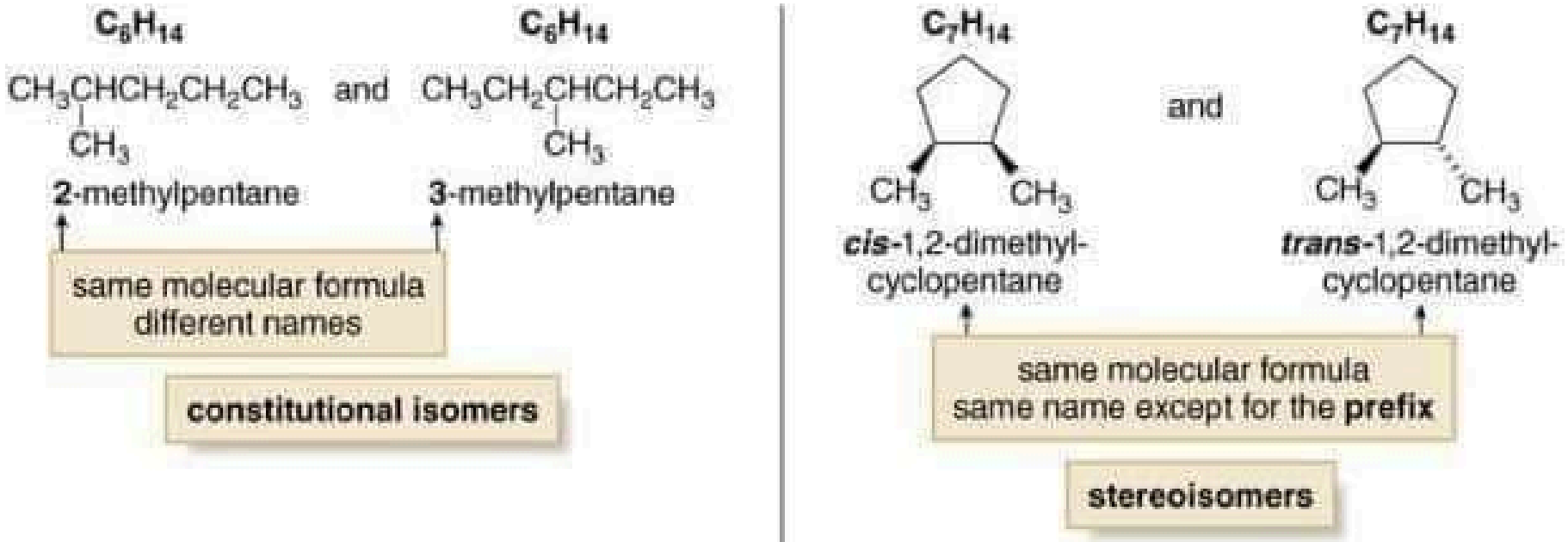
Stereochemistry

The Two Major Classes of Isomers

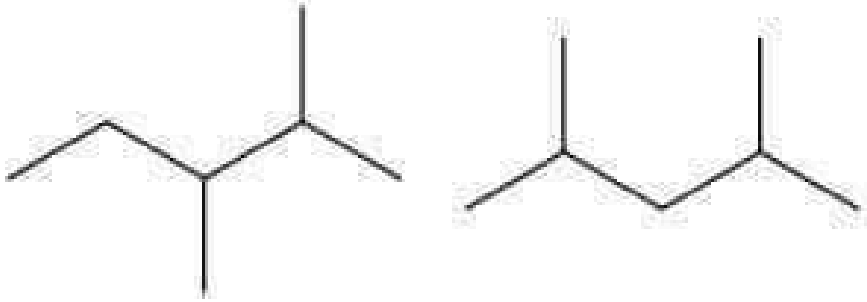
- Recall that isomers are different compounds with the same molecular formula.
- The two major classes of isomers are constitutional isomers and stereoisomers.
  - Constitutional/structural isomers have different IUPAC names, the same or different functional groups, different physical properties and 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.

Figure 5.3
A comparison of consitutional isomers and stereoisomers



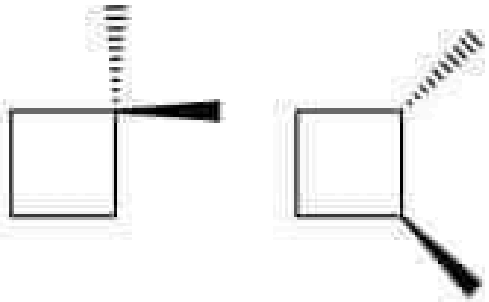
Are the following pairs of compounds consitutional isomers or stereoisomers?

a)



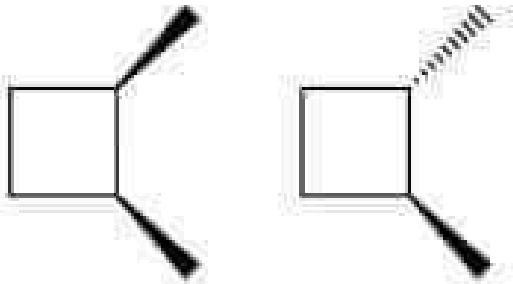
constitutional

b)



constitutional

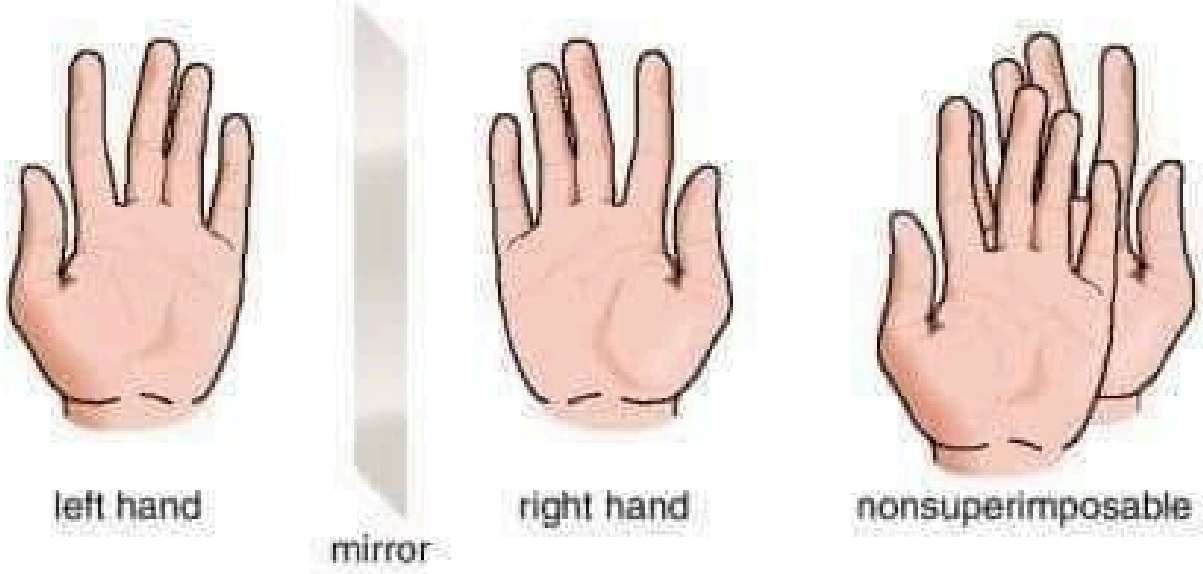
c)



stereoisomer

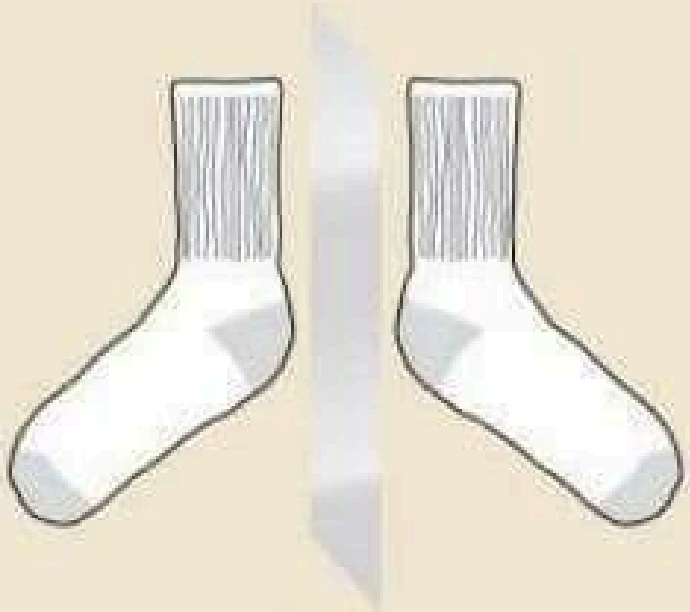
Chiral and Achiral Molecules

- Although everything has a mirror image, mirror images may or may not be superimposable.
- Some molecules are like hands. Left and right hands are mirror images, but they are not identical, or superimposable.



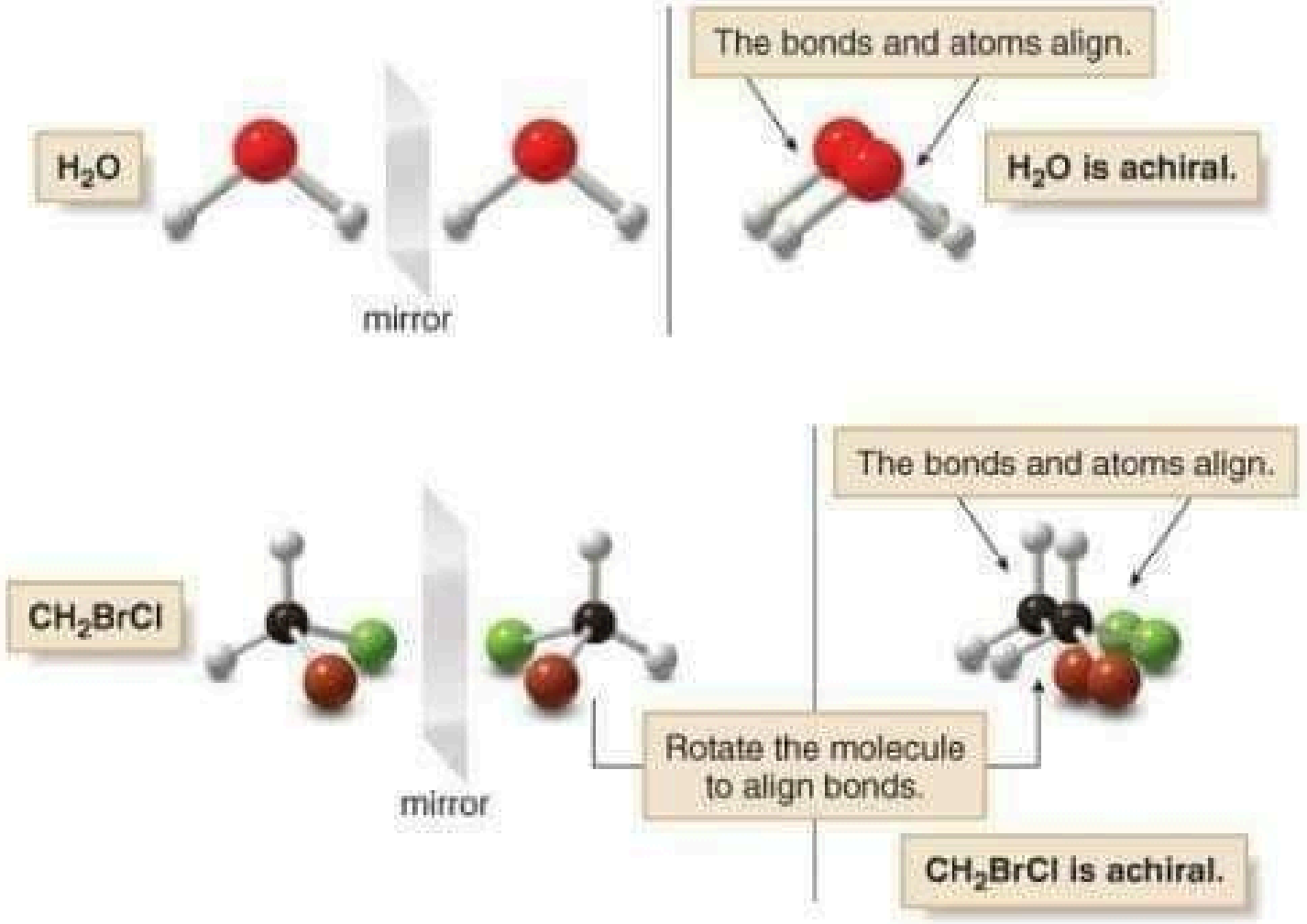
- A molecule (or object) that is *not* superimposable on its mirror image is said to be *chiral*.

- **Other molecules are like socks. Two socks from a pair are mirror images that are superimposable. A sock and its mirror image are identical.**
- **A molecule or object that is superimposable on its mirror image is said to be achiral.**
- **A molecule or object that is not superimposable on its mirror image is said to be chiral.**

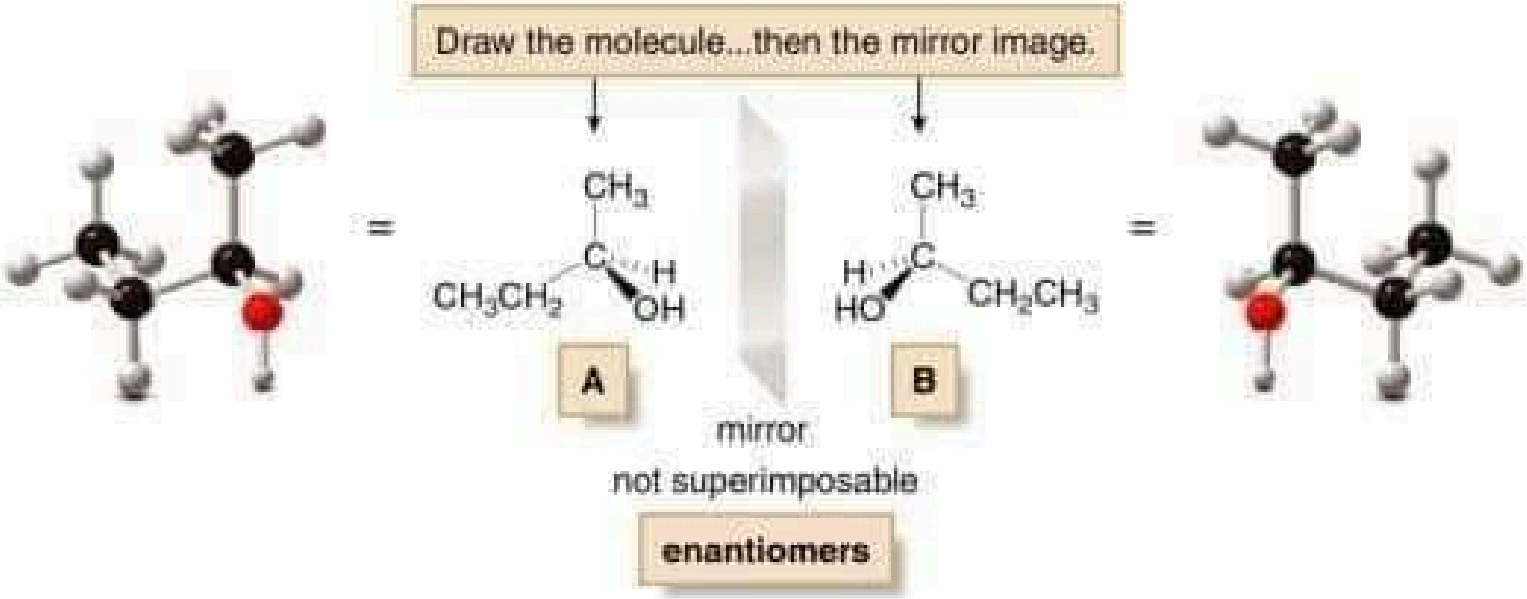


Socks are **achiral:** they are mirror images that are superimposable.

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



- 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.



- In general, a molecule with no stereogenic centers will not be chiral. There are exceptions to this that will be considered in Chapter 17.
- With one stereogenic center, a molecule will always be chiral.
- With two or more stereogenic centers, a molecule may or may not be chiral.
- 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.

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

CH_2BrCl

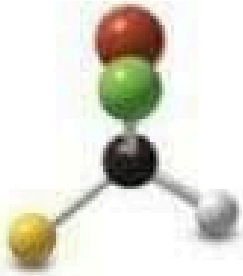
plane of symmetry

This molecule has **two identical halves.**

CH_2BrCl is **achiral.**

CHBrClF

NO plane of symmetry



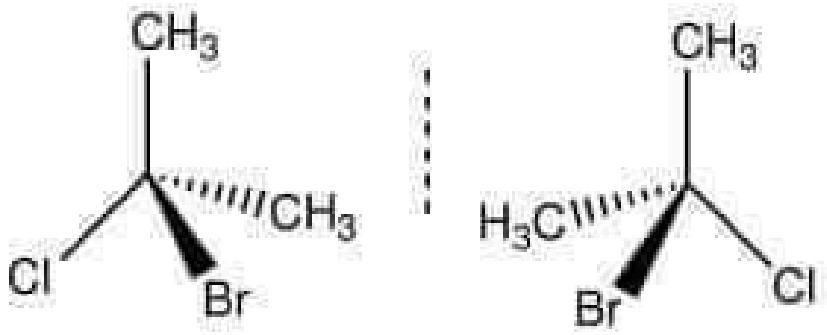
CHBrClF is **chiral.**

Summary of the Basic Principles of Chirality:

- Everything has a mirror image. The fundamental question is whether the molecule and its mirror image are superimposable.
- If a molecule and its mirror image are not superimposable, the molecule and its mirror image are chiral.
- The terms stereogenic center and chiral molecule are related but distinct. In general, a chiral molecule must have one or more stereogenic centers.
- The presence of a plane of symmetry makes a molecule achiral.

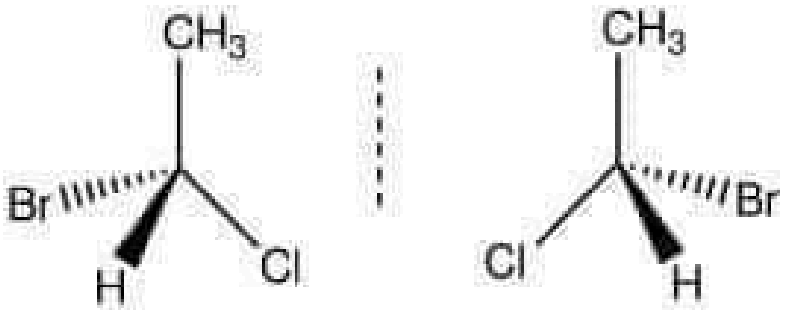
Clasiffy each of the following pairs as chiral or achiral.

a)



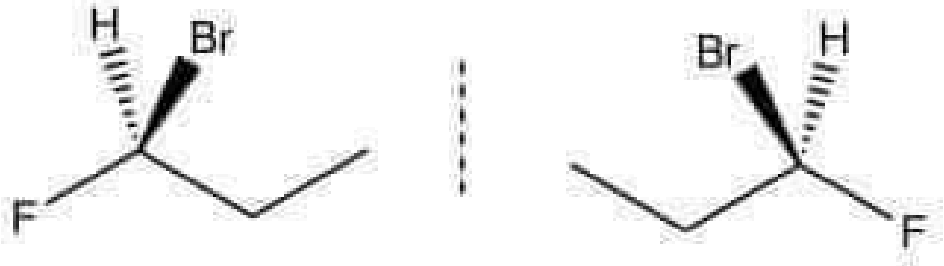
achiral

b)



chiral

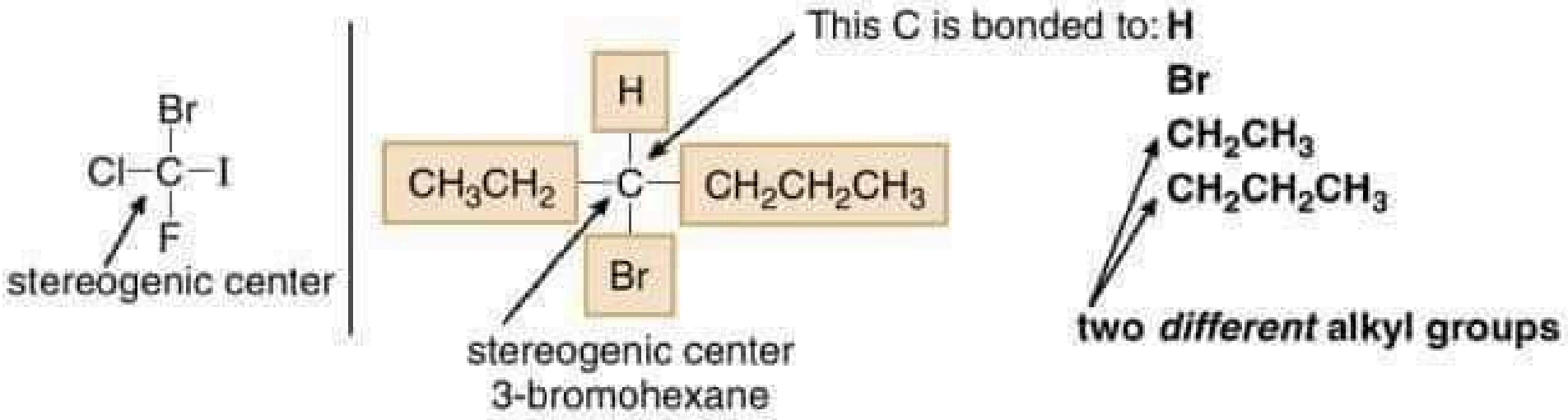
c)



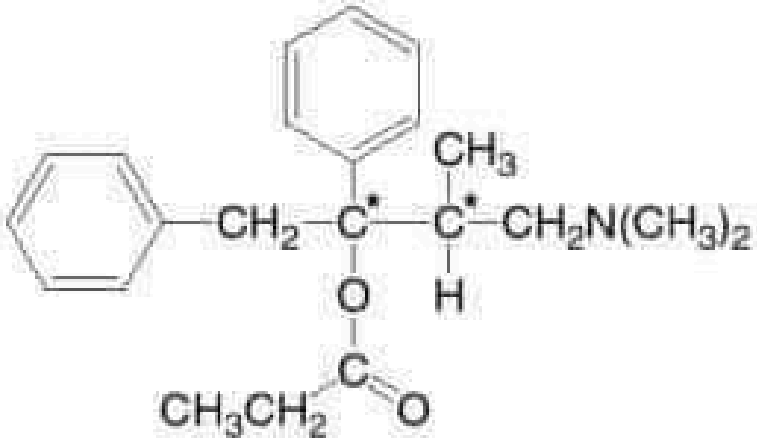
chiral

Stereogenic Centers

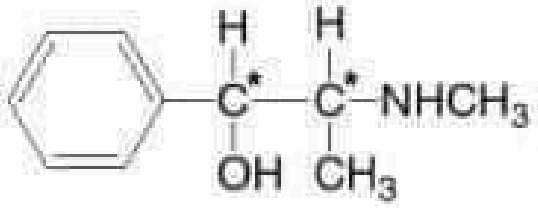
- To locate a stereogenic center, examine each tetrahedral carbon atom in a molecule, and look at the four groups—not the four atoms—bonded to it.
- Always omit from consideration all C atoms that cannot be tetrahedral stereogenic centers. These include
  - CH_2 and CH_3 groups
  - Any *sp* or sp^2 hybridized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



- **Larger organic molecules can have two, three or even hundreds of stereogenic centers.**

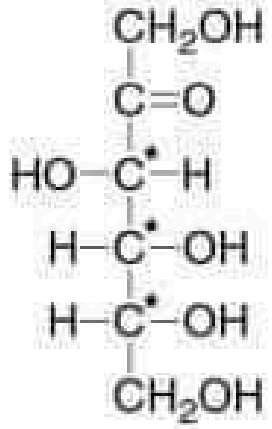


propoxyphene
Trade name: Darvon
(analgesic)



ephedrine
(bronchodilator, decongestant)

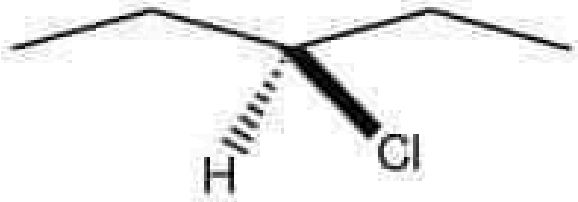
[* = stereogenic center]



fructose
(a simple sugar)

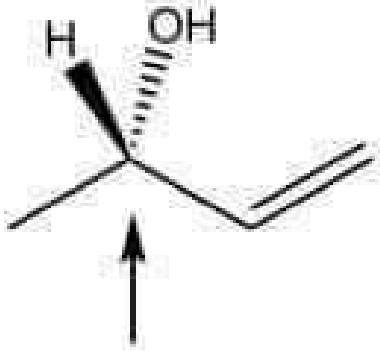
Label the stereogenic centers in each molecule and decide if it is chiral.

a) $CH_3CH_2CH(Cl)CH_2CH_3$



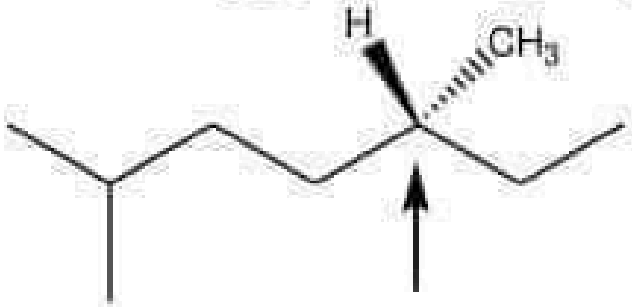
achiral

b) $CH_3CH(OH)CH{=}CH_2$



chiral

c) $(CH_3)_2CHCH_2CH_2CH(CH_3)CH_2CH_3$



chiral

- **To draw both enantiomers of a chiral compound such as 2-butanol, use the typical convention for depicting a tetrahedron: place two bonds in the plane, one in front of the plane on a wedge, and one behind the plane on a dash. Then, to form the first enantiomer, arbitrarily place the four groups—H, OH, CH_3 and CH_2CH_3—on any bond to the stereogenic center. Then draw the mirror image.**

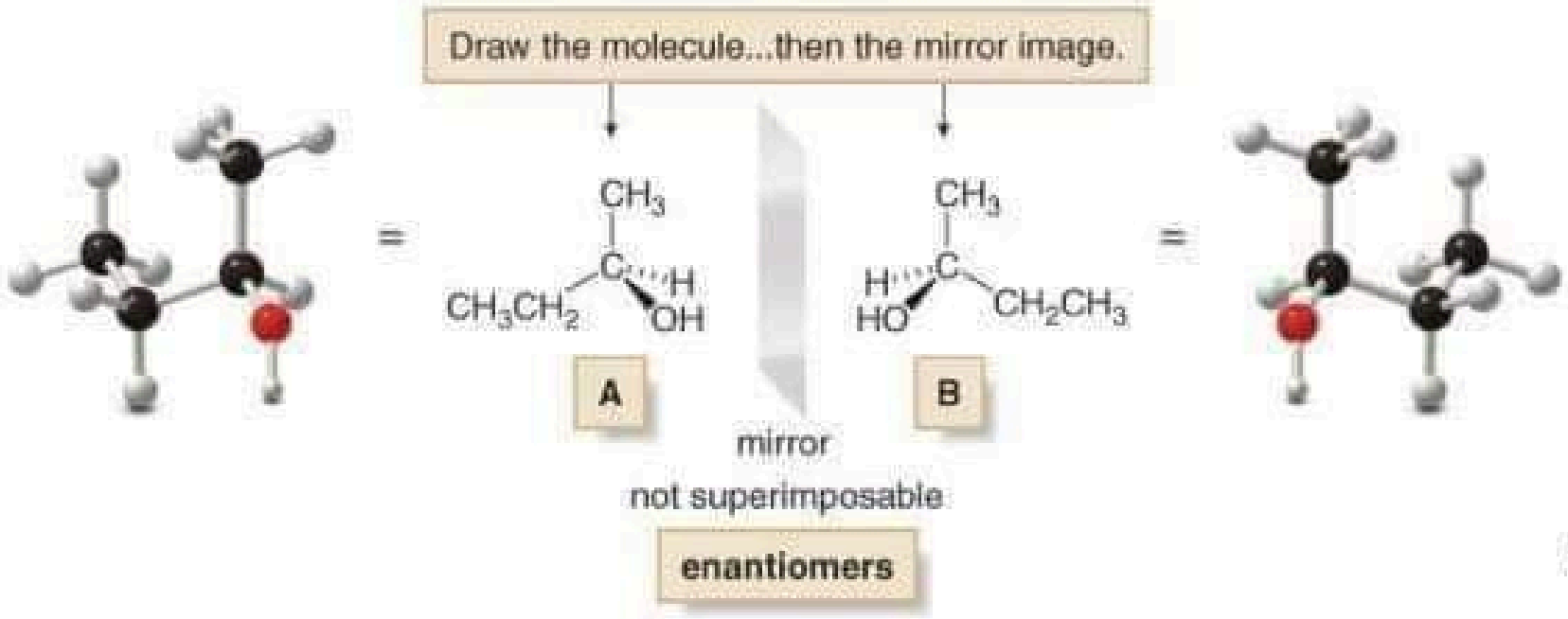
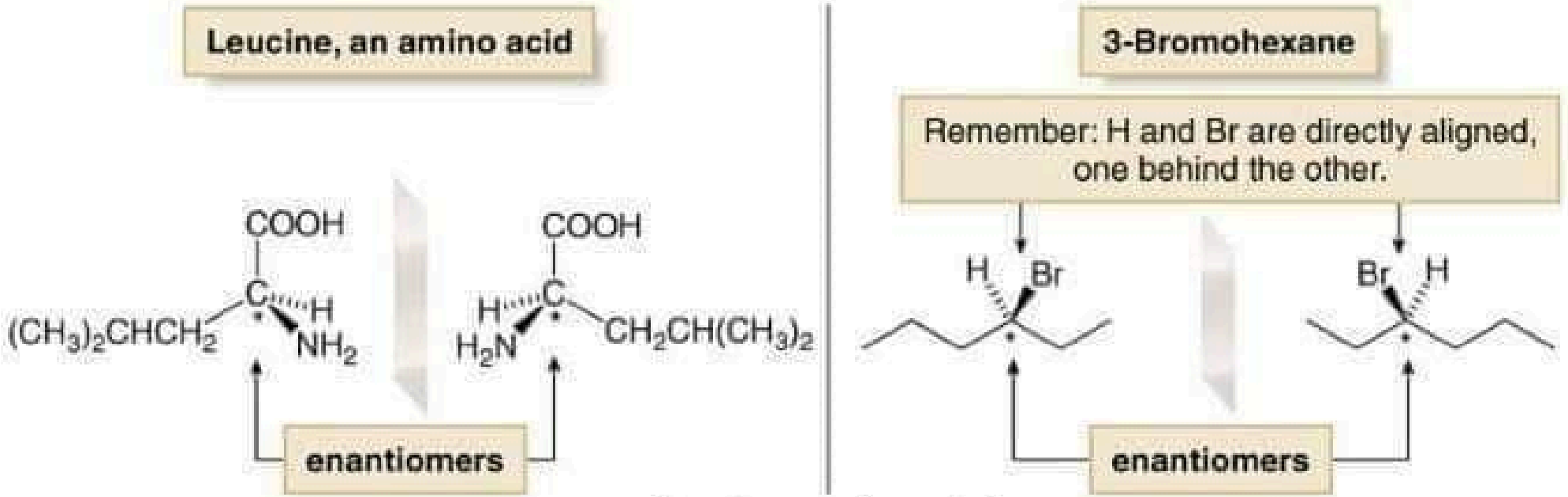
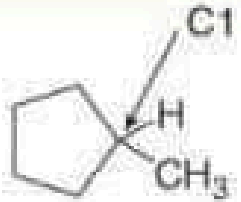


Figure 5.5
Three-dimensional representations for pairs of enantiomers



- **Stereogenic centers may also occur at carbon atoms that are part of a ring.**
- **To find stereogenic centers on ring carbons, always draw the rings as flat polygons, and look for tetrahedral carbons that are bonded to four different groups.**

Is C1 a stereogenic center?

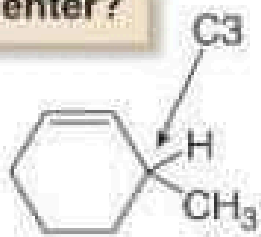


methylcyclopentane

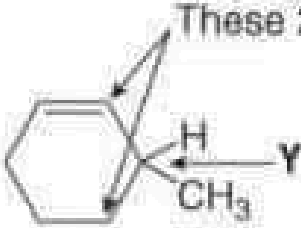
two identical groups, equidistant from C1

NO, C1 is **not** a stereogenic center.

Is C3 a stereogenic center?



3-methylcyclohexene



YES, C3 is a stereogenic center.

- **In 3-methylcyclohexene, the CH_3 and H substituents that are above and below the plane of the ring are drawn with wedges and dashes as usual.**