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Organic Chemistry

Chemical Bonding and Structure (2)

by
Dr. Seema Zareen & Dr. Izan Izwan Misnon
Faculty of Industrial Science & Technology
seema@ump.edu.my & iezwan@ump.edu.my

Chemical Bonding and Structure (3)
By Seema Zareen
http://ocw.ump.edu.my/course/view.php?id=152

Expected Outcomes

In the end of this chapter, student will have the ability to:

- Draw Lewis structure
- Identify ionic and covalent bond in a compounds
- Differentiate isomers and resonance Lewis drawing
- Explain characteristic and properties of constitutional isomers, enantiomers, diastereoisomers, and racemic mixture
- Predict the shape of molecules
- Draw condensed structures and skeletal structure

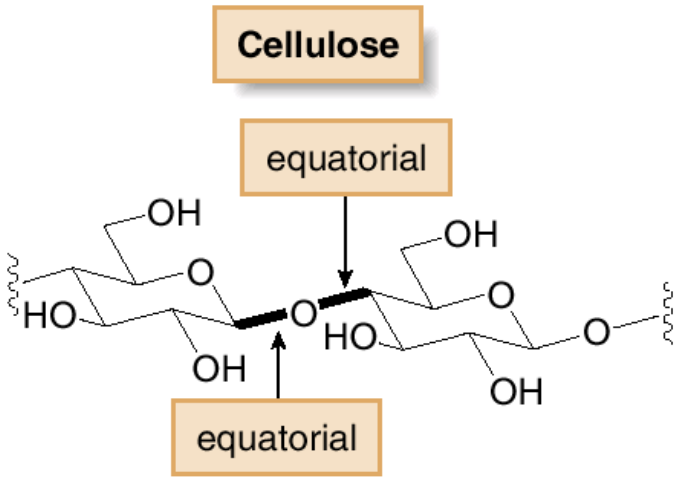
Contents

- Bonding
- Lewis Structure
- Resonance
- Stereochemistry
- Molecular shapes
- Drawing organic structure

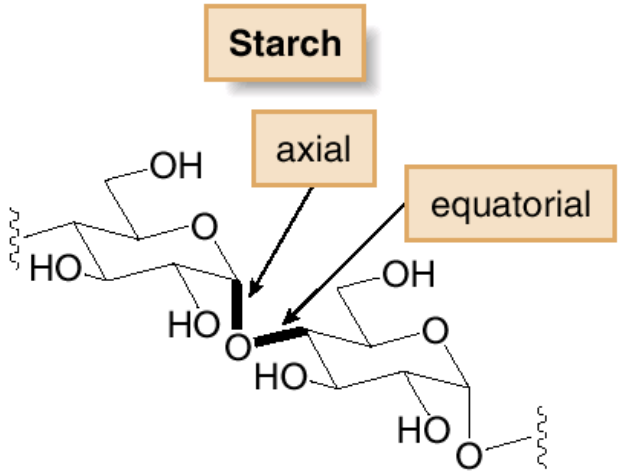
Stereochemistry

- Stereochemistry refers to the three-dimensional structure of a molecule.

- In cellulose, the O atom joins two rings using two equatorial bonds.
- In starch, the O atom joins two rings using one equatorial and one axial bond.



two equatorial bonds



one axial, one equatorial bond

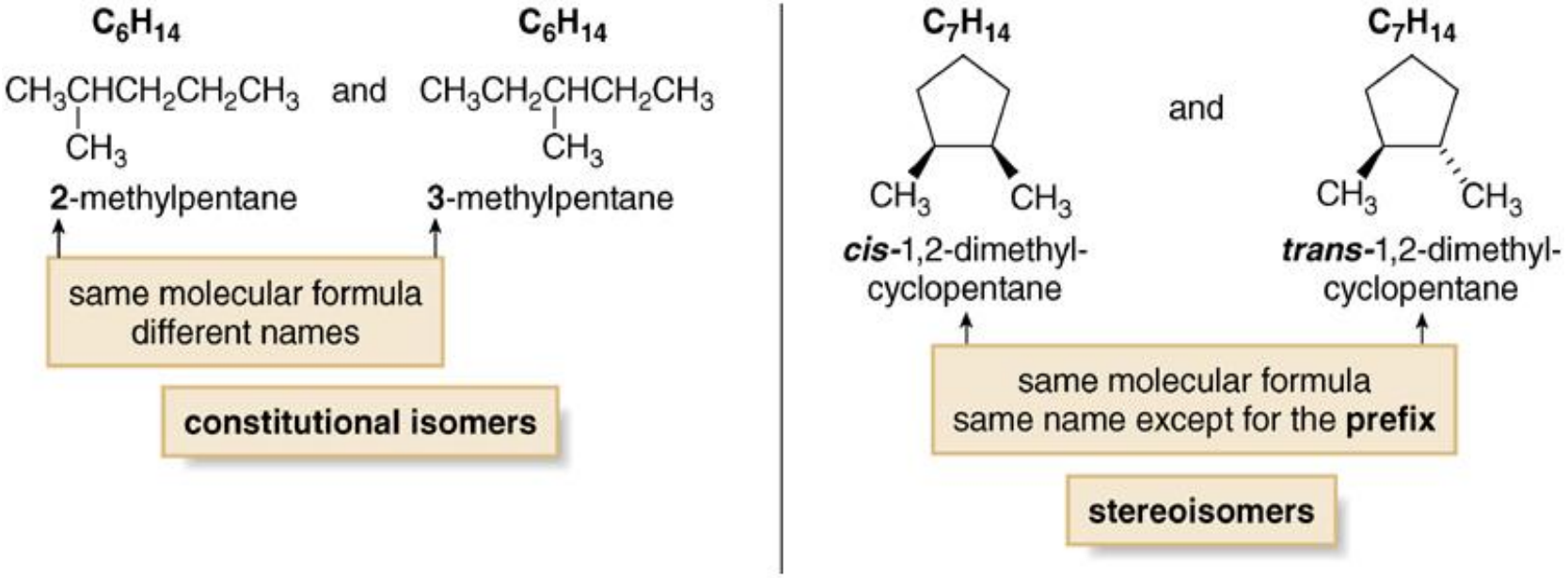
Stereochemistry

The Two Major Classes of Isomers

- The two major classes of isomers are constitutional isomers and stereoisomers.
  - Constitutional/structural isomers have different IUPAC names, the same or different functional groups, different physical properties and different chemical properties.
  - Stereoisomers differ only in the way the atoms are oriented in space. They have identical IUPAC names (except for a prefix like *cis* or *trans*). They always have the same functional group(s).
- A particular three-dimensional arrangement is called a configuration. Stereoisomers differ in configuration.

Stereochemistry

A comparison of constitutional isomers and stereoisomers



Stereochemistry

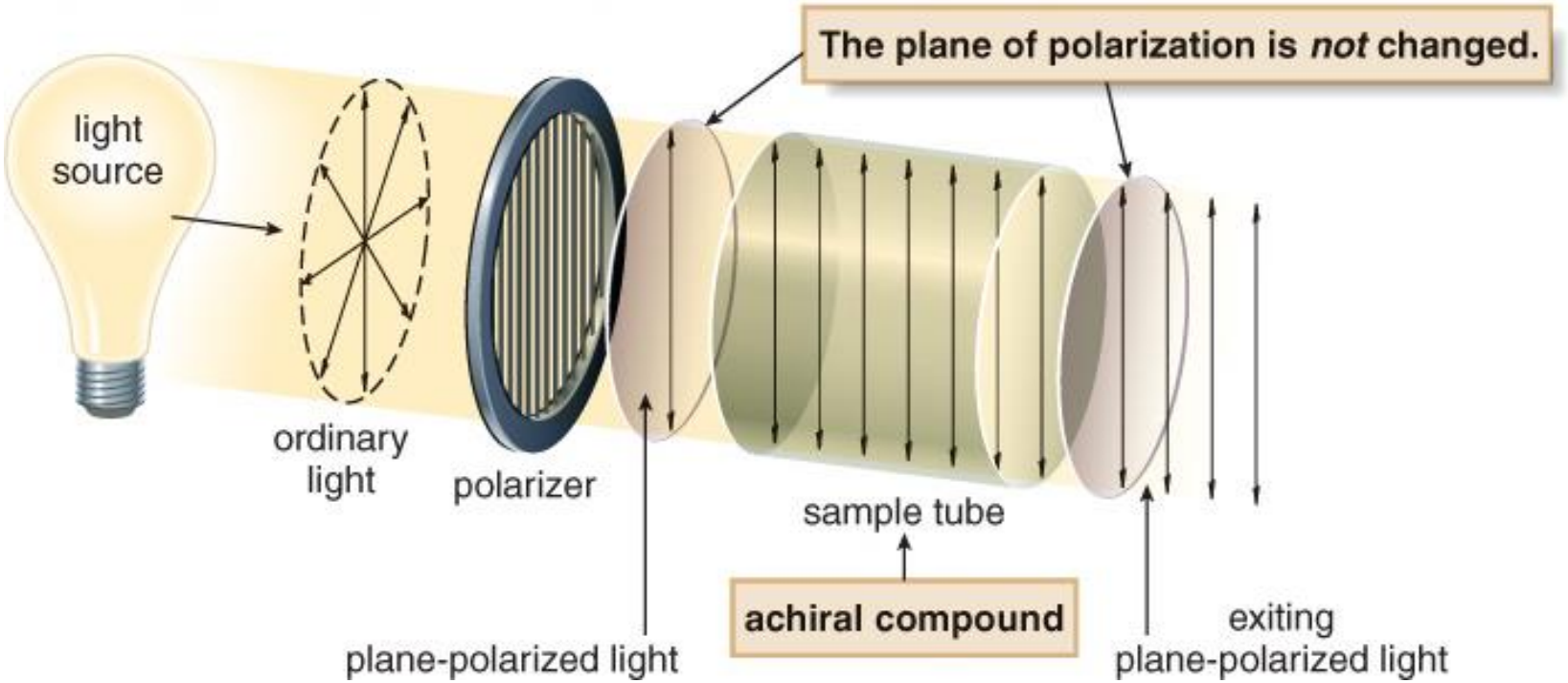
Physical Properties of Stereoisomers—Optical Activity

- The chemical and physical properties of two enantiomers are identical except in their interaction with chiral substances. They have identical physical properties, except for how they interact with plane-polarized light.
- Plane-polarized (polarized) light is light that has an electric vector that oscillates in a single plane. Plane-polarized light arises from passing ordinary light through a polarizer.
- A polarimeter is an instrument that allows polarized light to travel through a sample tube containing an organic compound. It permits the measurement of the degree to which an organic compound rotates plane-polarized light.

Stereochemistry

Physical Properties of Stereoisomers—Optical Activity

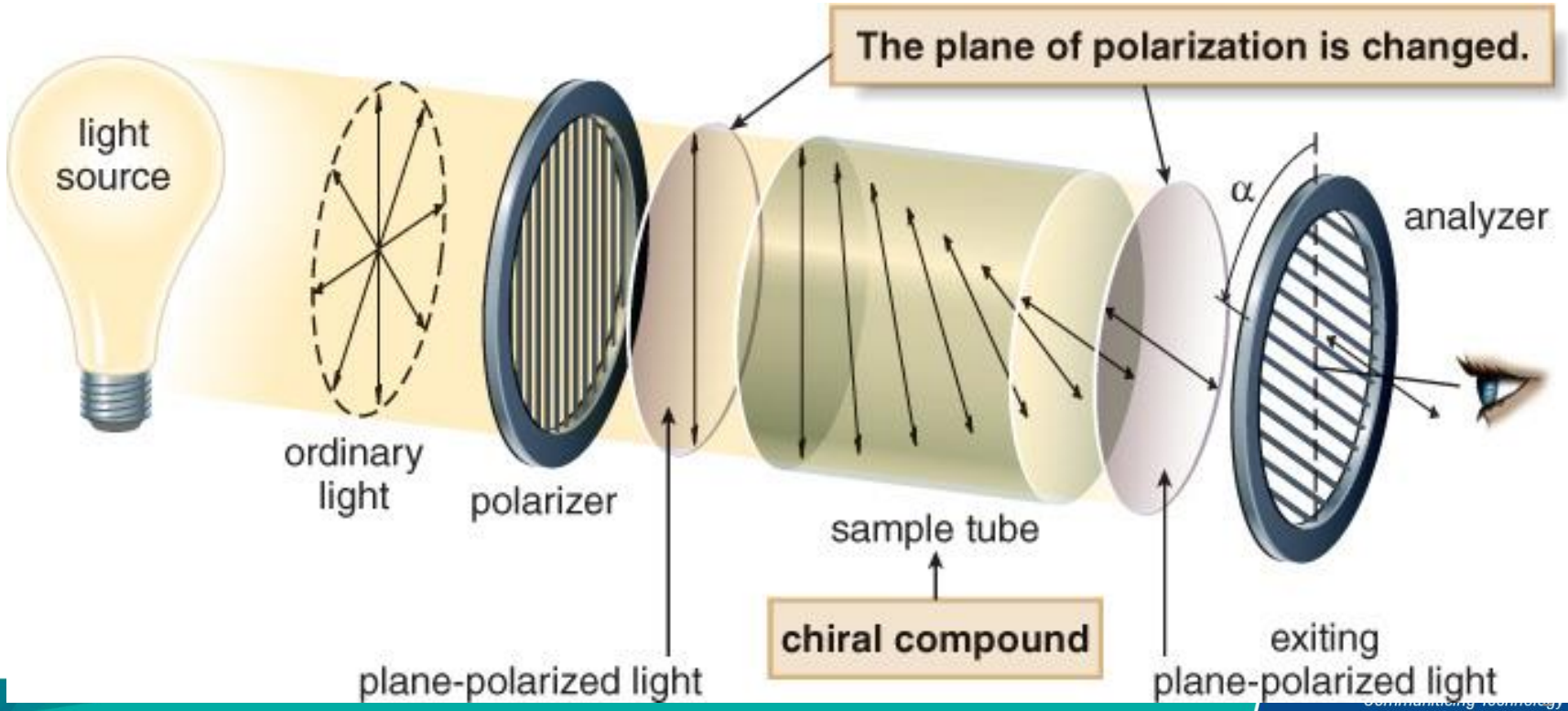
- With achiral compounds, the light that exits the sample tube remains unchanged. A compound that does not change the plane of polarized light is said to be optically inactive.



Stereochemistry

Physical Properties of Stereoisomers—Optical Activity

- With chiral compounds, the plane of the polarized light is rotated through an angle α. The angle α is measured in degrees (°), and is called the observed rotation. A compound that rotates polarized light is said to be optically active.



Stereochemistry

Physical Properties of Stereoisomers—Optical Activity

- The rotation of polarized light can be clockwise or anticlockwise.
- If the rotation is clockwise (to the right of the noon position), the compound is called dextrorotatory. The rotation is labeled *d* or (+).
- If the rotation is counterclockwise, (to the left of noon), the compound is called levorotatory. The rotation is labeled *l* or (-).
- Two enantiomers rotate plane-polarized light to an equal extent but in opposite directions. Thus, if enantiomer A rotates polarized light +5°, the same concentration of enantiomer B rotates it –5°.
- No relationship exists between *R* and *S* prefixes and the (+) and (-) designations that indicate optical rotation.

Stereochemistry

Physical Properties of Stereoisomers—Optical Activity

- Specific rotation is a standardized physical constant for the amount that a chiral compound rotates plane-polarized light. Specific rotation is denoted by the symbol [α] and defined using a specific sample tube length (l, in dm), concentration (c in g/mL), temperature (25^0C) and wavelength (589 nm).

$$\text{specific rotation} = [\alpha] = \frac{\alpha}{l \times c}$$

α = observed rotation (°)
l = length of sample tube (dm)
c = concentration (g/mL)

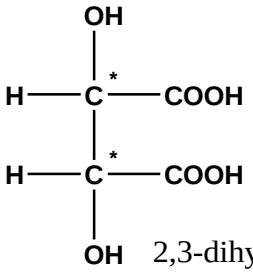
[dm = decimeter
1 dm = 10 cm]

Terms used to describe optical isomers:

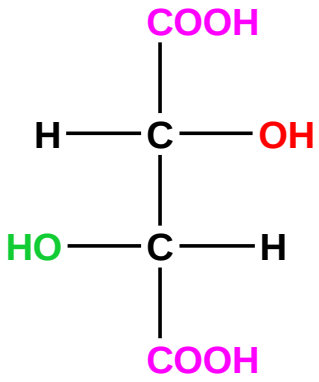
An optically active compound can exist in two isomeric forms which rotate the plane-polarized light in OPPOSITE DIRECTIONS. These are called OPTICAL ISOMERS.

1. Optically active molecule is a molecule that can not be superimposed on its mirror image. It is also called chiral molecule.
2. Asymmetric carbon is a carbon atom that is bonded to four (4) different groups. It is also called chiral carbon.
3. Enantiomers (Greek, *enantio* = opposite) are optical active that are mirror images.
4. Diastereomers are optical isomer but not mirror images.
5. Racemic mixture is a mixture of equal parts of enantiomers. Racemic mixtures optically inactive.
6. Meso compounds is a compound that has more than one asymmetric carbon and that is superimposable on its mirror image. Meso compounds are optically inactive.

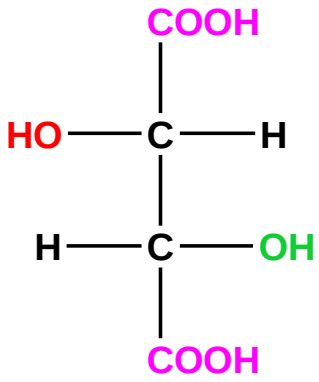
Isomers of Tartaric acid



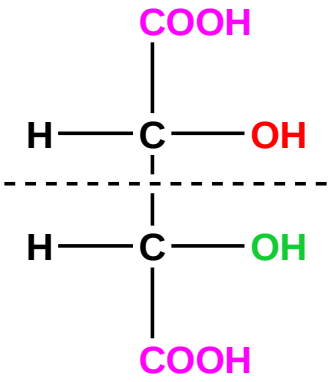
2,3-dihydroxysuccinic acid



(+) Tartaric acid
mp = 170 ^{o}C



(-) Tartaric acid
mp = 170 ^{o}C



meso-Acid
mp = 143^{o}C

Equimolar mixture of (+) and (-) forms (Racemix mixture)

(±) Acid
mp = 206 ^{o}C

Stereochemistry

Physical Properties of Stereoisomers—Racemic Mixtures

- An equal amount of two enantiomers is called a racemic mixture or a racemate. A racemic mixture is optically inactive. Because two enantiomers rotate plane-polarized light to an equal extent but in opposite directions, the rotations cancel, and no rotation is observed.

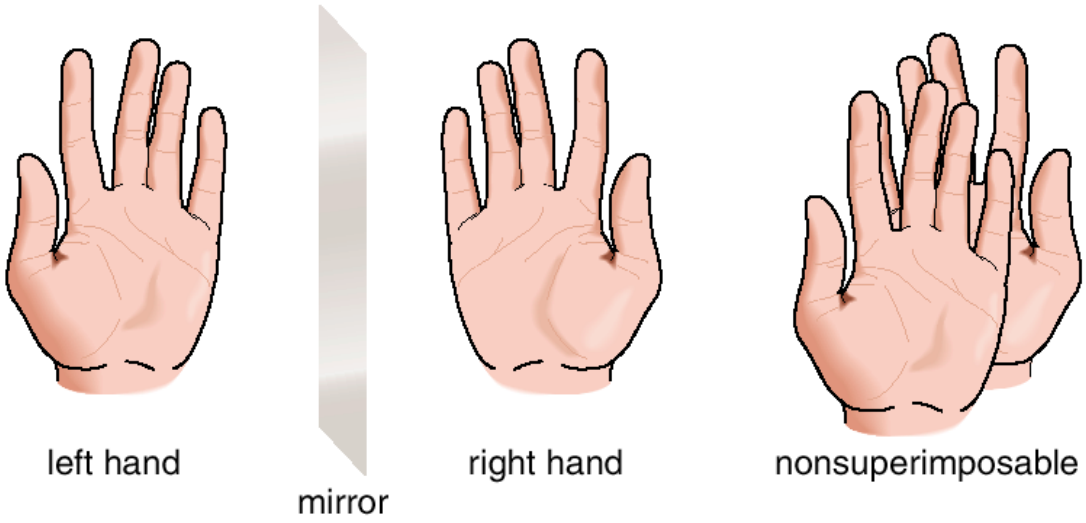
The Physical Properties of Enantiomers A and B Compared

Property	A alone	B alone	Racemic A + B
Melting point	identical to **B**	identical to **A**	may be different from **A** and **B**
Boiling point	identical to **B**	identical to **A**	may be different from **A** and **B**
Optical rotation	equal in magnitude but opposite in sign to **B**	equal in magnitude but opposite in sign to **A**	0°

Stereochemistry

Chiral and Achiral Molecules

- Some molecules are like hands. Left and right hands are mirror images, but they are not identical, or superimposable.

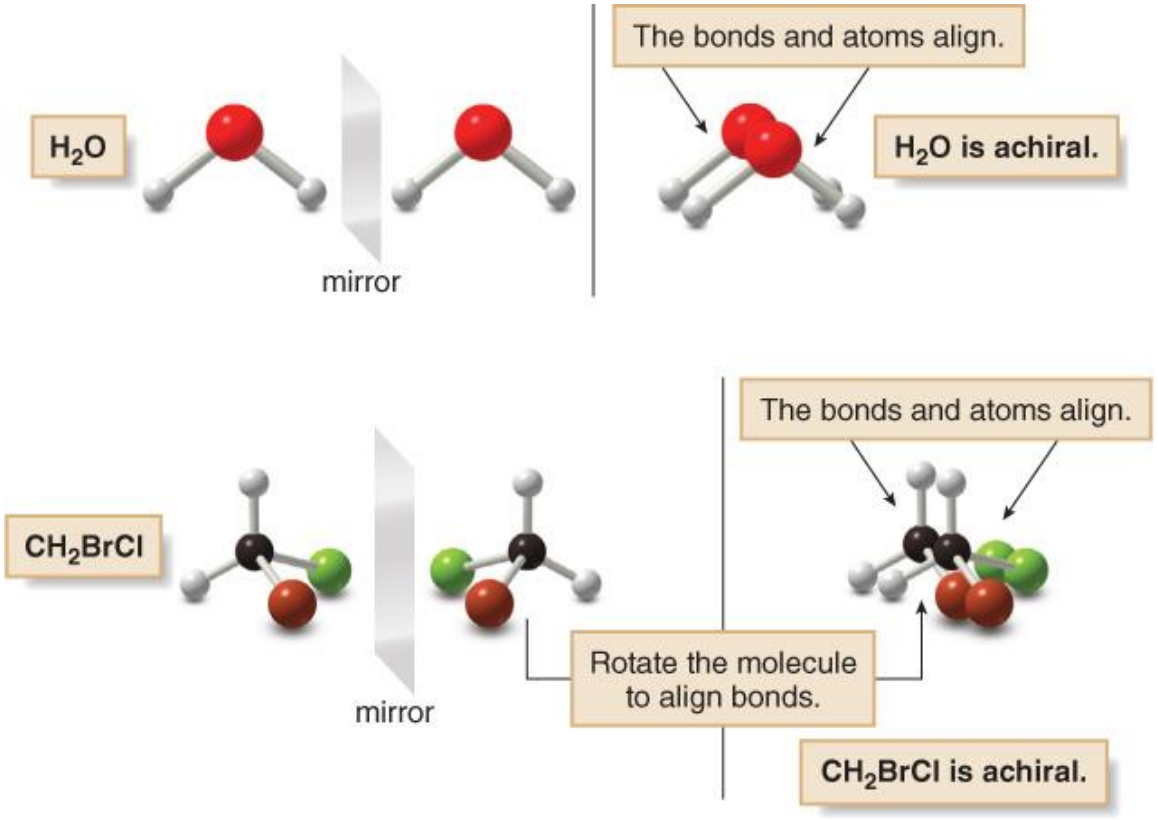


- A molecule (or object) that is *not* superimposable on its mirror image is said to be *chiral.*

Stereochemistry

Chiral and Achiral Molecules

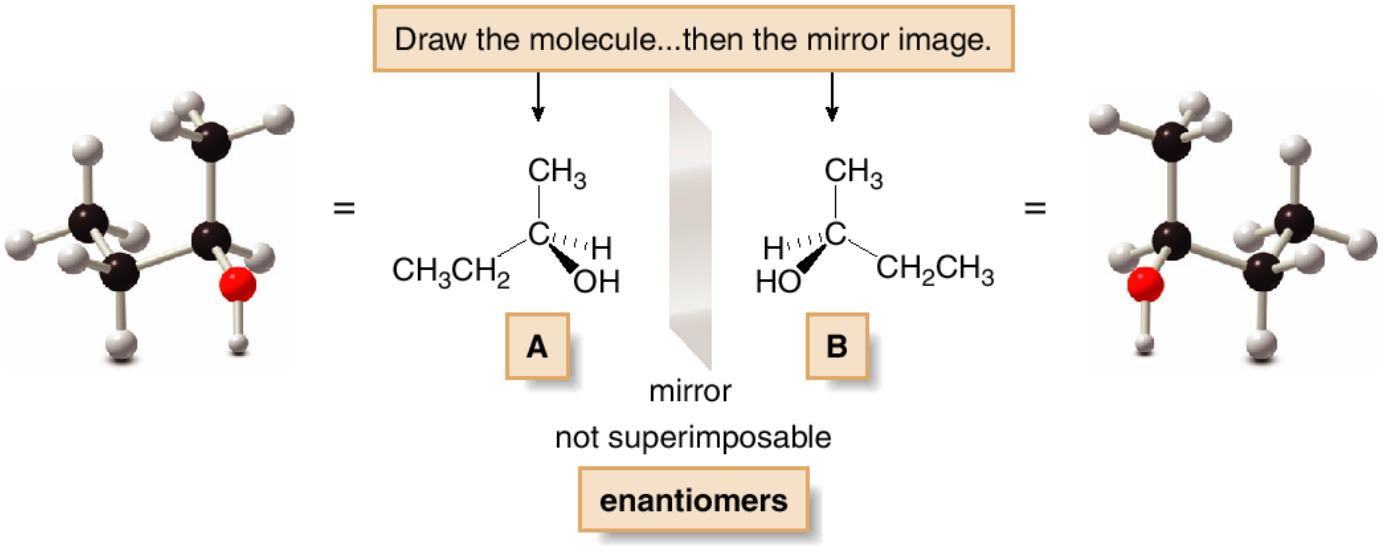
- We can now consider several molecules to determine whether or not they are chiral.



Stereochemistry

Chiral and Achiral Molecules

- The molecule labeled A and its mirror image labeled B are not superimposable. No matter how you rotate A and B, all the atoms never align. Thus, CHBrClF is a chiral molecule, and A and B are different compounds.
- A and B are stereoisomers—specifically, they are enantiomers.
- A carbon atom with four different groups is a tetrahedral stereogenic center.



Chiral and Achiral Molecules

- Achiral molecules usually contain a plane of symmetry but chiral molecules do not.
- A plane of symmetry is a mirror plane that cuts the molecule in half, so that one half of the molecule is a reflection of the other half.

Chiral and Achiral Molecules

Aligning the C–Cl and C–Br bonds in each molecule.

CH_2BrCl

plane of symmetry

This molecule has **two identical halves.**

CH_2BrCl is **achiral.**

CHBrClF

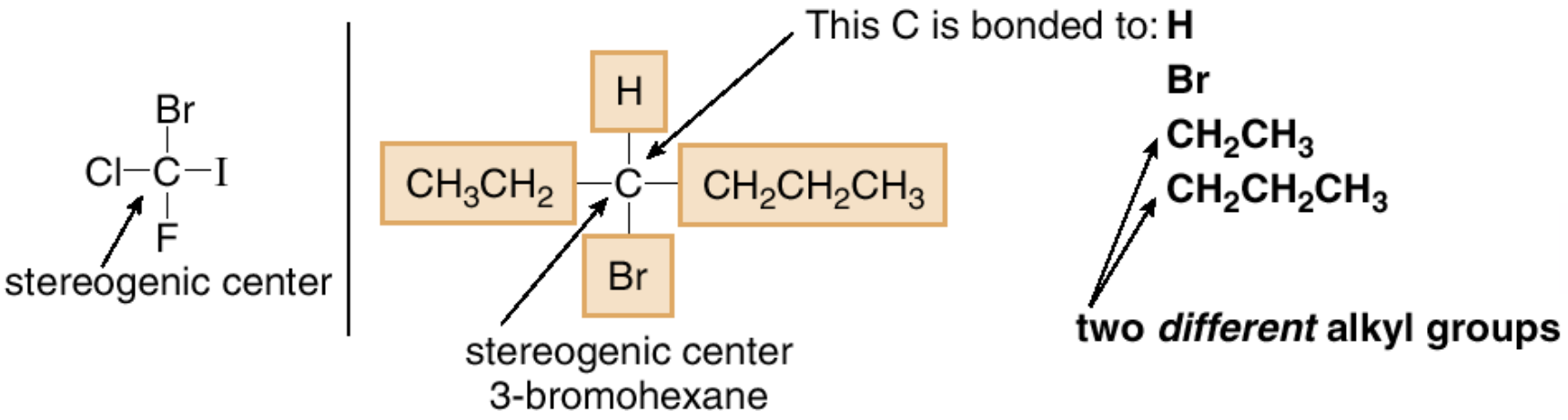
NO plane of symmetry

CHBrClF is **chiral.**

Stereochemistry

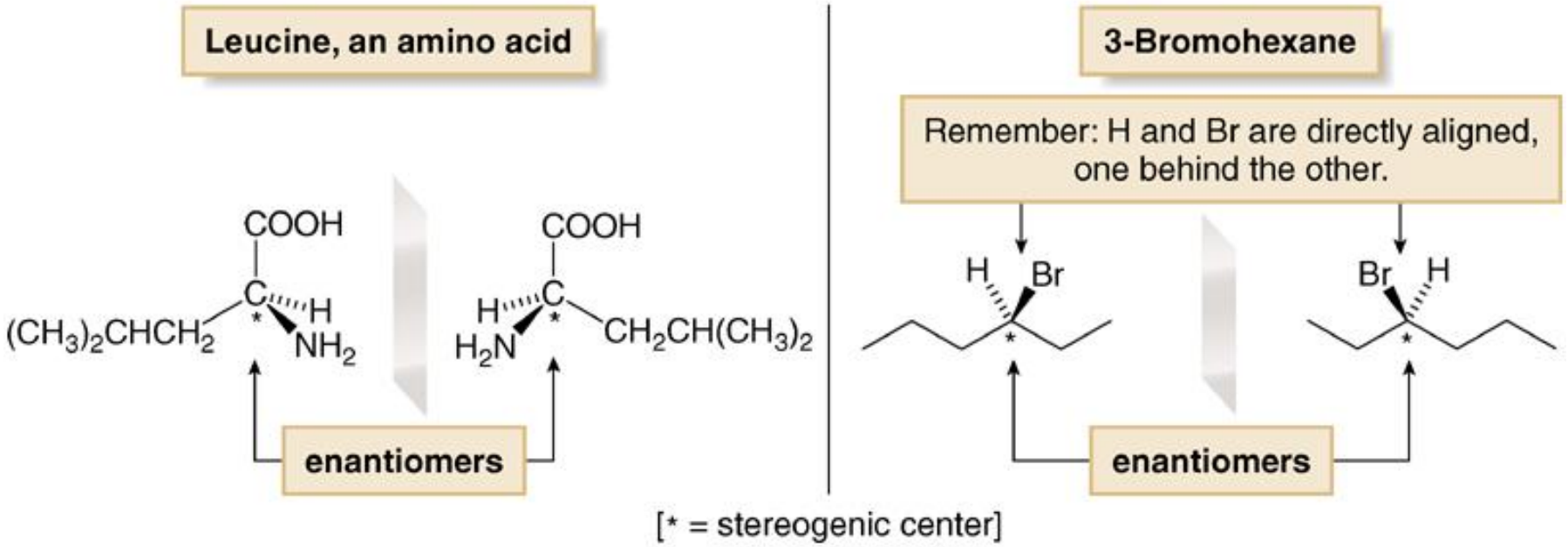
Stereogenic Centers

- **To locate a stereogenic center, examine each tetrahedral carbon atom in a molecule, and look at the four groups—not the four atoms—bonded to it.**
- **Always omit from consideration all C atoms that cannot be tetrahedral stereogenic centers. These include**
  - **CH_2 and CH_3 groups**
  - **Any *sp* or sp^2 hybridized C**



Stereogenic Centers

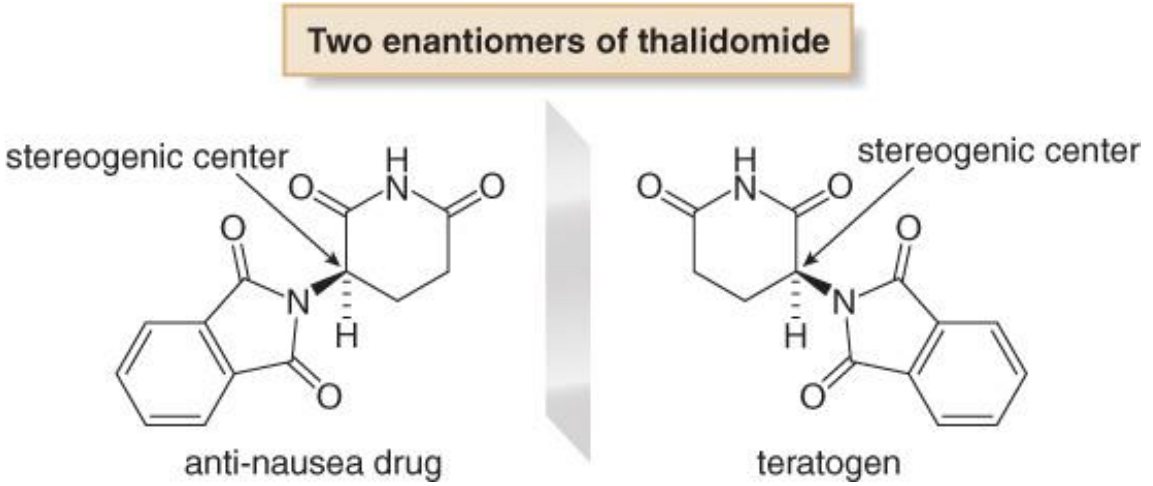
Three-dimensional representations for pairs of enantiomers

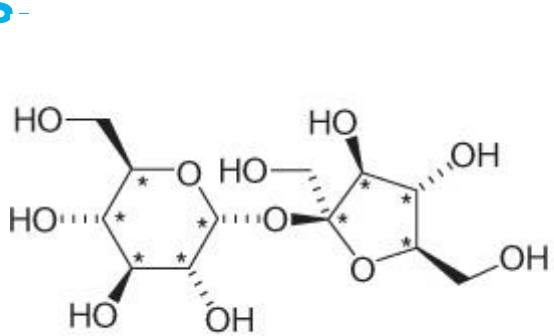


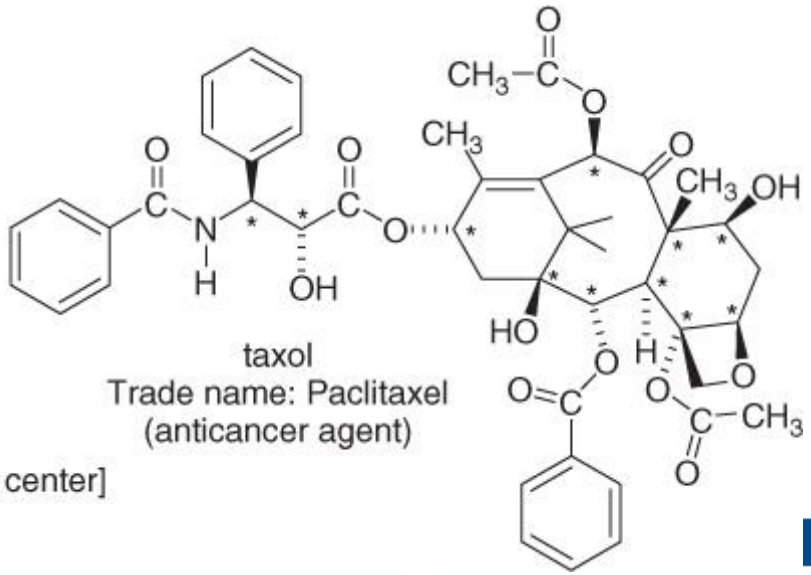
Stereochemistry

Stereogenic Centers

- **Many biologically active molecules contain stereogenic centers at ring carbons**







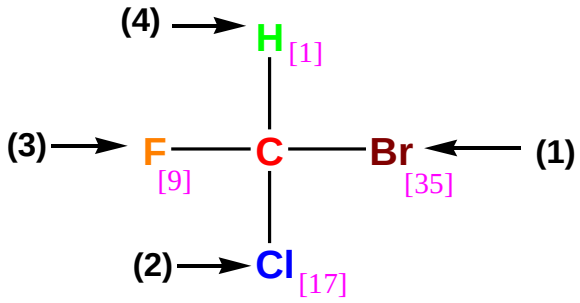
[* = stereogenic center]

Stereochemistry

Labeling Stereogenic Centers with *R* or *S*

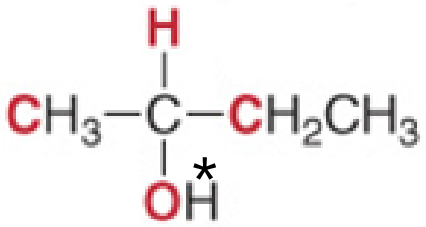
- Since enantiomers are two different compounds, they need to be distinguished by name. This is done by adding the prefix *R* or *S* to the IUPAC name of the enantiomer.
- Naming enantiomers with the prefixes *R* or *S* is called the *Cahn-Ingold-Prelog* system (CIP Rule).
- To designate enantiomers 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).

H (1)
F (9)
Cl (17)
Br (35)



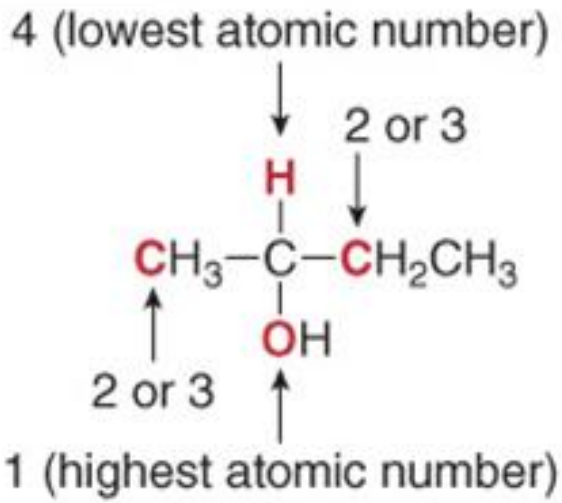
Labeling Stereogenic Centers with *R* or *S*

- 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.

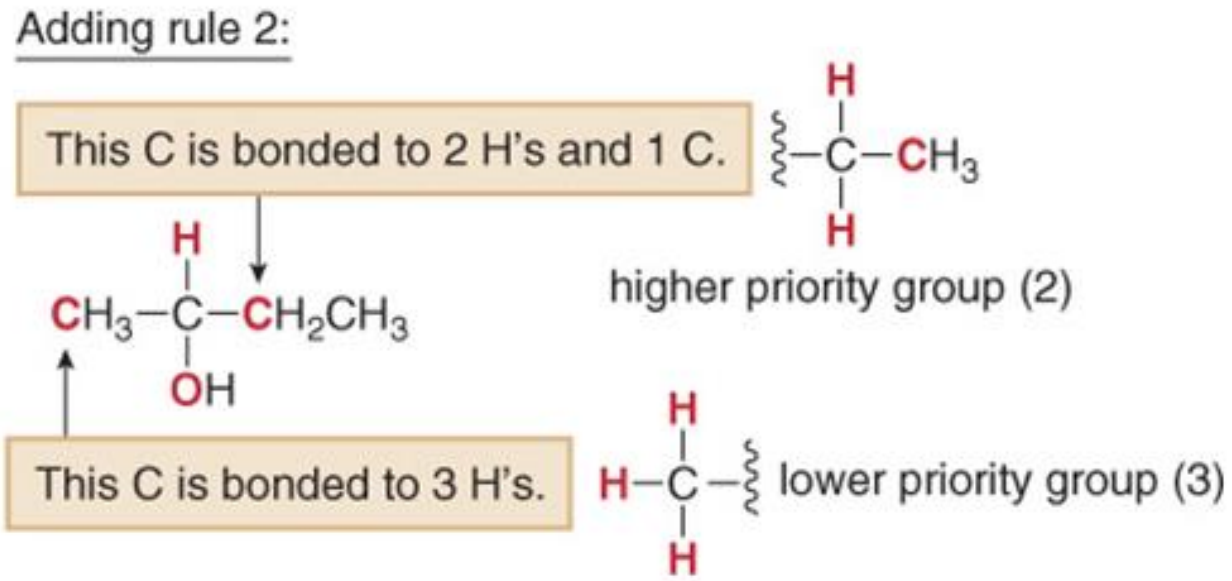


2-butanol

Following rule 1:

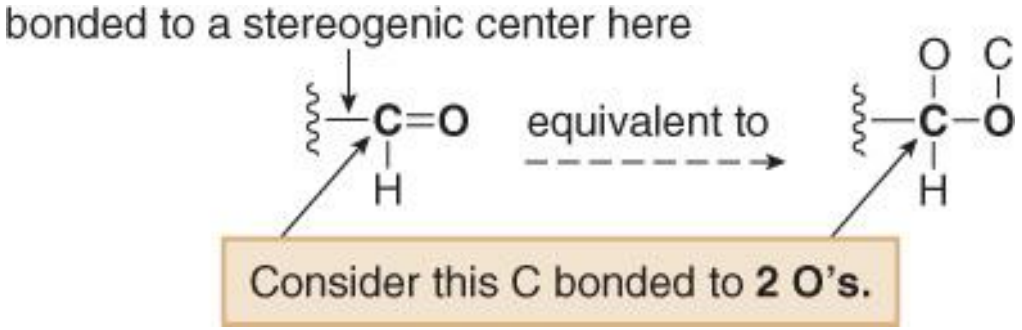


Labeling Stereogenic Centers with *R* or *S*

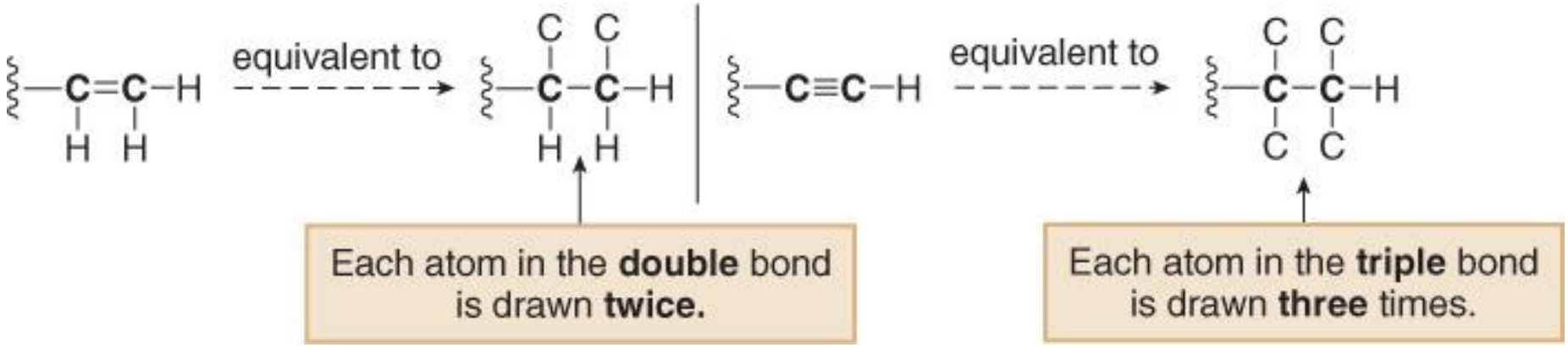


Labeling Stereogenic Centers with *R* or *S*

- 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.



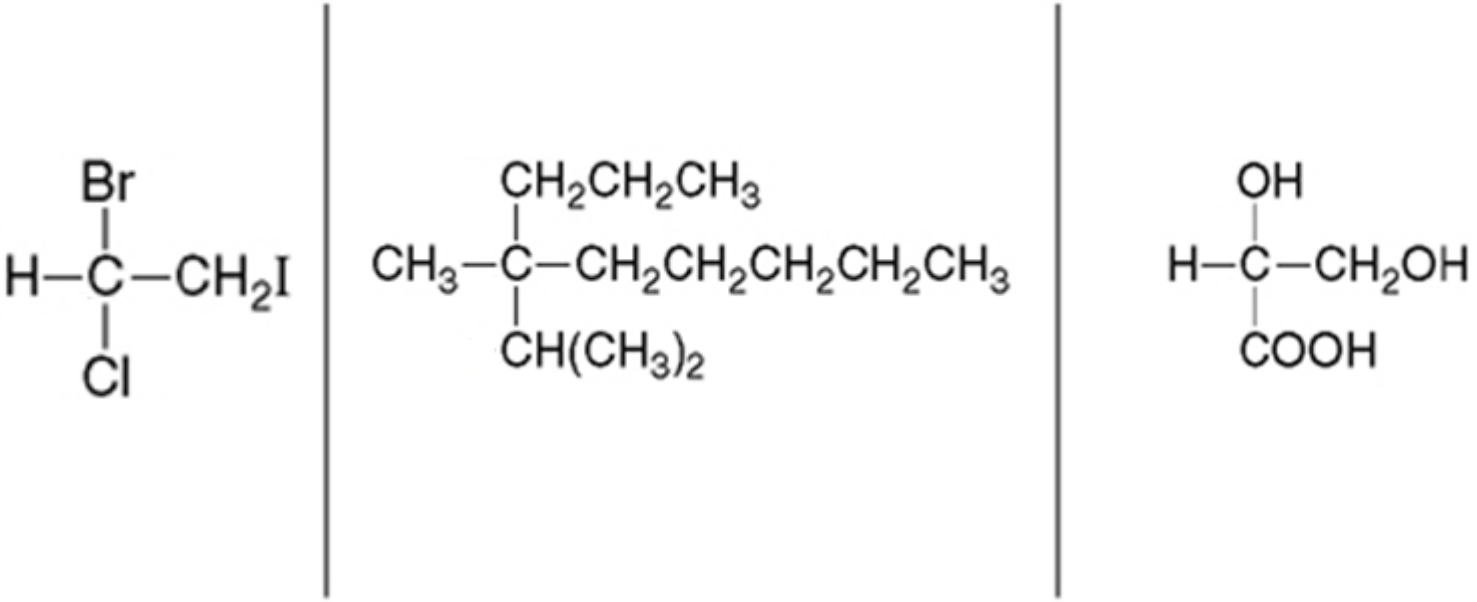
- Other common multiple bonds are drawn below:



Stereochemistry

Labeling Stereogenic Centers with *R* or *S*

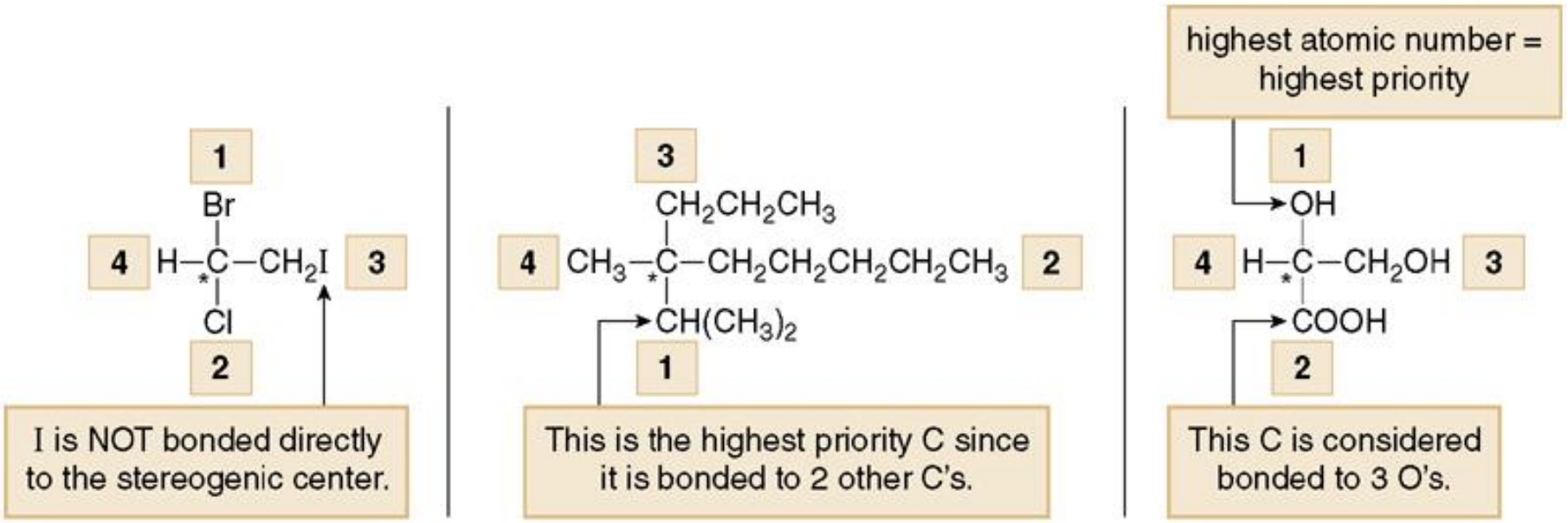
Examples of assigning priorities to stereogenic centers



Stereochemistry

Labeling Stereogenic Centers with *R* or *S*

Examples of assigning priorities to stereogenic centers

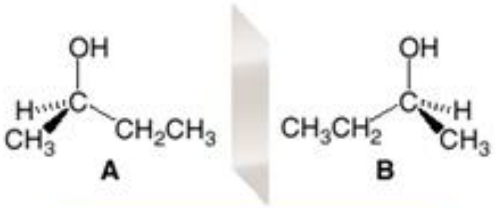


[* = stereogenic center]

Labeling Stereogenic Centers with *R* or *S*

How To Assign *R* or *S* to a Stereogenic Center

Example Label each enantiomer as *R* or *S*.



two enantiomers of 2-butanol

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 ·

−OH	$-CH_2CH_3$	$-CH_3$	−H
1	2	3	4
highest			lowest

Decreasing priority

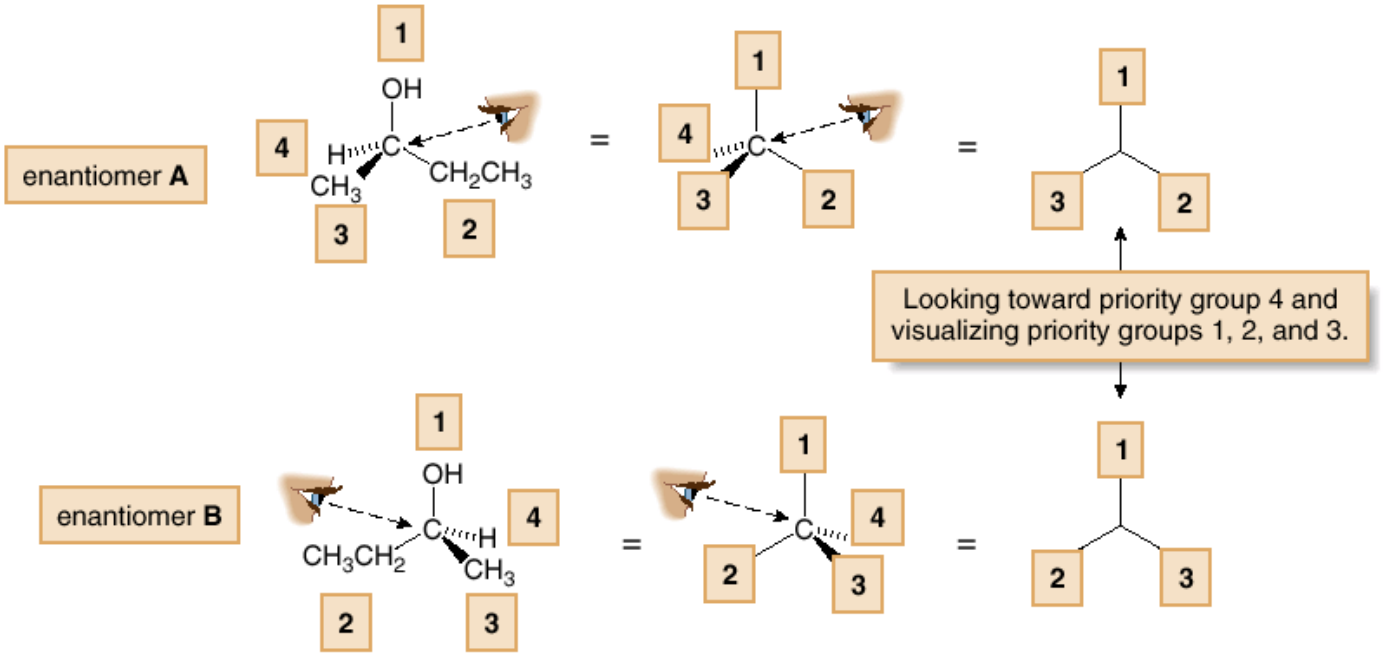
Stereochemistry

Labeling Stereogenic Centers with *R* or *S*

How To, continued . . .

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.

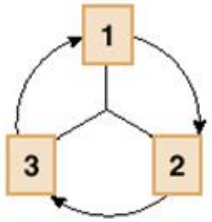


Stereochemistry

Labeling Stereogenic Centers with *R* or *S*

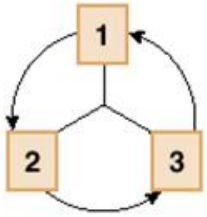
Step [3] Trace a circle from priority group 1 → 2 → 3.

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



clockwise

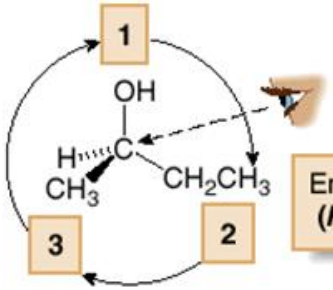
***R* isomer**



counterclockwise

***S* isomer**

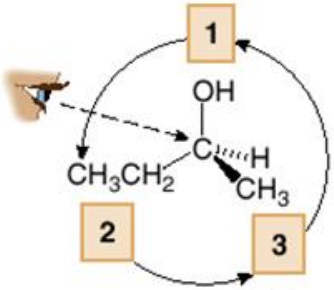
- The letters *R* or *S* precede the IUPAC name of the molecule. For the enantiomers of 2-butanol:



clockwise

***R* isomer**

Enantiomer **A** is **(*R*)-2-butanol.**



counterclockwise

***S* isomer**

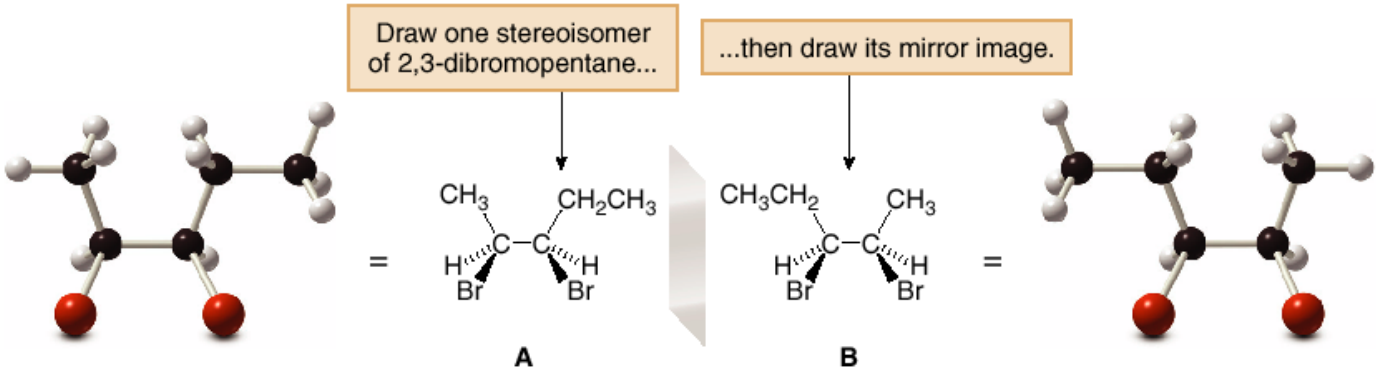
Enantiomer **B** is **(*S*)-2-butanol.**

Diastereomers

- For a molecule with *n* stereogenic centers, the maximum number of stereoisomers is 2^n. Let us consider the stepwise procedure for finding all the possible stereoisomers of 2,3-dibromopentane.

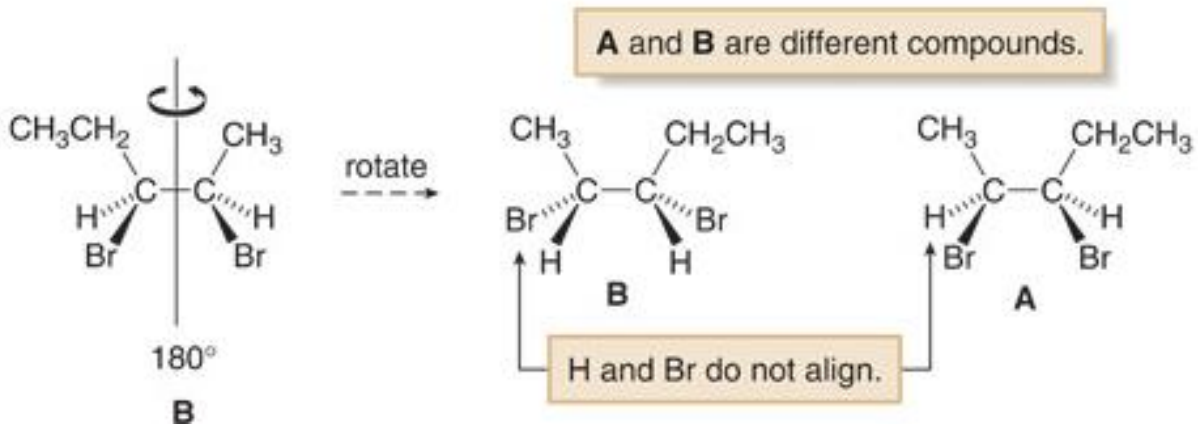
How To Find and Draw All Possible Stereoisomers for a Compound with Two Stereogenic Centers

Step [1] Draw one stereoisomer by arbitrarily arranging substituents around the stereogenic centers. Then draw its mirror image.



Diastereomers

- If you have drawn the compound and the mirror image in the described manner, you have only to do two operations to see if the atoms align. Place B directly on top of A; and rotate B 180° and place it on top of A to see if the atoms align.



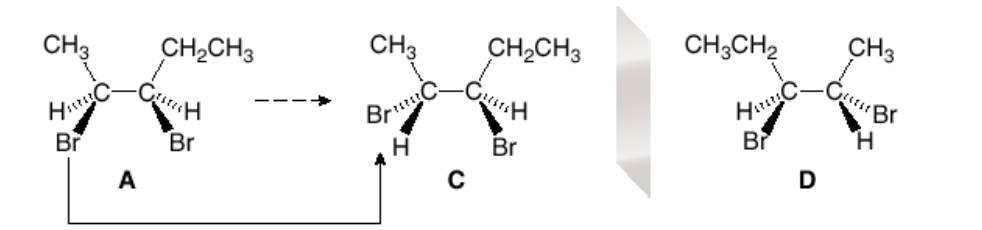
- In this case, the atoms of A and B do not align, making A and B nonsuperimposable mirror images—i.e., enantiomers. Thus, A and B are two of the four possible stereoisomers of 2,3-dibromopentane.

Stereochemistry

Diastereomers

- Switching the positions of H and Br (or any two groups) on one stereogenic center of either A or B forms a new stereoisomer (labeled C in this example), which is different from A and B. The mirror image of C is labeled D. C and D are enantiomers.

How To, continued . . .

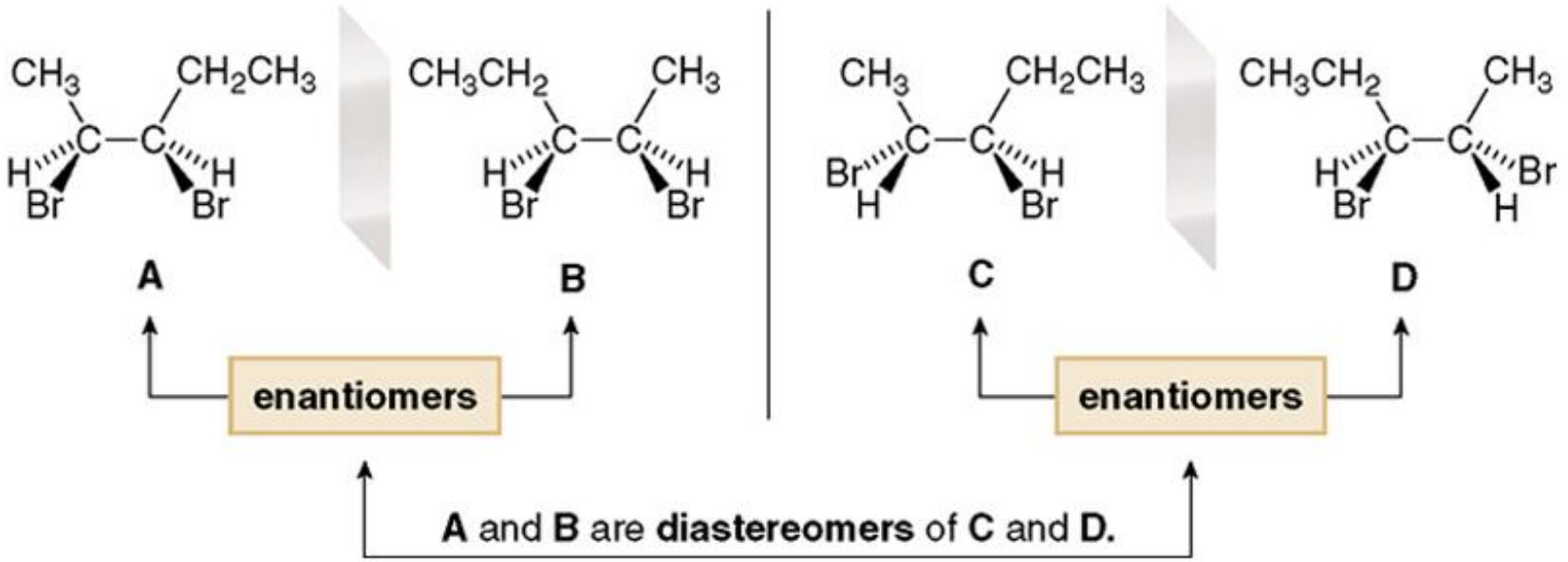


With models...

- Stereoisomers that are not mirror images of one another are called diastereomers. For example, A and C are diastereomers.

Diastereomers

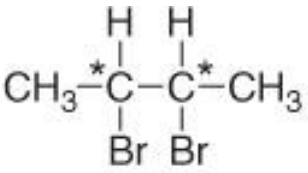
Summary: The four stereoisomers of 2,3-dibromopentane



- Pairs of enantiomers: **A** and **B; C** and **D.**
- Pairs of diastereomers: **A** and **C; A** and **D; B** and **C; B** and **D.**

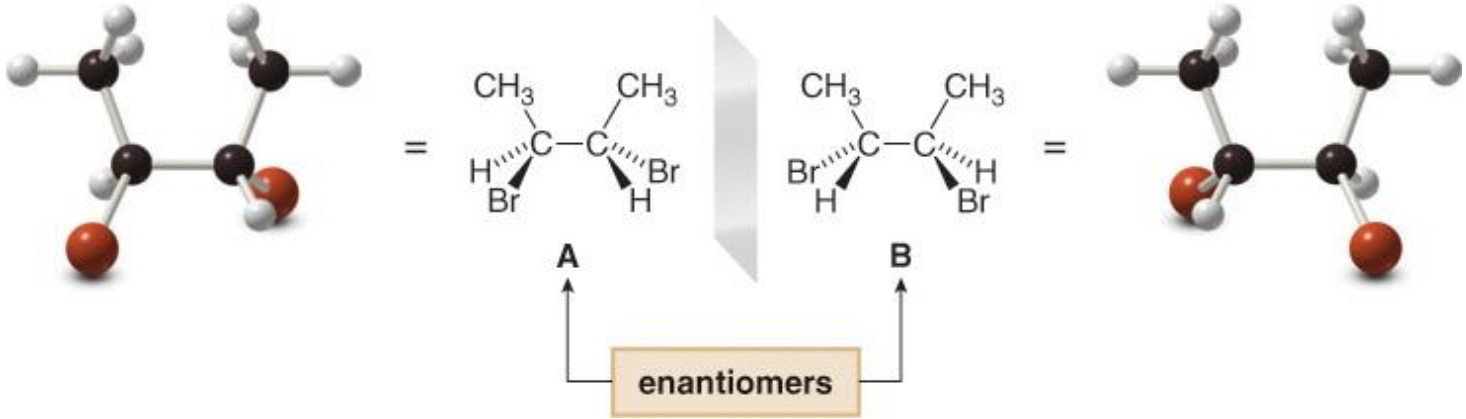
Meso Compounds

- Let us now consider the stereoisomers of 2,3-dibromobutane. Since this molecule has two stereogenic centers, the maximum number of stereoisomers is 4.



2,3-dibromobutane
[* = stereogenic center]

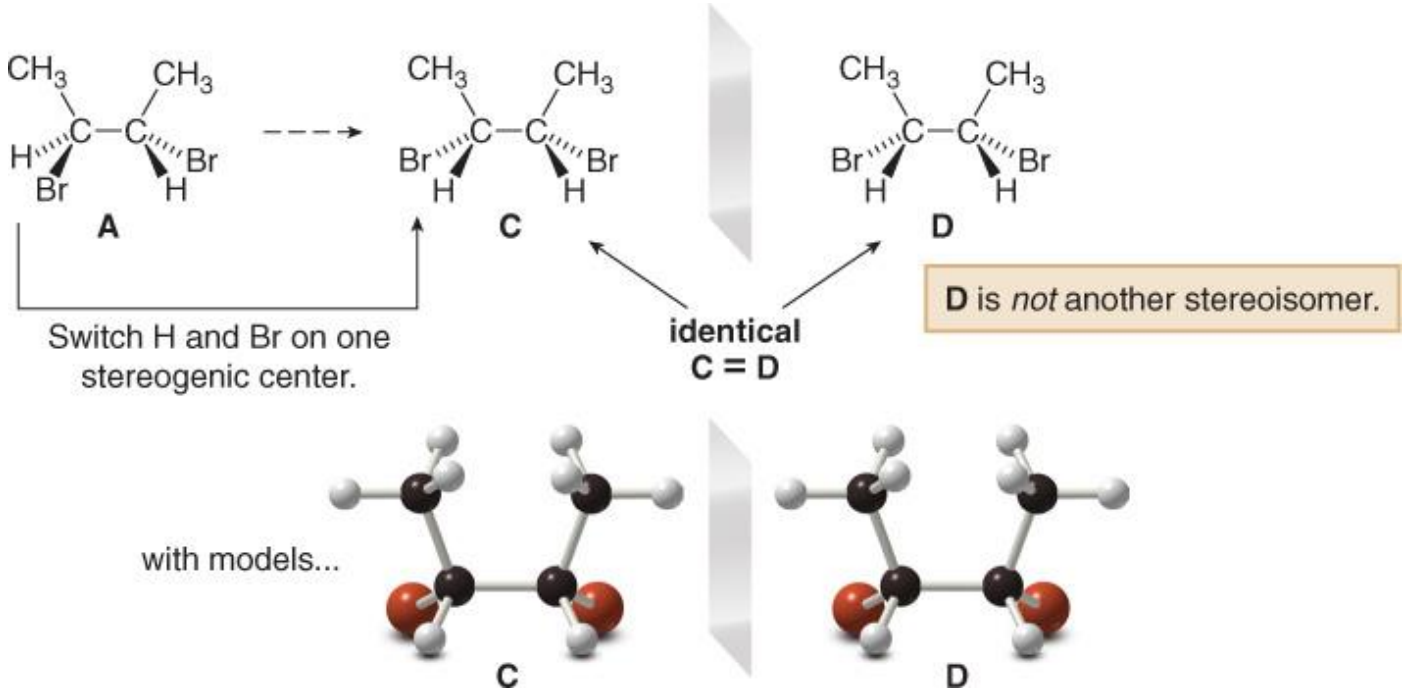
- To find all the stereoisomers of 2,3-dibromobutane, add the H, Br, and CH_3 groups to the stereogenic centers, forming one stereoisomer A, and then draw its mirror image, B.



Stereochemistry

Meso Compounds

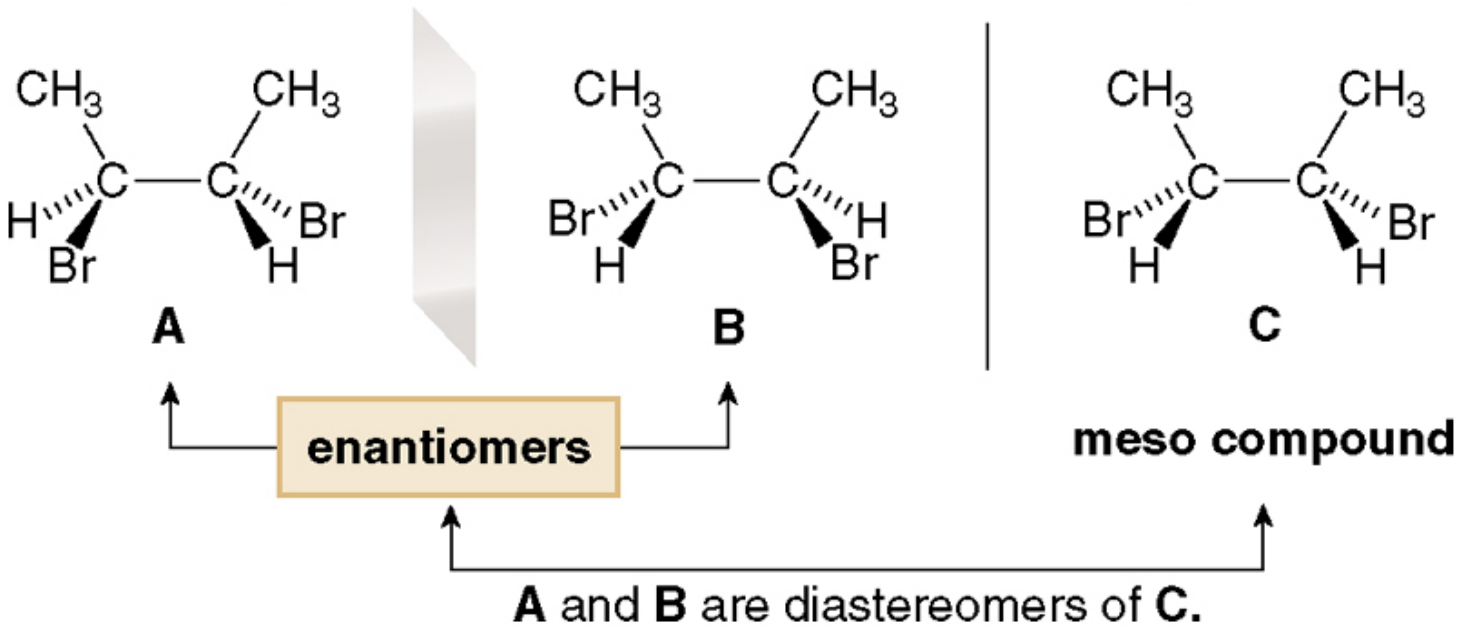
- To find the other two stereoisomers if they exist, switch the position of two groups on one stereogenic center of one enantiomer only. In this case, switching the positions of H and Br on one stereogenic center of A forms C, which is different from both A and D.



- A meso compound is an achiral compound that contains tetrahedral stereogenic centers. C is a meso compound.

Meso Compounds

Summary: The three stereoisomers 2,3-dibromobutane

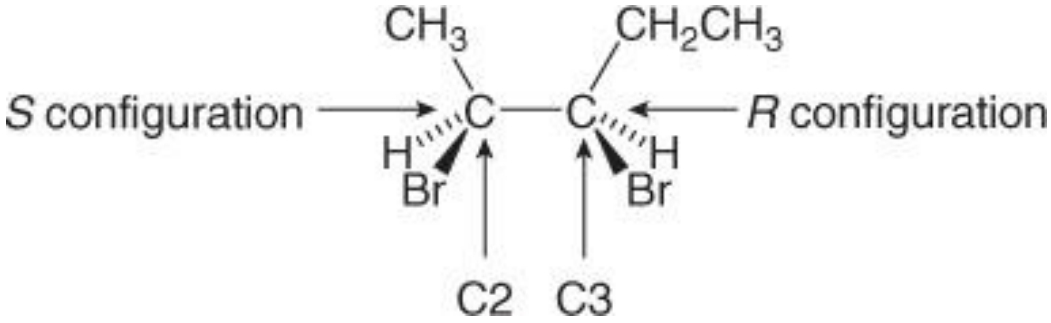


- Pair of enantiomers: **A** and **B.**
- Pairs of diastereomers: **A** and **C; B** and **C.**

Stereochemistry

R and *S* Assignments in Compounds with Two or More Stereogenic Centers.

- When a compound has more than one stereogenic center, *R* and *S* configurations must be assigned to each of them.



One stereoisomer of 2,3-dibromopentane

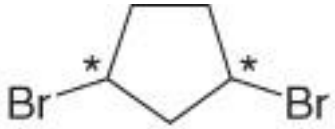
The complete name is (2*S*,3*R*)-2,3-dibromopentane

- Identical compounds have the *same R,S* designations at every tetrahedral stereogenic center.
- Enantiomers have exactly *opposite R,S* designations.
- Diastereomers have the *same R,S* designation for at least one stereogenic center and the *opposite* for at least one of the other stereogenic centers.

Stereochemistry

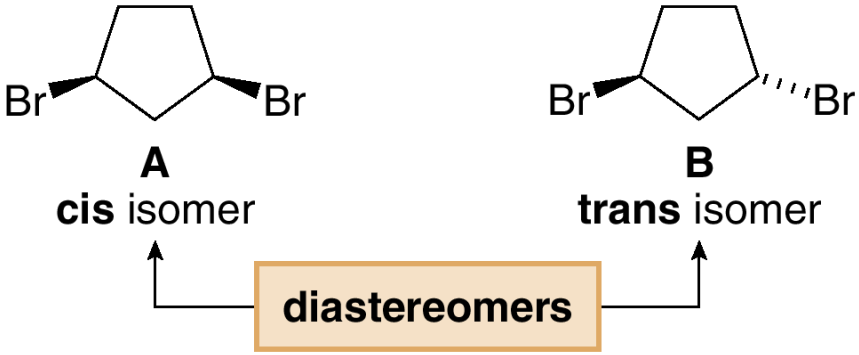
Disubstituted Cycloalkanes

- Consider 1,3-dibromocyclopentane. Since it has two stereogenic centers, it has a maximum of four stereoisomers.



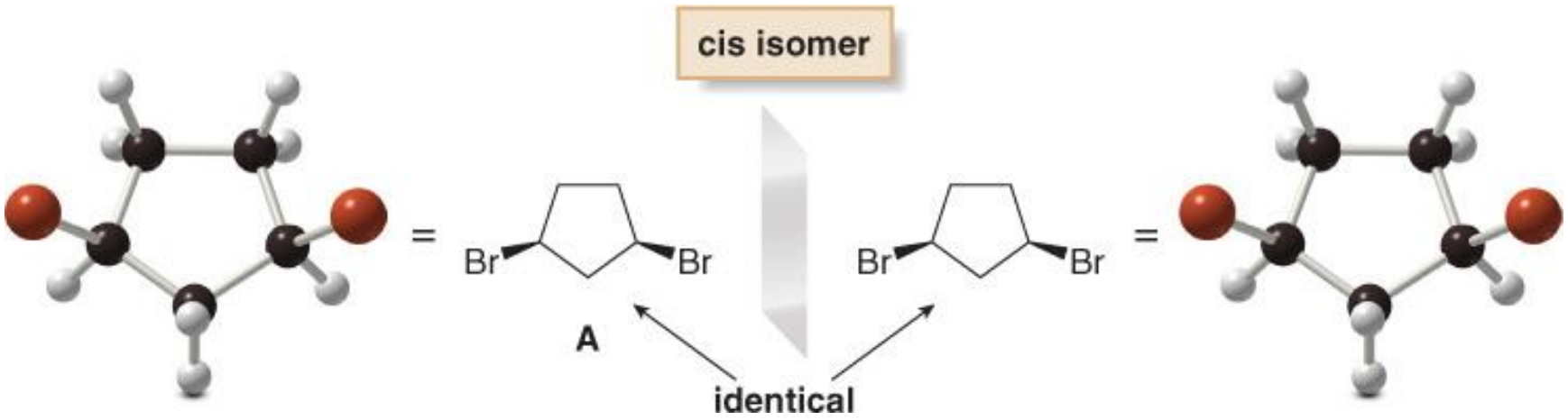
1,3-dibromocyclopentane
[* = stereogenic center]

- Recall that a disubstituted cycloalkane can have two substituents on the same side of the ring (*cis* isomer, A) or on opposite sides of the ring (*trans* isomer, B). These compounds are stereoisomers but not mirror images.



Disubstituted Cycloalkanes

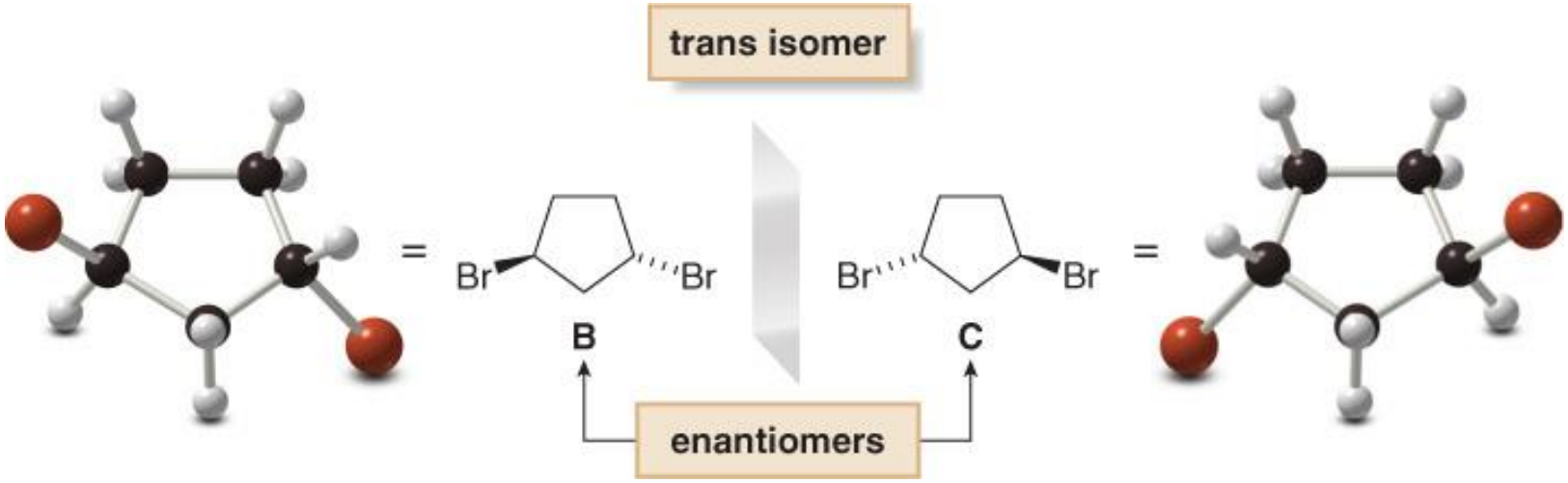
- To find the other two stereoisomers if they exist, draw the mirror images of each compound and determine whether the compound and its mirror image are superimposable.



- The *cis* isomer is superimposable on its mirror image, making the images identical. Thus, A is an achiral meso compound.

Disubstituted Cycloalkanes

- The trans isomer is not superimposable on its mirror image, labeled C, making B and C different compounds. B and C are enantiomers.

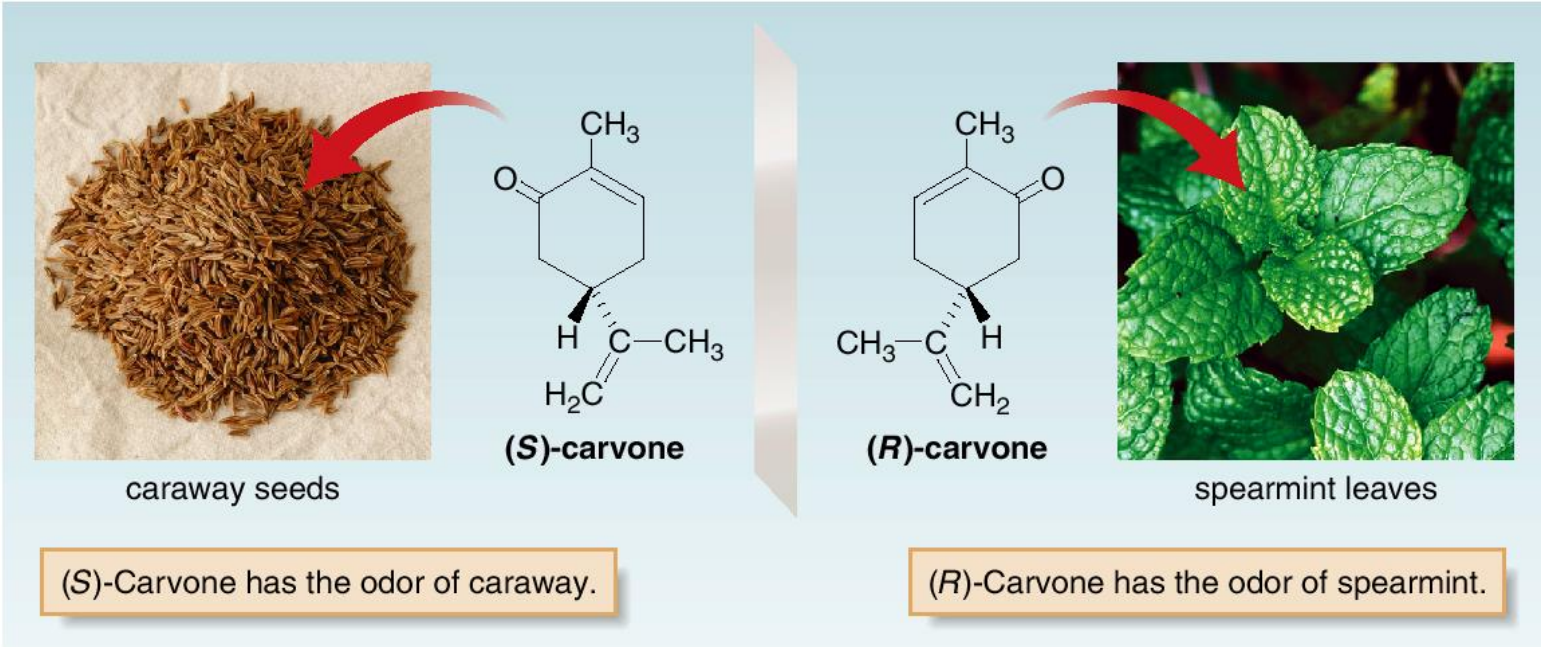


- Because one stereoisomer of 1,3-dibromocyclopentane is superimposable on its mirror image, there are only three stereoisomers, not four.

Stereochemistry

Enantiomers and the Sense of Smell

- Research suggests that the odor of a particular molecule is determined more by its shape than by the presence of a particular functional group.
- Because enantiomers interact with chiral smell receptors, some enantiomers have different odors.



Stereochemistry

Summary—Types of isomers