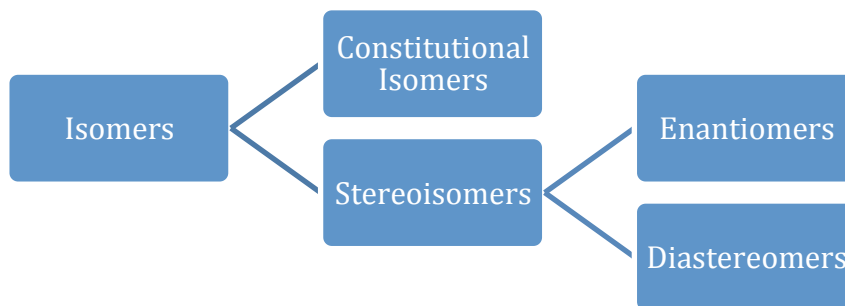
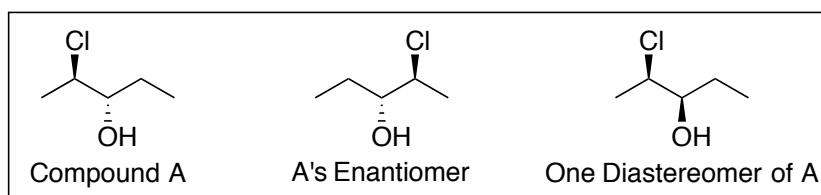


Chapter 4 - Stereochemistry Review

Chemistry 233

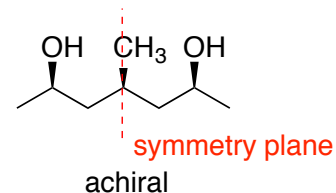
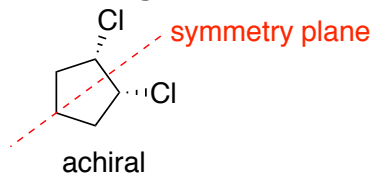
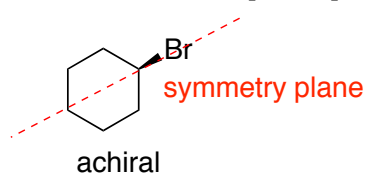


- Isomers – Different compounds with the same molecular formula.
- Constitutional Isomers – Compounds with the same molecular formula but different atom connectivity.
- Stereoisomers – Compounds with the same atom connectivity but a different orientation of the atoms in space.
- Enantiomers – Stereoisomers that are non-superimposable mirror images.
- Diastereomers – Stereoisomers that are non-superimposable and are not mirror images.

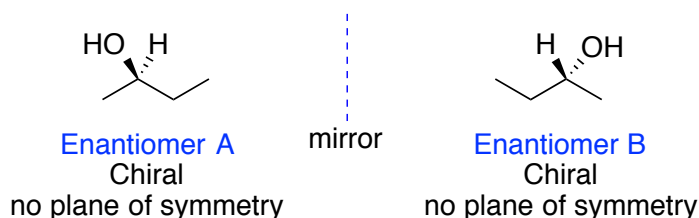


Chirality

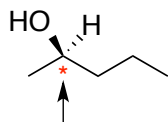
A molecule will be **achiral** if it has a plane of symmetry or a center of symmetry. If a molecule is achiral it can be superimposed on its mirror image and thus does not have an enantiomer.



A compound is **chiral** if it cannot be superimposed on its mirror image. A chiral compound will have two enantiomeric forms.

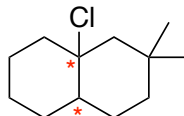


Asymmetric Center (Chiral Center) – An atom (usually C) containing four different groups.



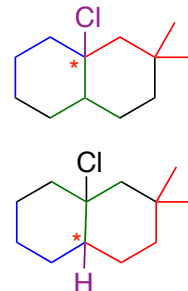
4 different things attached

- methyl group
- propyl group
- OH
- H

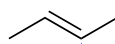
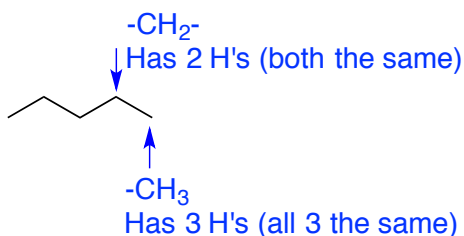


Two asymmetric centers

Sometimes you have to trace around to look for a point of difference in order to determine if you have 4 different groups.



Certain types of carbon can immediately be excluded from consideration as an asymmetric center because it can never have four different groups around it.

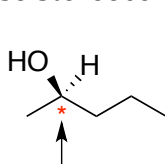


an sp^2 carbon
only has 3
groups (never 4)



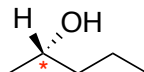
an sp carbon
only has 2
groups (never 4)

Stereocenter – An atom about which an exchange of two groups produces a stereoisomer. The stereocenter definition is more broad than the asymmetric center definition. All asymmetric centers are also stereocenters.

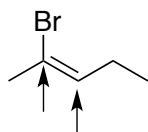


Asymmetric Center
Stereocenter

Switch groups at
the stereocenter

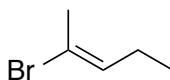


Stereoisomer of the first molecule
(Pair of enantiomers)



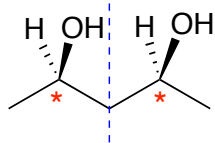
Stereocenters, but
not asymmetric centers

Switch groups at
one stereocenter



Stereoisomer of the first molecule
Non-superimposable, not mirror images
(Pair of diastereomers)

Meso compound – a compound that contains two or more asymmetric centers, but is achiral due to a plane of symmetry.

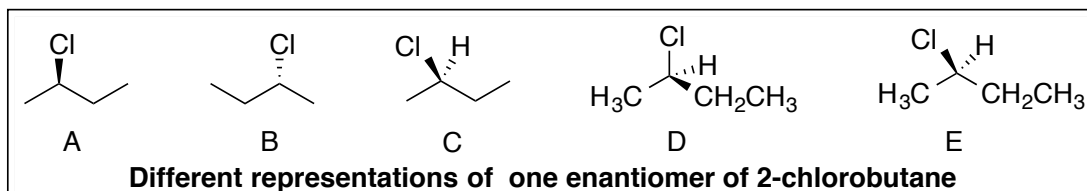


Symmetry Plane

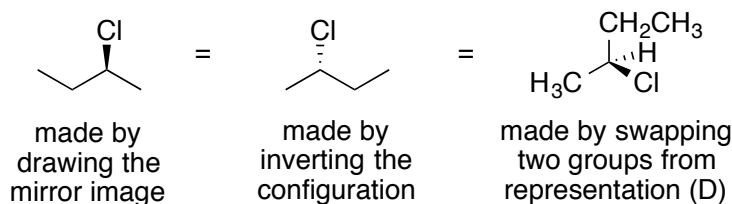
This compound has two asymmetric centers, however, it has a plane of symmetry. This plane of symmetry makes it achiral. This is by definition a meso-compound.

Drawing Chiral Molecules

It should be noted that there are several different, yet correct, ways to represent the 3D structure of a chiral molecule. Below are five different representations of one enantiomer of 2-chlorobutane. Convince yourself that these are all the same molecule. Representation (A) simply shows the stereochemistry of the chlorine. Since the two carbon bonds are in the plane and $-Cl$ is out, you can assume $-H$ is back. Representation (C) is the same as (A) with the $-H$ drawn in. Representation (B) is just (A) flipped horizontally. Representations (D) and (E) show only the bonds at the chiral center while all others are condensed. Using one of these structures we can also draw the other enantiomer by 1. Drawing the mirror image or 2. Inverting the configuration (swapping 2 groups).



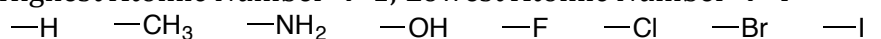
The Enantiomer of A:



R/S Configurations

- Look at the four atoms directly attached to the asymmetric center.
- Prioritize these atoms based on atomic number

- Highest Atomic Number \rightarrow 1; Lowest Atomic Number \rightarrow 4



Increasing Atomic Number
Increasing Priority

- If there is a tie between two or more groups, move to the next atom out in the chain and compare.

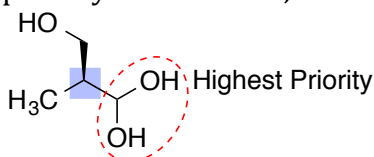


Increasing Atomic Number of the 2nd Atom Out
Increasing Priority

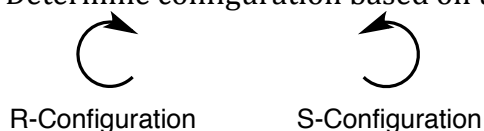
- Atoms with a double or triple bond are considered as having two (or three) bonds to phantom atoms.



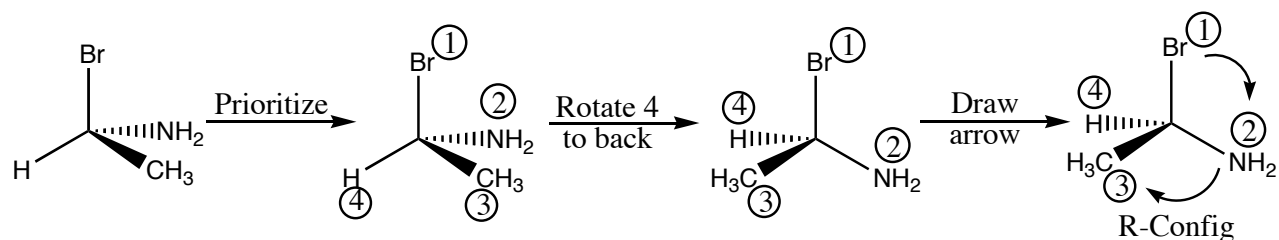
- When two carbons have substituents of the same priority, but one has more of the priority substituents, this carbon is given priority.



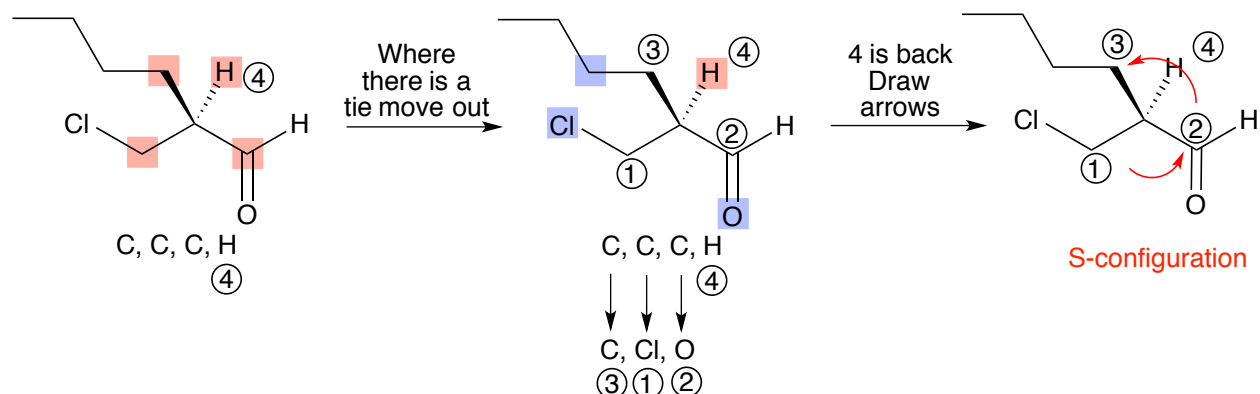
3. Orient molecule so that the lowest priority group (group 4) is pointing to the back.
4. Draw a curved arrow from group 1→2 and from 2→3.
5. Determine configuration based on the direction of the curved arrows.



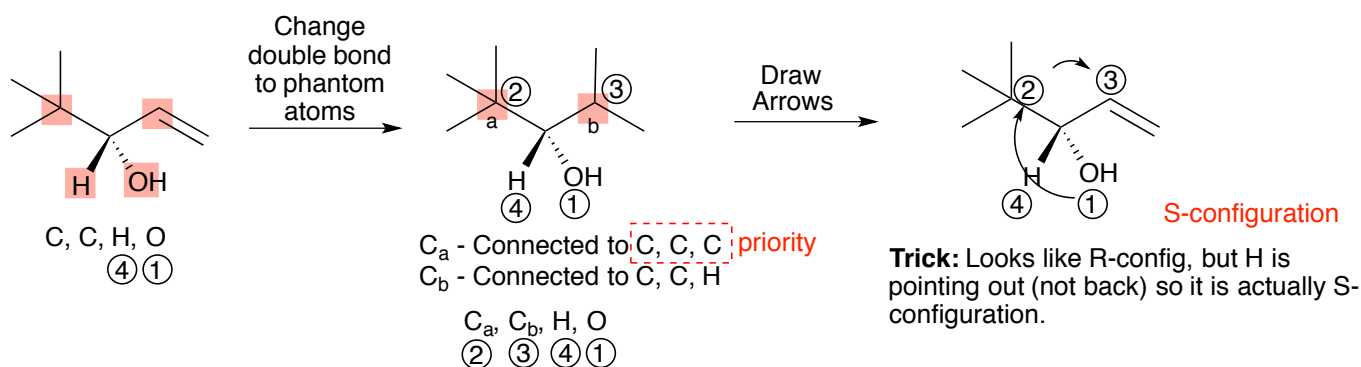
Example 1:



Example 2:



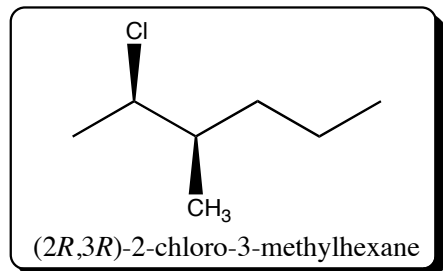
Example 3:



In example 3, a common and very useful trick was used. Rather than rotating the molecule to put the priority 4 group in the back, you can leave it pointing out. Draw your arrows as usual, but reverse the configuration.

Naming using the *R/S* Convention

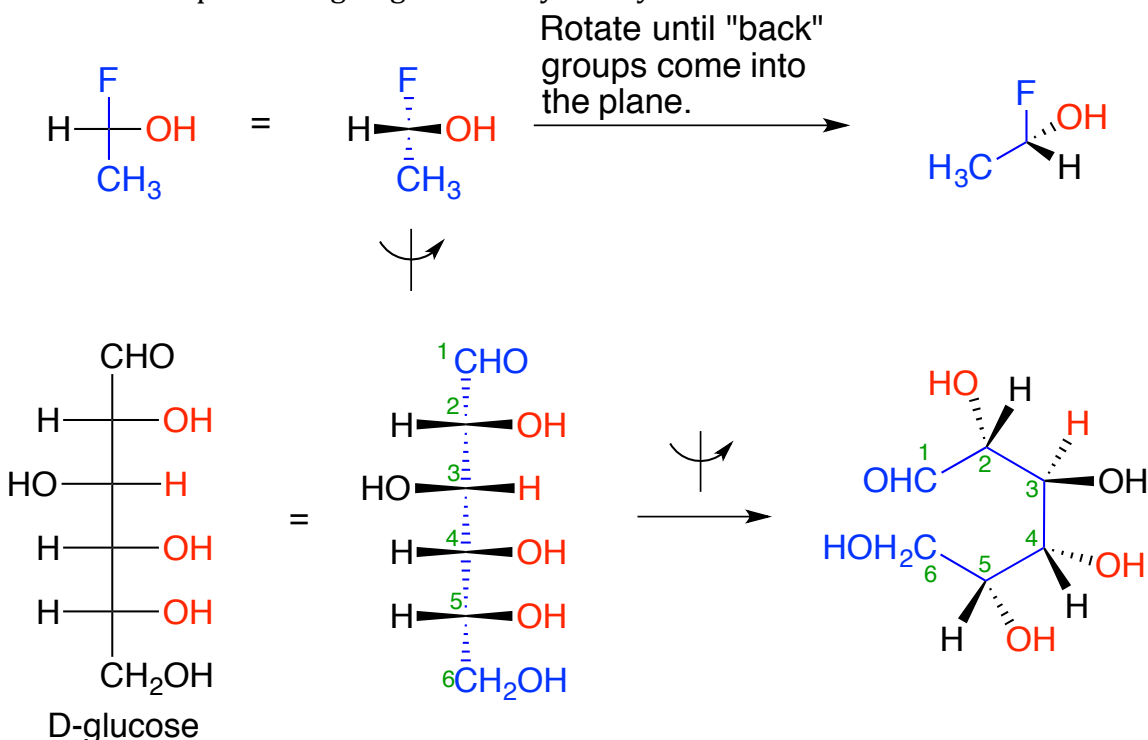
- Name chiral compound as usual with IUPAC nomenclature
- Identify the configuration of the chiral center(s) by placing the configuration of the chiral center(s) in parenthesis before the regular IUPAC name.
- Within the parentheses, list the carbon number of the stereocenter followed by the configuration at that carbon. If more than one stereocenter is present separate the configurations by a comma.



Fisher Projections

The Fisher projection is a different way to view molecules. Fisher projections are most useful for compounds with multiple chiral centers (such as monosaccharides).

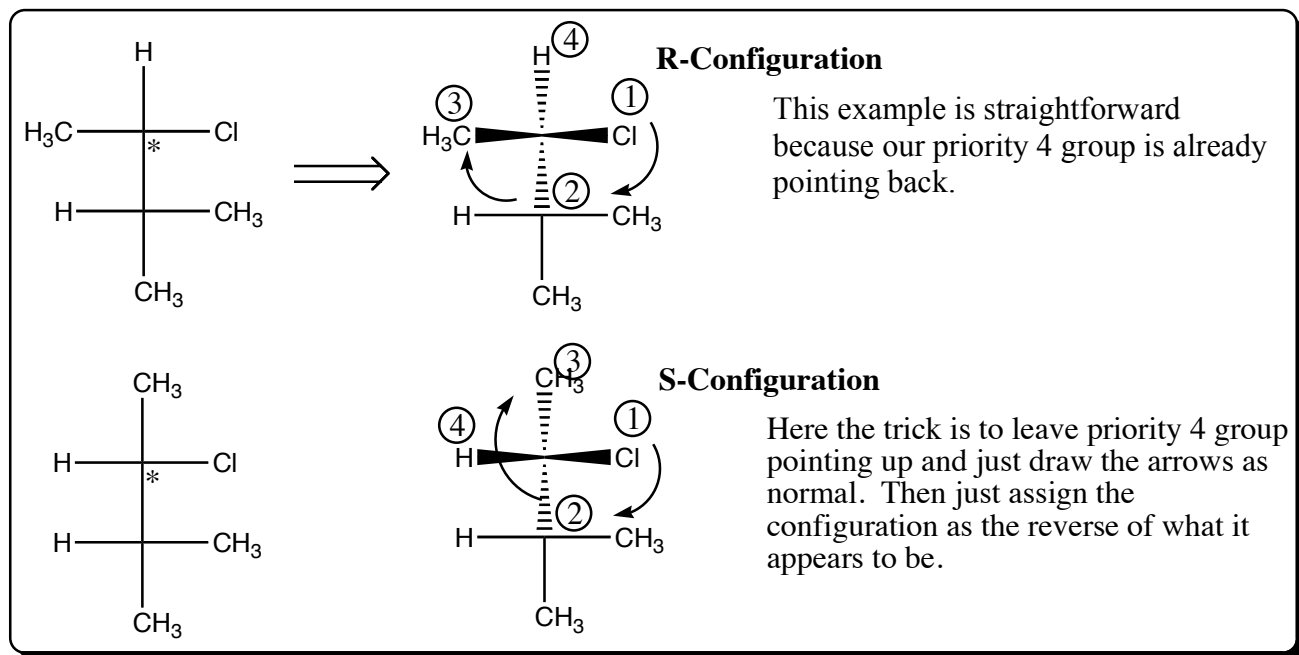
In the Fisher projection, groups along the horizontal plane are coming out towards you, while groups in the vertical plane are going back away from you.



All three structures listed above are exactly same. They are just different representations.

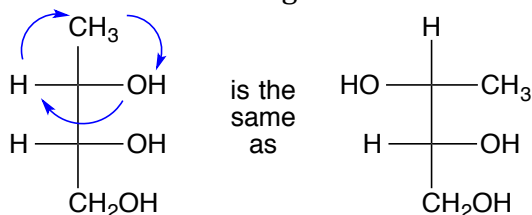
You should notice that there are 4 chiral centers in D-glucose. You should be able to assign *R/S* configuration for each of these asymmetric centers by looking at the Fisher Projection.

Example: Determining R/S Configuration from a Fischer Projection

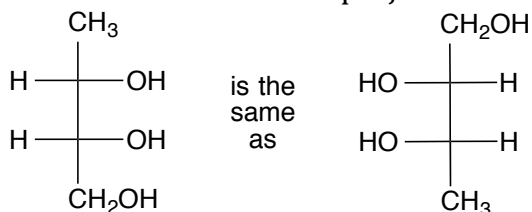


Some Tricks for Working With Fischer Projections

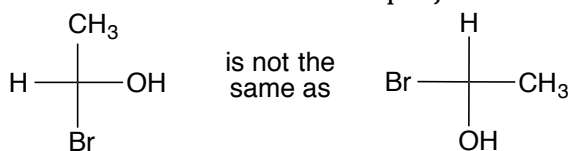
- You can rotate the top three groups or bottom three groups on a Fischer projection at will without changing the identity of the compound. You must rotate all three groups the same direction when doing this.



- You can rotate a Fischer projection 180°



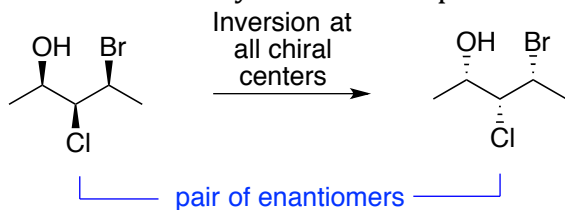
- You can **not** rotate a Fischer projection 90°



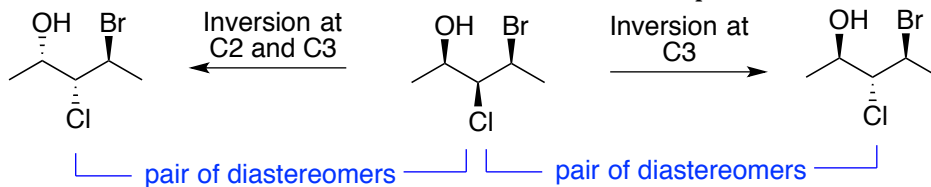
R-configuration $\xrightarrow{\text{switches to}}$ S-configuration
during a 90° rotation

Some Tricks for Compounds that Have 2 or More Chiral Centers

- Inversion at every chiral center produces an enantiomer of your starting compound.



- Inversion of one or more, but not all chiral centers produces a diastereomer.



- Sometimes you have to rotate around some single bonds to orient molecules in an easy to compare fashion.

