

# Lecture VI: Chirality

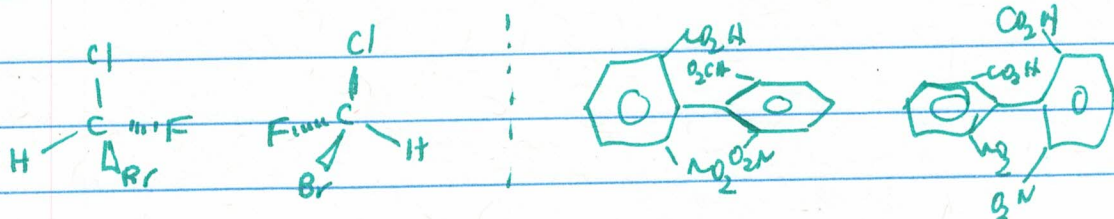
01-27-2020

When looking at point groups, we've seen that objects belonging to  $C_1$ ,  $C_n$ , and  $D_n$  <sup>point</sup> space groups cannot be superimposed to their mirror images — they are CHIRAL.

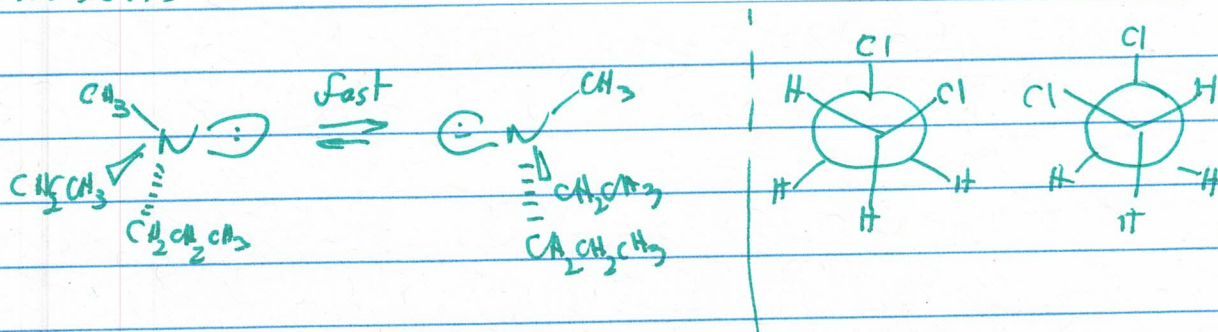
Chirality is the property of objects that cannot be superimposed to their mirror images. Hands, feet, corkscrews, gloves, spiral staircases all belong to this class.

Stereoisomers that are non-superimposable mirror images of one another are called ENANTIOMERS (or antipodes, optical antipodes, or enantiomorphs in older literature). All other stereoisomers are DIASTEREOMERS. Two molecules can either be enantiomers or diastereomers of each other — but not both!

Enantiomers can be stable and isolable:



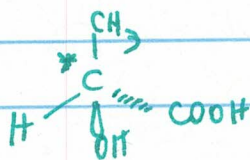
Or transient:





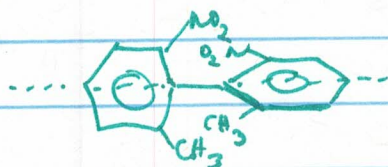
Residual stereoisomers are those that can be distinguished under specific conditions by a given technique. The compounds in the top row would have two enantiomers. Those on the bottom - only one.

Chirality is a property of the molecule as a whole, and it is ultimately symmetry-related. But because of the focus on the atomic structure, a concept of a chiral center is introduced:



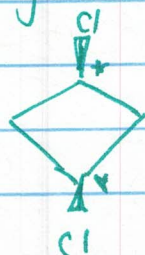
\* Carbon (or another element), which is tetrahedral and substituted with four different groups

This leads to problems:

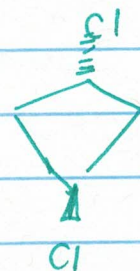
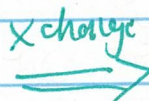


no chiral center, but chiral axis  
point chirality vs. axial chirality  
will come back to this

More general concept is that of a stereogenic center: atom on which an exchange of two ligands results in a set of stereoisomers. All chiral centers are also stereogenic, but not all stereogenic centers are chiral:



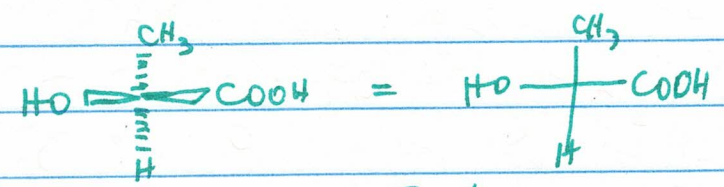
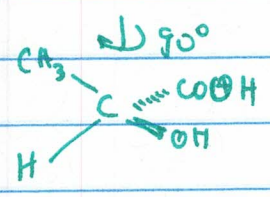
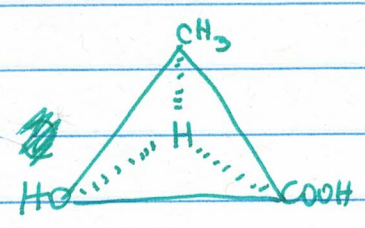
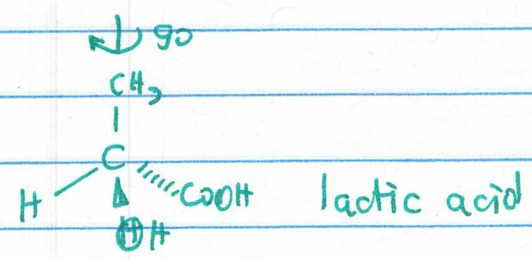
\* = stereogenic  
but not chiral



diastereomer

A chirotopic point is any point in a molecule that has a chiral environment. In a chiral molecule, any point is chirotopic.

Representing enantiomers

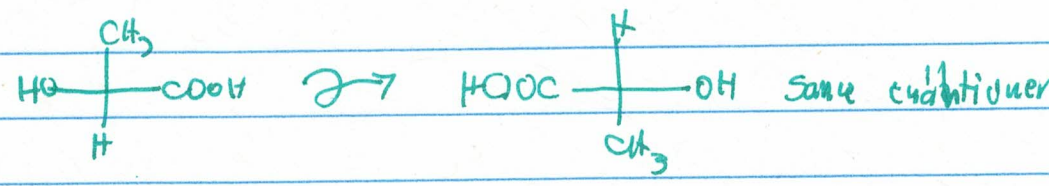


implied

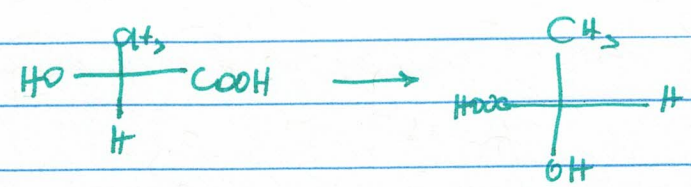
Fischer projection

For a chiral center, there are 24 (=4!) ways of writing a Fischer formula: 12 for one enantiomer, and 12 for the other. Allowed manipulations of Fischer formulas:

- ① Rotation by 180°



- ② Three-way permutations:



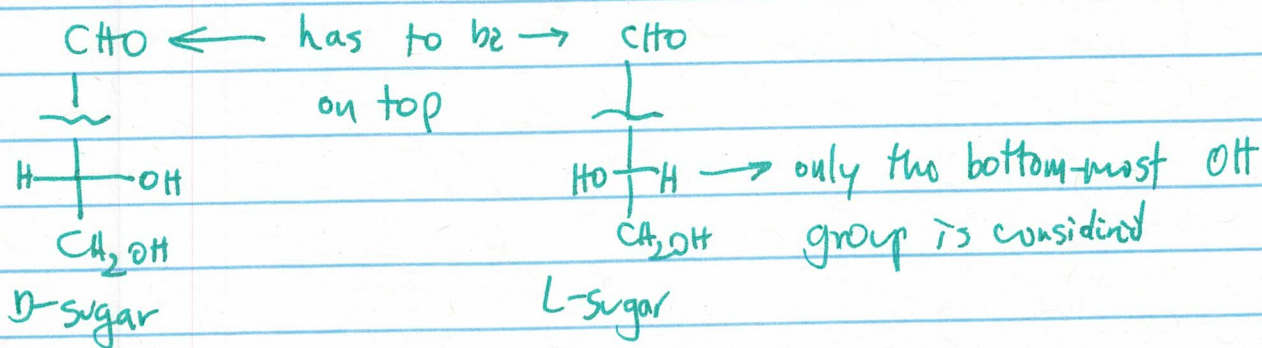
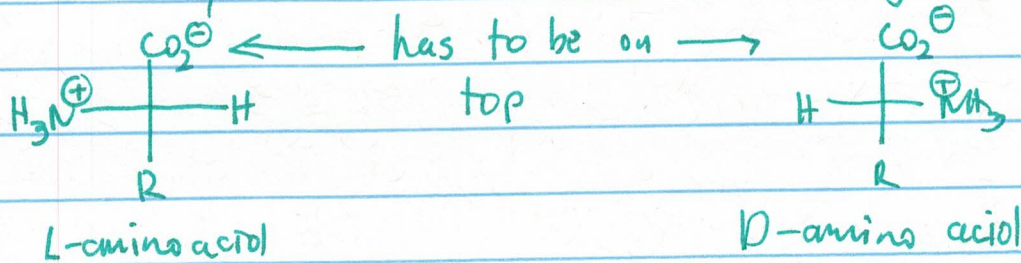
Forbidden:

- ① Rotation by 90° turns it into a different enantiomer
- ② Pairwise switching of ligands does the same

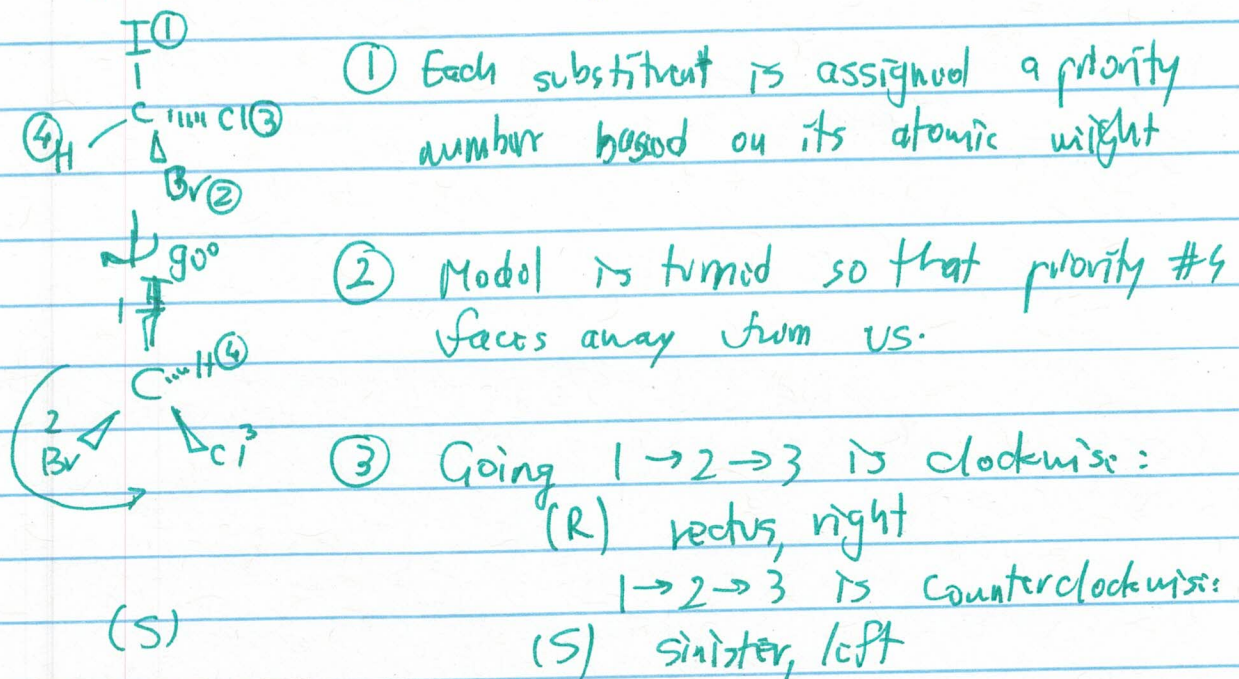


## Naming enantiomers

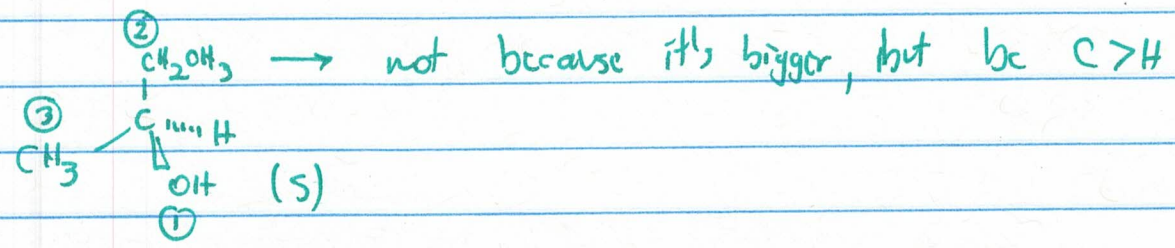
In the old literature, D- and L- notations were used. They today persist only for amino acids and sugars:



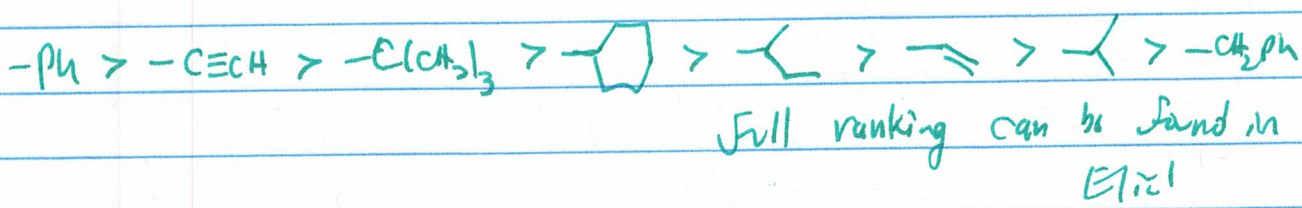
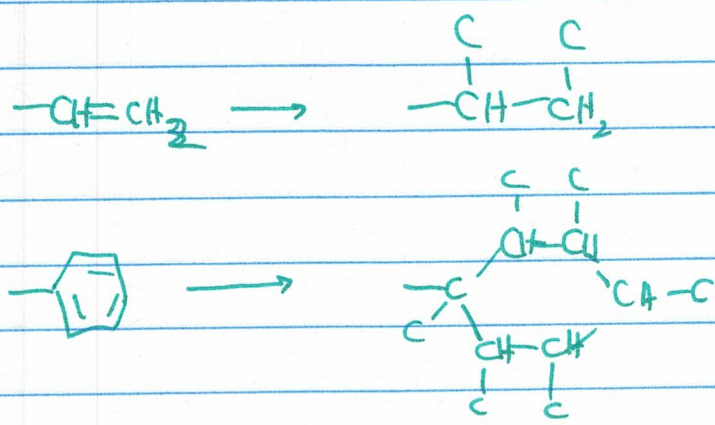
Today, the Cahn-Ingold-Prelog notation is being used:



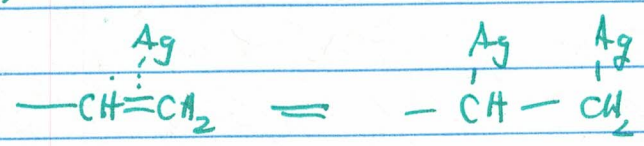
If two groups start with the same atom, go to the next level:



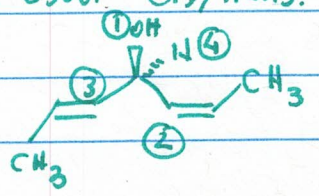
If a group has double or triple bonds, they are converted into "phantom atoms":



Metals also count:



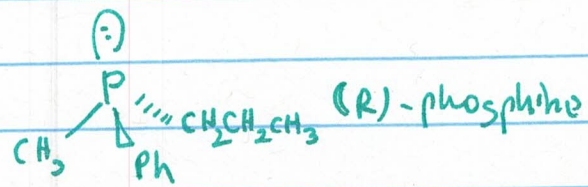
What about cis/trans:



Double bond where CH<sub>3</sub> is on the same side as the chiral center takes precedence

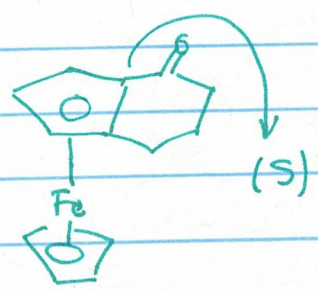
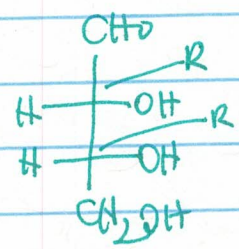


In atoms where lone pair is one of the substituents, it counts as having atomic number zero - below hydrogen:



We'll continue with properties of other chiral elements.

Practice problems for configuration assignment:



Fe counts as a substituent

In isotopically substituted compounds:

$D > H$ ,  $^{13}C > ^{12}C$   
 but  $-\text{CH}_2\text{CH}_2\text{CH}_3$  is still higher than  $-\text{CHDOCH}_3$