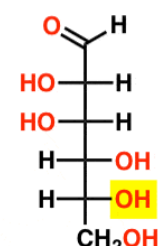
D-Glucose



D-Altrose



D-Idose



D-Mannose

Labeling Stereogenic Centers with *R* or *S*

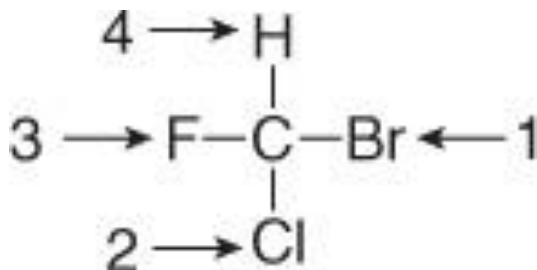
- Since enantiomers are two different compounds, they need to be distinguished by name. This is done by adding the prefix

R ("rectus" → Latin= "right")

or *S* ("Sinister" → Latin= "left")

to the IUPAC name of the enantiomer.

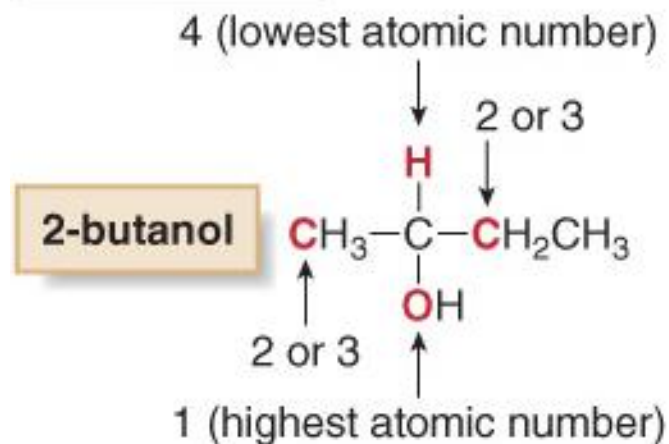
- Naming enantiomers with the prefixes *R* or *S* is called the **Cahn-Ingold-Prelog** [**CIP** system (1951-1966)].
- To designate enantiomers as *R* or *S*, priorities must be assigned to each group bonded to the stereogenic center, *in order of decreasing atomic number*. The atom of highest atomic number gets the highest priority (1).



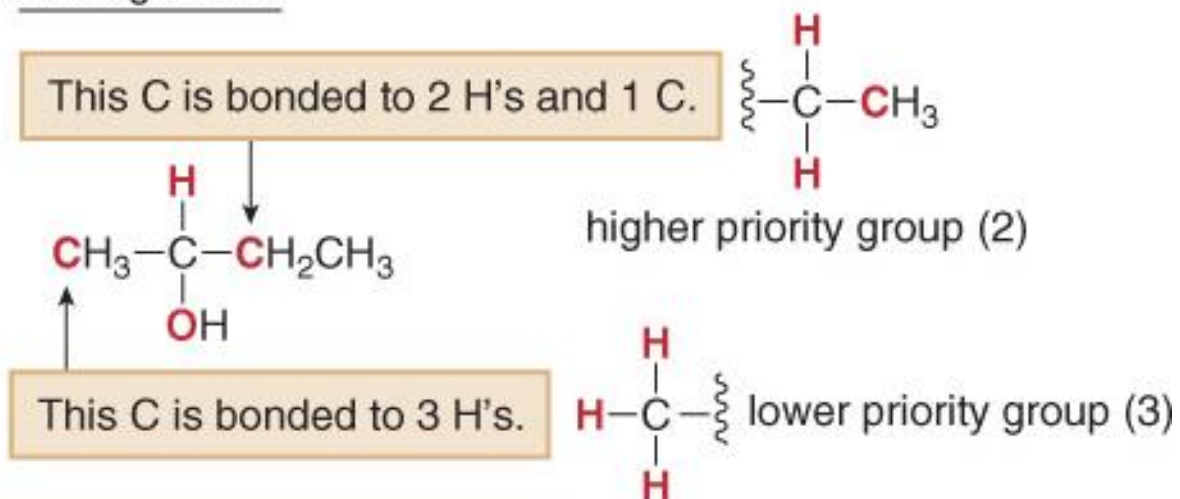
Labeling Stereogenic Centers with *R* or *S*

- If two atoms on a stereogenic center are the same, assign priority based on the atomic number of the atoms bonded to these atoms. *One atom of higher atomic number determines the higher priority.*

Following rule 1:



Adding rule 2:



Labeling Stereogenic Centers with R or S

- If two isotopes are bonded to the stereogenic center, *assign priorities in order of decreasing mass number*. Thus, in comparing the three isotopes of hydrogen, the order of priorities is:

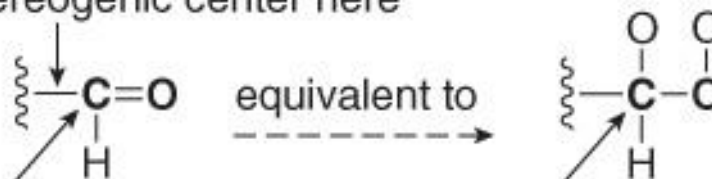
Tritium (T) > Deuterium (D) > Hydrogen (H)

	Mass number	Priority
T (tritium)	3 (1 proton + 2 neutrons)	1
D (deuterium)	2 (1 proton + 1 neutron)	2
H (hydrogen)	1 (1 proton)	3

Labeling Stereogenic Centers with *R* or *S*

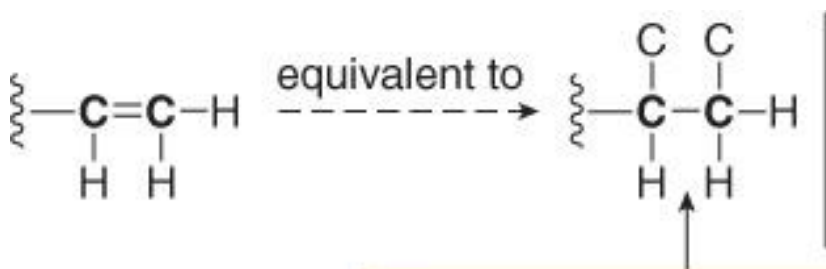
- To assign a priority to an atom that is part of a multiple bond, *treat a multiply bonded atom as an equivalent number of singly bonded atoms*. For example, the C of a C=O is considered to be bonded to two O atoms.

bonded to a stereogenic center here

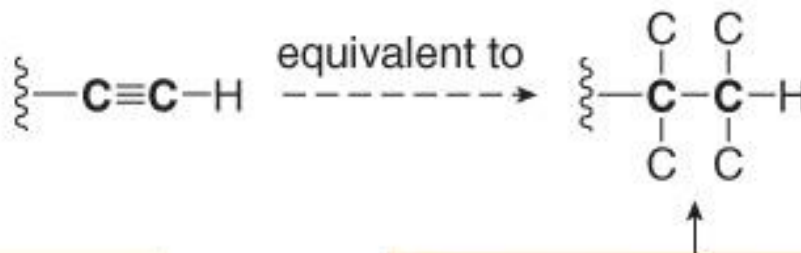


Consider this C bonded to 2 O's.

- Other common multiple bonds are drawn below:

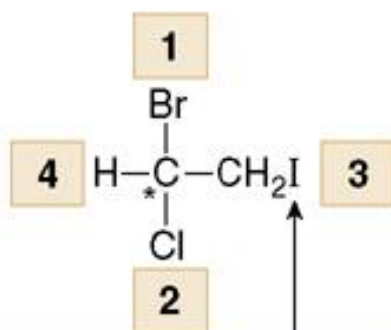


Each atom in the **double** bond is drawn **twice**.

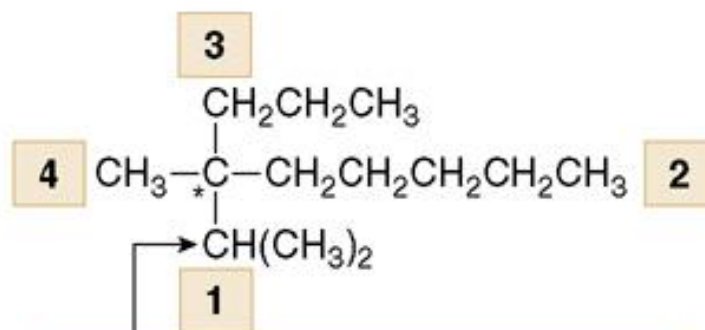


Each atom in the **triple** bond is drawn **three** times.

Labeling Stereogenic Centers with *R* or *S*

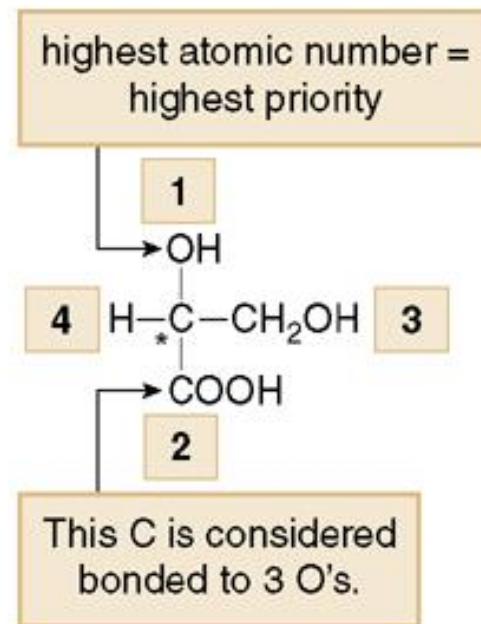


I is NOT bonded directly to the stereogenic center.



This is the highest priority C since it is bonded to 2 other C's.

[* = stereogenic center]

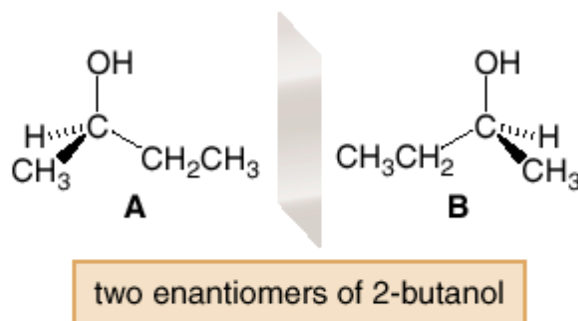


This C is considered bonded to 3 O's.

Labeling Stereogenic Centers with *R* or *S*

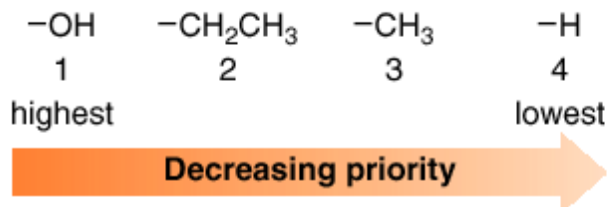
- Assign ***R*** or ***S*** to a Stereogenic Center
- Example: Label each enantiomer as *R* or *S*

Step [1]:



Assign priorities from 1 to 4 to each group bonded to the stereogenic center.

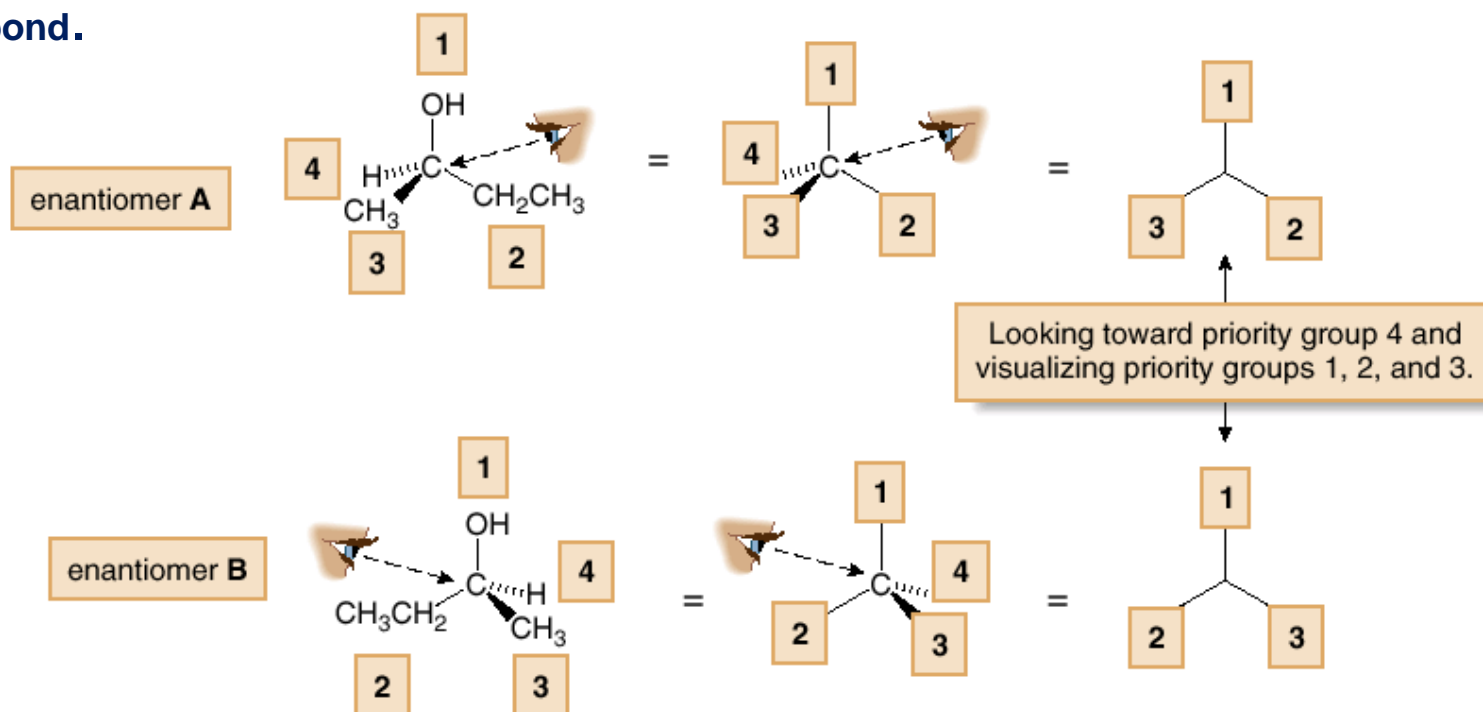
- The priorities for the four groups around the stereogenic center in 2-butanol were given in Rule 2, on page 172.



Labeling Stereogenic Centers with *R* or *S*

Step [2]: Orient the molecule with the lowest priority group (4) back (on a dash), and visualize the relative positions of the remaining three groups (priorities 1, 2 and 3).

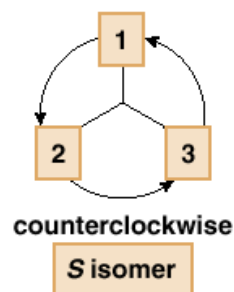
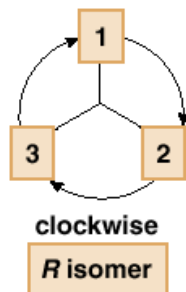
- For each enantiomer of 2-butanol, look toward the lowest priority group, drawn behind the plane, down the C-H bond.



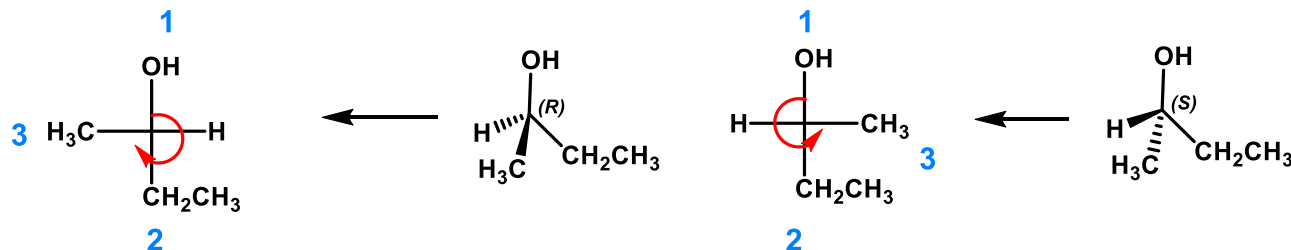
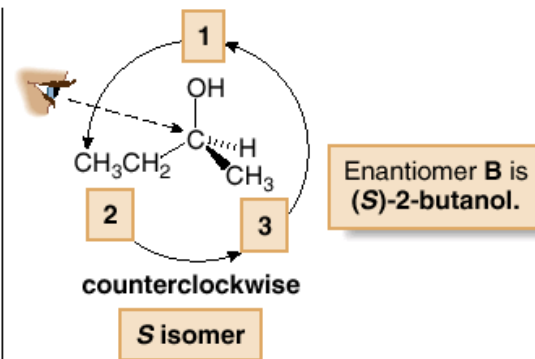
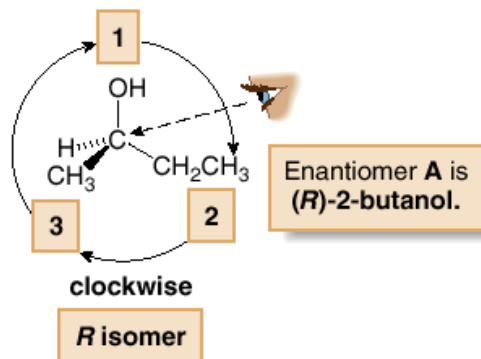
Labeling Stereogenic Centers with *R* or *S*

Step [3]: Trace a circle 1 \rightarrow 2 \rightarrow 3

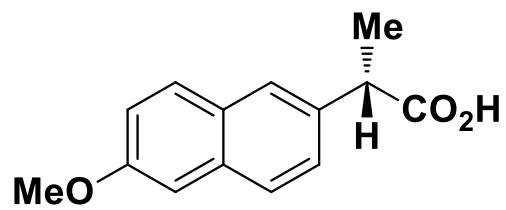
- If tracing the circle goes in the **clockwise** direction-to the right from the noon position-the isomer is named ***R***
- If **counterclockwise** direction-to the left from the noon position-the isomer is named ***S***



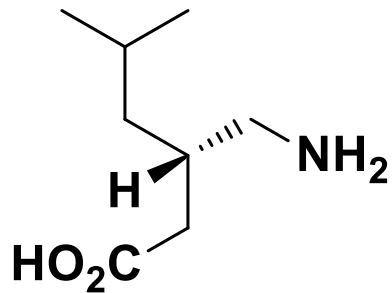
- The letters *R* or *S* precede the IUPAC name of the molecule. For the enantiomers of 2-butanol:



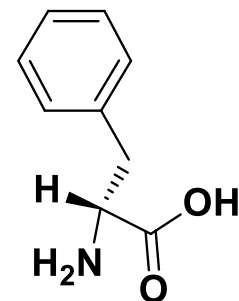
Quick Test



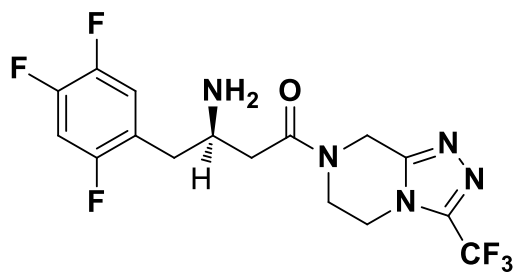
(S)



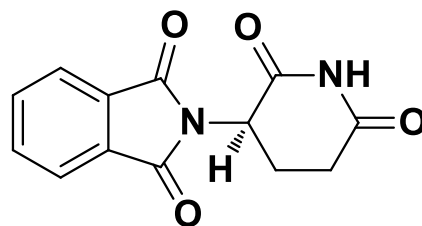
(S)



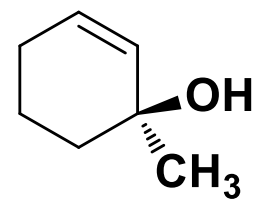
(R)



(R)



(R)

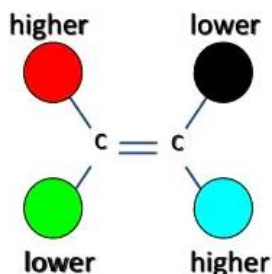


(S)

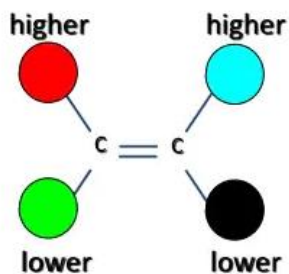
The E (Trans) / Z (Cis) Notational System

E–Z configuration, or the **E–Z** convention, is the **IUPAC** preferred method of describing the absolute stereochemistry of double bonds in organic chemistry.

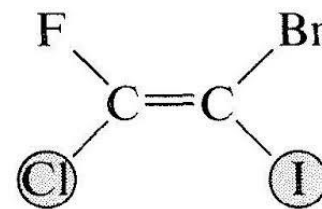
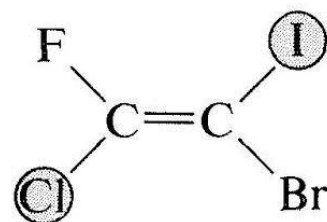
- **E** : higher ranked substituents on opposite sides
- **Z** : higher ranked substituents on same side



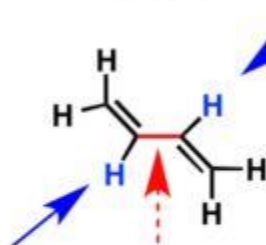
Entgegen



Zusammen



" s-trans "

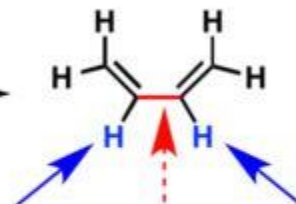


C–C sigma bond

Notice that the two hydrogens are on the **opposite side ("trans")** of the (red) C–C sigma bond

rotation about the
(red) C–C bond

" s-cis "



C–C sigma bond

Notice that the two hydrogens are on the **same side ("cis")** of the (red) C–C sigma bond