

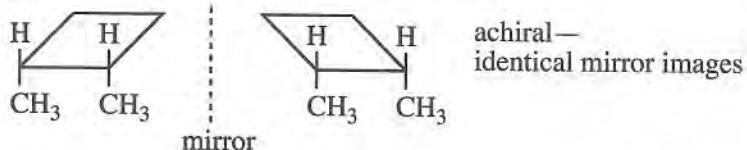
CHAPTER 5—STEREOCHEMISTRY

Note to the student: Stereochemistry is the study of molecular structure and reactions in three dimensions. Molecular models will be especially helpful in this chapter.

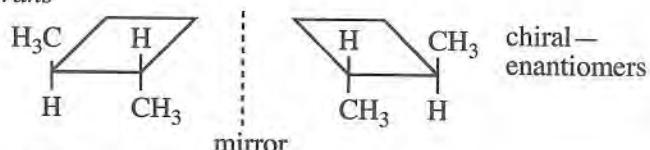
5-1 The best test of whether a household object is chiral is whether it would be used equally well by a left- or right-handed person. The chiral objects are the corkscrew, the writing desk, the can opener, the screw-cap bottle (only for refilling, however; in use, it would not be chiral), the rifle and the knotted rope. The corkscrew, the bottle top, and the rope each have a twist in one direction. The rifle, corkscrew, and desk are clearly made for right-handed users; the can opener is for a left-handed person. All the other objects are achiral and would feel equivalent to right- or left-handed users.

5-2

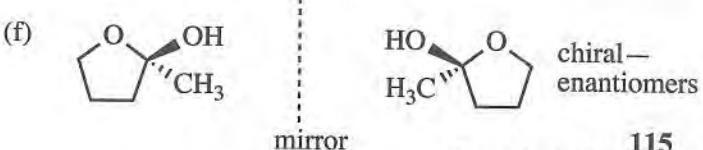
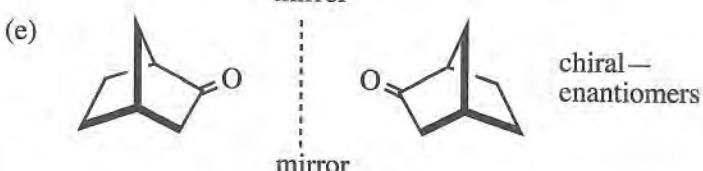
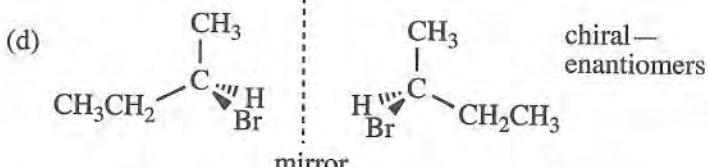
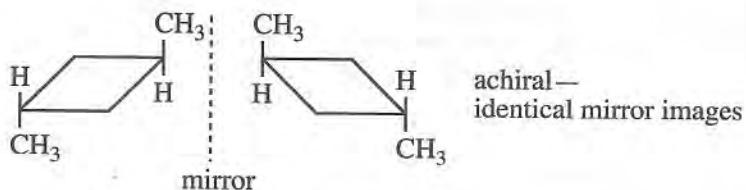
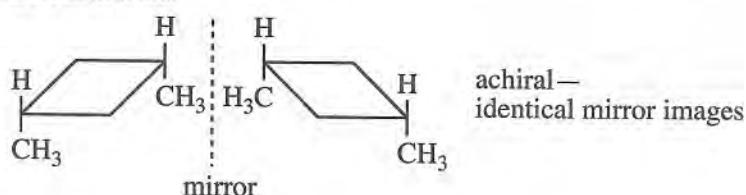
(a) *cis*



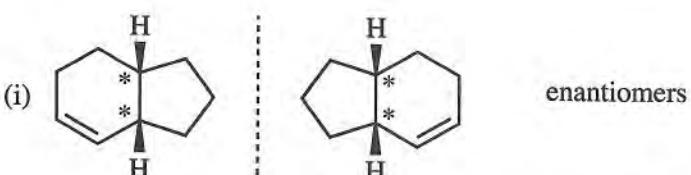
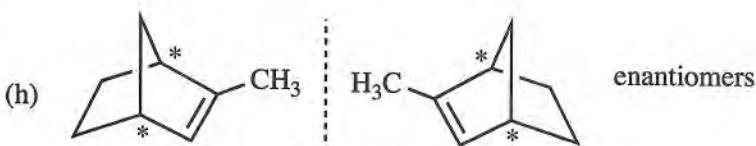
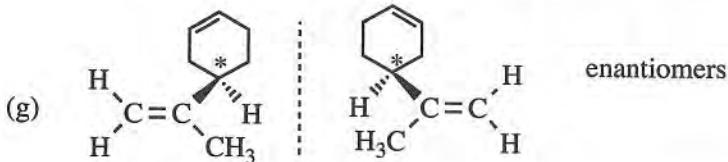
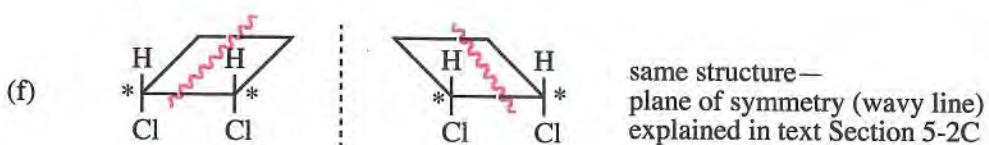
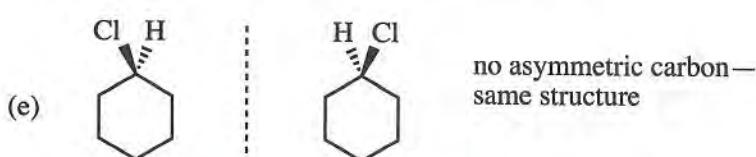
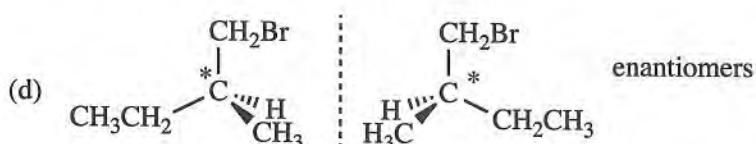
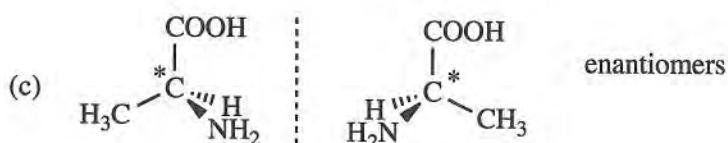
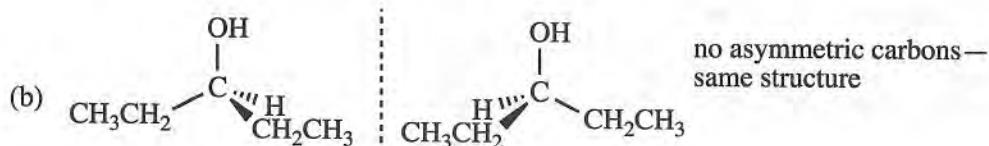
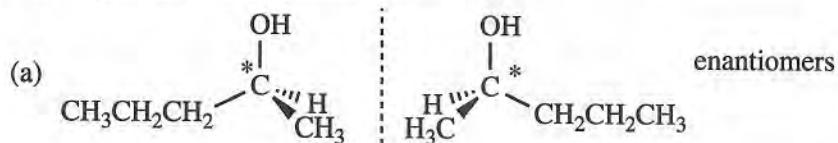
(b) *trans*



(c) *cis* first, then *trans*

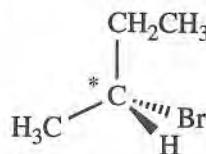


5-3 Asymmetric carbon atoms are starred.

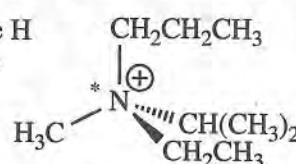


5-4 You may have chosen to interchange two groups different from the ones shown here. The type of isomer produced will still be the same as listed here.

Interchanging any two groups around a chiral center (*) will create an enantiomer of the first structure.

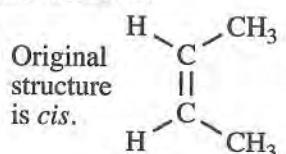


Interchanging the Br and the H creates an enantiomer of the structure in Figure 5-5.

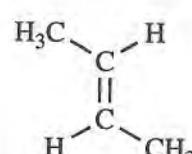


Interchanging the ethyl and the isopropyl creates an enantiomer of the structure in Figure 5-5.

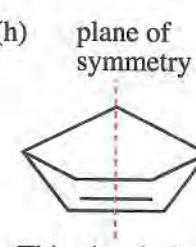
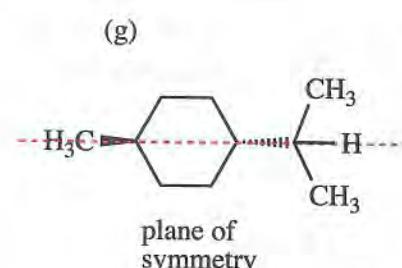
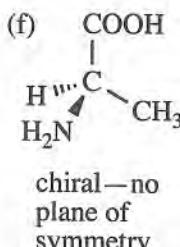
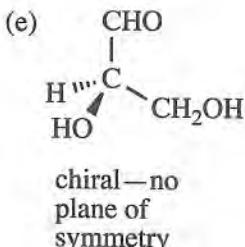
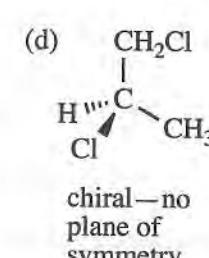
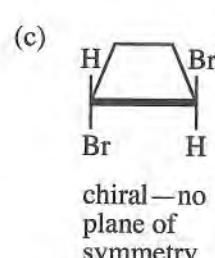
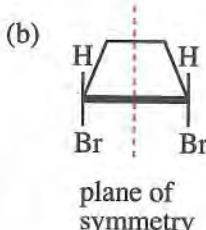
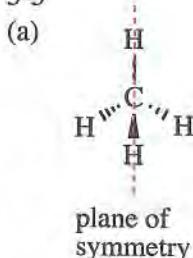
On a double bond, interchanging the two groups on ONE of the stereocenters will create the other geometric (*cis-trans*) isomer. However, interchanging the two groups on BOTH of the stereocenters will give the original structure.



Interchange H and CH₃ on top stereocenter to produce *trans* (interchanging bottom two groups will give the same structure).

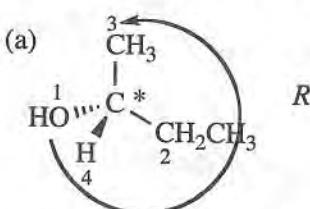


5-5

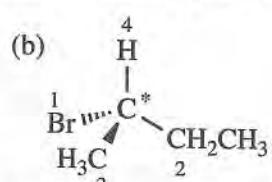


This view is from the right side of the structure as drawn in the text.

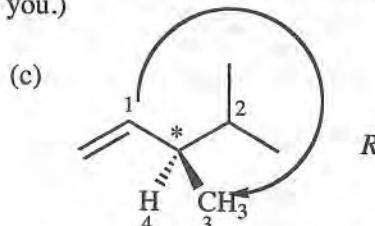
5-6 Place the 4th priority group away from you, where possible. Then determine if the sequence 1→2→3 is clockwise (R) or counter-clockwise (S). (There is a Problem-Solving Hint near the end of section 5-3 in the text that describes what to do when the 4th priority group is closest to you.)



This appears to be *S*, but group 4 is coming toward the viewer, so the opposite chirality must be assigned; it is actually *R*.

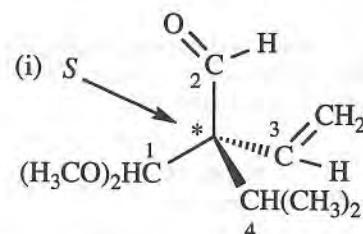
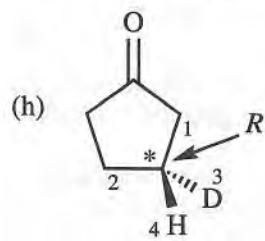
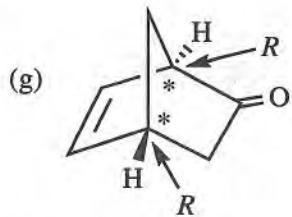
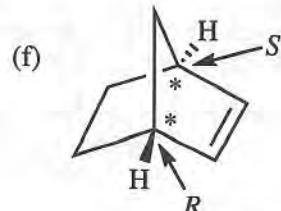
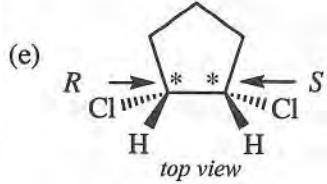
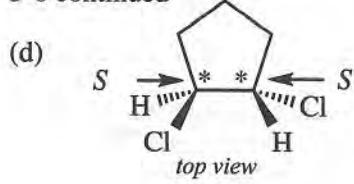


Viewing from the bottom to put group 4 going away, the arrow is counterclockwise; the chirality is *S*.

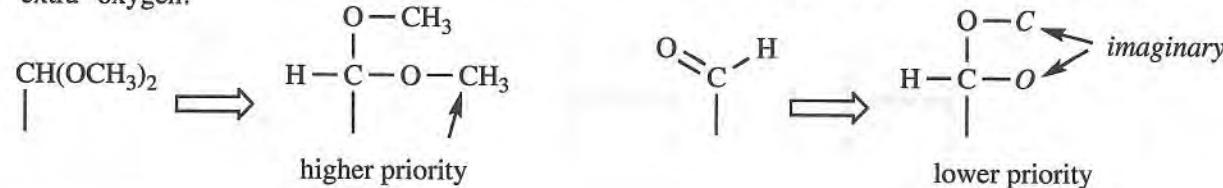


Viewing from the front to put group 4 going away, the arrow is clockwise; the chirality is *R*.

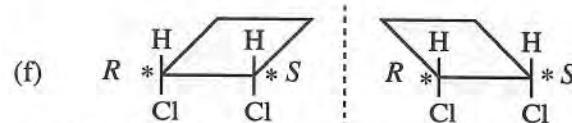
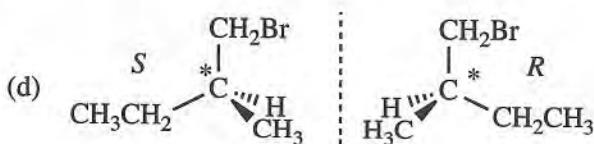
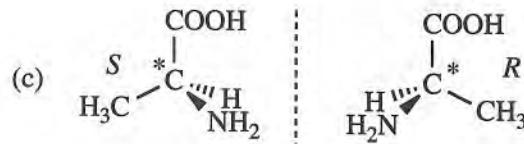
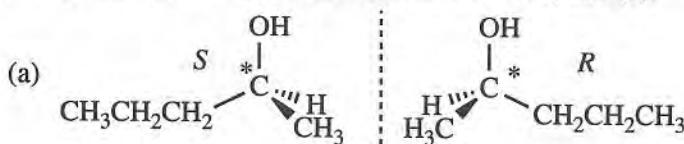
5-6 continued



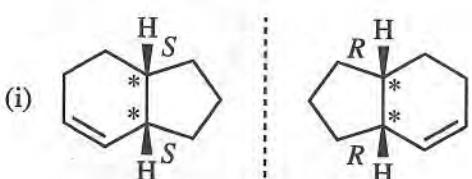
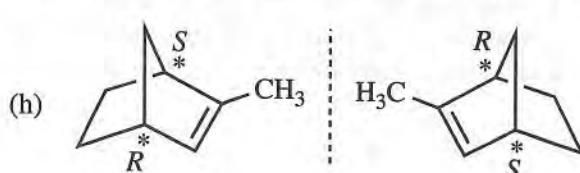
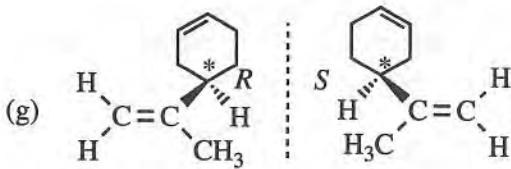
Part (i) deserves some explanation. The difference between groups 1 and 2 hinges on what is on the "extra" oxygen.



5-7 There are no asymmetric carbons in 5-3 (b) and (e).



The identity of these two structures becomes more clear with the assignments of configuration.



What can you conclude about the designation of configuration between two enantiomers?

5-8

$$2.0 \text{ g} / 10.0 \text{ mL} = 0.20 \text{ g/mL}; 100 \text{ mm} = 1 \text{ dm}$$

$$[\alpha]_D^{25} = \frac{+1.74^\circ}{(0.20)(1)} = +8.7^\circ \text{ for (+)-glyceraldehyde}$$

5-9

$$0.50 \text{ g} / 10.0 \text{ mL} = 0.050 \text{ g/mL}; 20 \text{ cm} = 2 \text{ dm}$$

$$[\alpha]_D^{25} = \frac{-5.1^\circ}{(0.050)(2)} = -51^\circ \text{ for (-)-epinephrine}$$

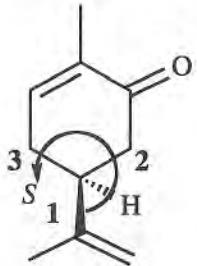
5-10

Measure using a solution of about one-fourth the concentration of the first. The value will be either $+45^\circ$ or -45° , which gives the sign of the rotation.

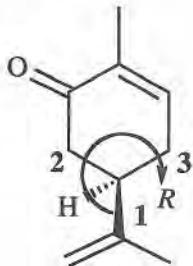
5-11

Whether a sample is dextrorotatory (abbreviated "(+)") or levorotatory (abbreviated "(-)") is determined experimentally by a polarimeter. Except for the molecule glyceraldehyde (see text Section 5-14), there is no direct, universal correlation between direction of optical rotation ((+) and (-)) and designation of configuration (*R* and *S*). In other words, one dextrorotatory compound might have *R* configuration while a different dextrorotatory compound might have *S* configuration.

- (a) Yes, both of these are determined experimentally: the (+) or (-) by the polarimeter and the smell by the nose.
(b) No, *R* or *S* cannot be determined by either the polarimeter or the nose.
(c) The drawings show that (+)-carvone from caraway has the *S* configuration and (-)-carvone from spearmint has the *R* configuration.



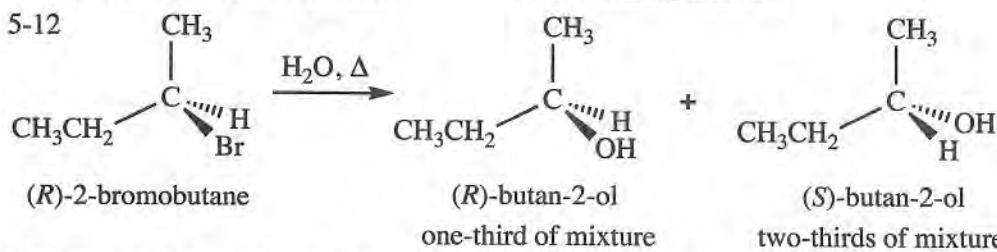
(+)-carvone (caraway seed)



(-)-carvone (spearmint)

(For fun, ask your instructor if you can smell the two enantiomers of carvone. Some people are unable, presumably for genetic reasons, to distinguish the fragrance of the two enantiomers.)

5-12



Chapter 6 will explain how these mixtures come about. For this problem, the *S* enantiomer accounts for 66.7% of the butan-2-ol in the mixture and the rest, 33.3%, is the *R* enantiomer. Therefore, the excess of one enantiomer over the racemic mixture must be 33.3% of the *S*, the enantiomeric excess. (All of the *R* is "canceled" by an equal amount of the *S*, algebraically as well as in optical rotation.)

The optical rotation of pure *(S)*-butan-2-ol is $+13.5^\circ$. (If you had chosen the opposite sign, then the answer will be opposite. That is not the important part of this problem.) The optical rotation of this mixture is:

$$33.3\% \times (+13.5^\circ) = +4.5^\circ$$

see next page for an alternative solution

5-12 continued

(This algebraic approach has been suggested by Editorial Adviser Richard King.)
From the problem, the reaction produces twice as much (*S*)-(+)-butan-2-ol (the *d* isomer) as (*R*)(-)-butan-2-ol (the *l* isomer): $d = 2l$

$$\text{e.e.} = \frac{d-l}{d+l} \times 100\% = \frac{2l-l}{2l+l} \times 100\% = \frac{l}{3l} \times 100\% = 33.3\%$$

The calculation of optical rotation of the mixture is the same as on the previous page.

5-13 The rotation of pure (+)-butan-2-ol is $+13.5^\circ$.

$$\frac{\text{observed rotation}}{\text{rotation of pure enantiomer}} = \frac{+0.45^\circ}{+13.5^\circ} \times 100\% = 3.3\% \text{ optical purity}$$

$= 3.3\% \text{ e.e.} = \text{excess of (+) over (-)}$

To calculate percentages of (+) and (-): (two equations in two unknowns)

$$(+)+(-)=100\% \longrightarrow (-)=100\%-(+)$$

$$(+)-(-)=3.3\% \longrightarrow (+)-(100\%-(+))=3.3\%$$

$$2(+)=103.3\%$$

$(+)=51.6\%$ (rounded)
$(-) = 48.4\%$

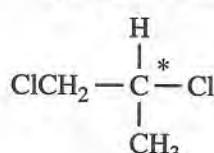
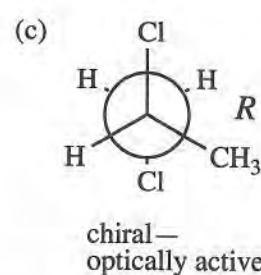
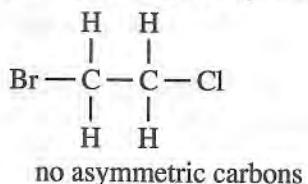
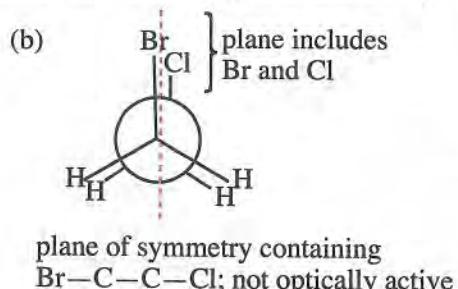
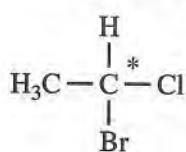
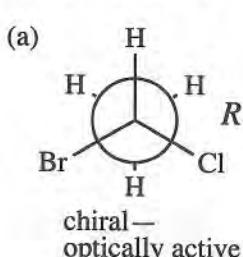
(This algebraic approach has been suggested by Editorial Adviser Richard King.)

$$\text{e.e.} = \frac{d-l}{d+l} \times 100\% = 3.33\% \longrightarrow \frac{d-l}{d+l} = \frac{3.33\%}{100\%} \longrightarrow$$

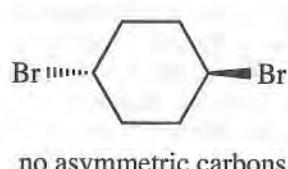
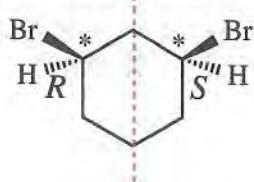
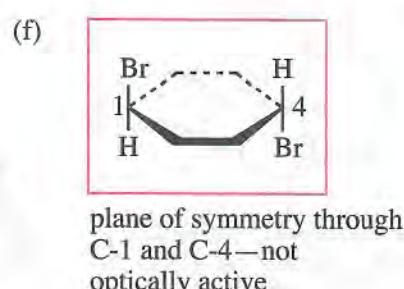
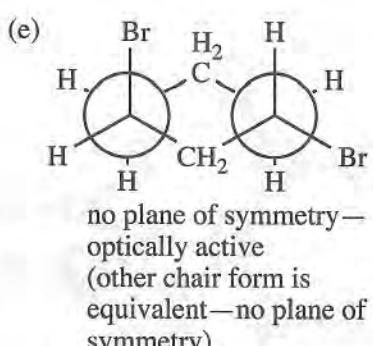
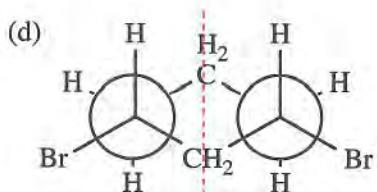
$$\left. \begin{array}{l} d-l = 3.33\% \\ \text{and } d+l = 100\% \end{array} \right\} \text{add these two equations}$$

$$2d = 103.33\% \longrightarrow d = 51.6\% \quad l = 100\% - d = 100\% - 51.6\% = 48.4\%$$

5-14 Drawing Newman projections is the clearest way to determine symmetry of conformations.

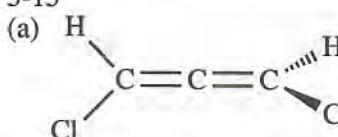


5-14 continued

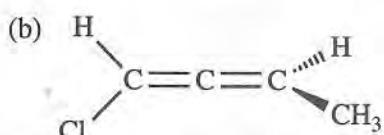
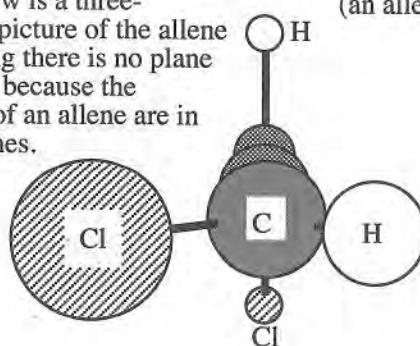


Part (2) Predictions of optical activity based on asymmetric centers give the same answers as predictions based on the most symmetric conformation. NOTE: The assignment of *R* and *S* above might be different from your answers if you happened to draw the enantiomer.

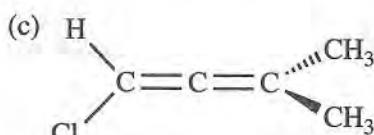
5-15



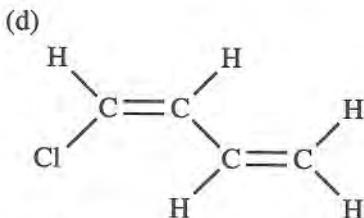
No asymmetric carbons, but the molecule is chiral (an allene); the drawing below is a three-dimensional picture of the allene in (a) showing there is no plane of symmetry because the substituents of an allene are in different planes.



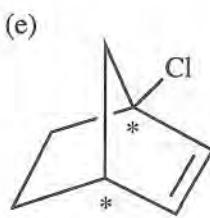
No asymmetric carbons, but the molecule is chiral (an allene).



No asymmetric carbons; this allene has a plane of symmetry between the two methyls (the plane of the paper), including all the other atoms because the two pi bonds of an allene are perpendicular, the Cl is in the plane of the paper and the plane of symmetry goes through it; not a chiral molecule.

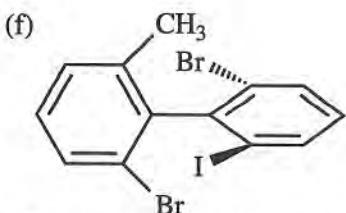


planar molecule—no asymmetric carbons; not a chiral molecule

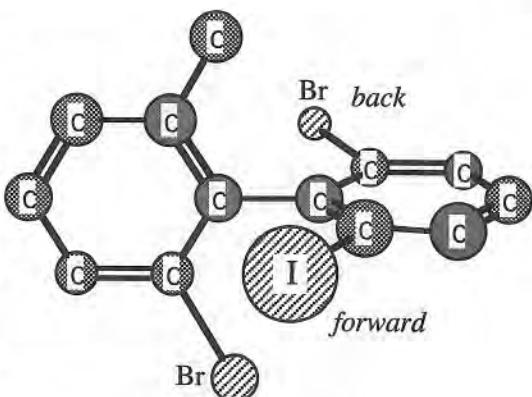


two asymmetric carbons and no plane of symmetry;
a chiral compound

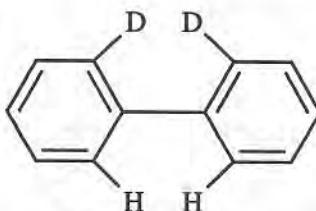
5-15 continued



No asymmetric carbons, but the molecule is chiral due to restricted rotation that precludes a plane of symmetry; the drawing below is a three-dimensional picture showing that the rings are perpendicular (hydrogens are not shown).

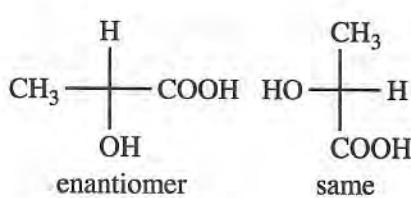
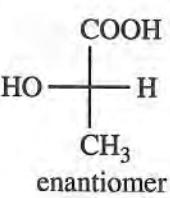
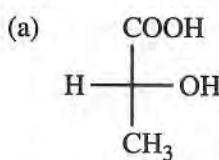


(g)



No asymmetric carbons, and the groups are not large enough to restrict rotation; thus, it has a plane of symmetry and is not a chiral compound.

5-16

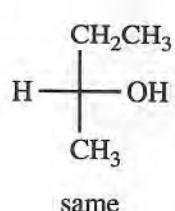
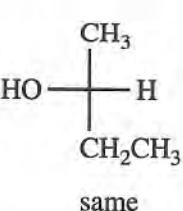
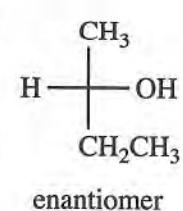
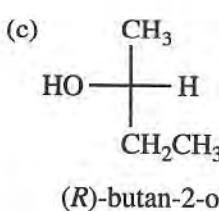
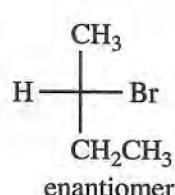
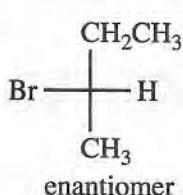
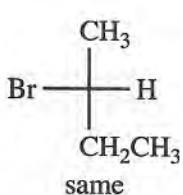
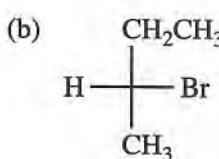


Rules for Fischer projections:

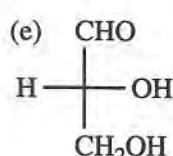
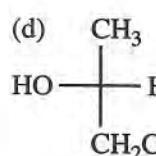
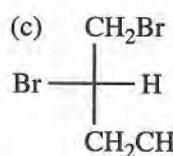
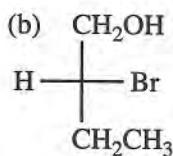
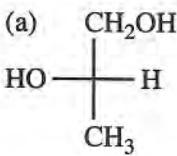
1. Interchanging any two groups an odd number of times (once, three times, etc.) makes an enantiomer.

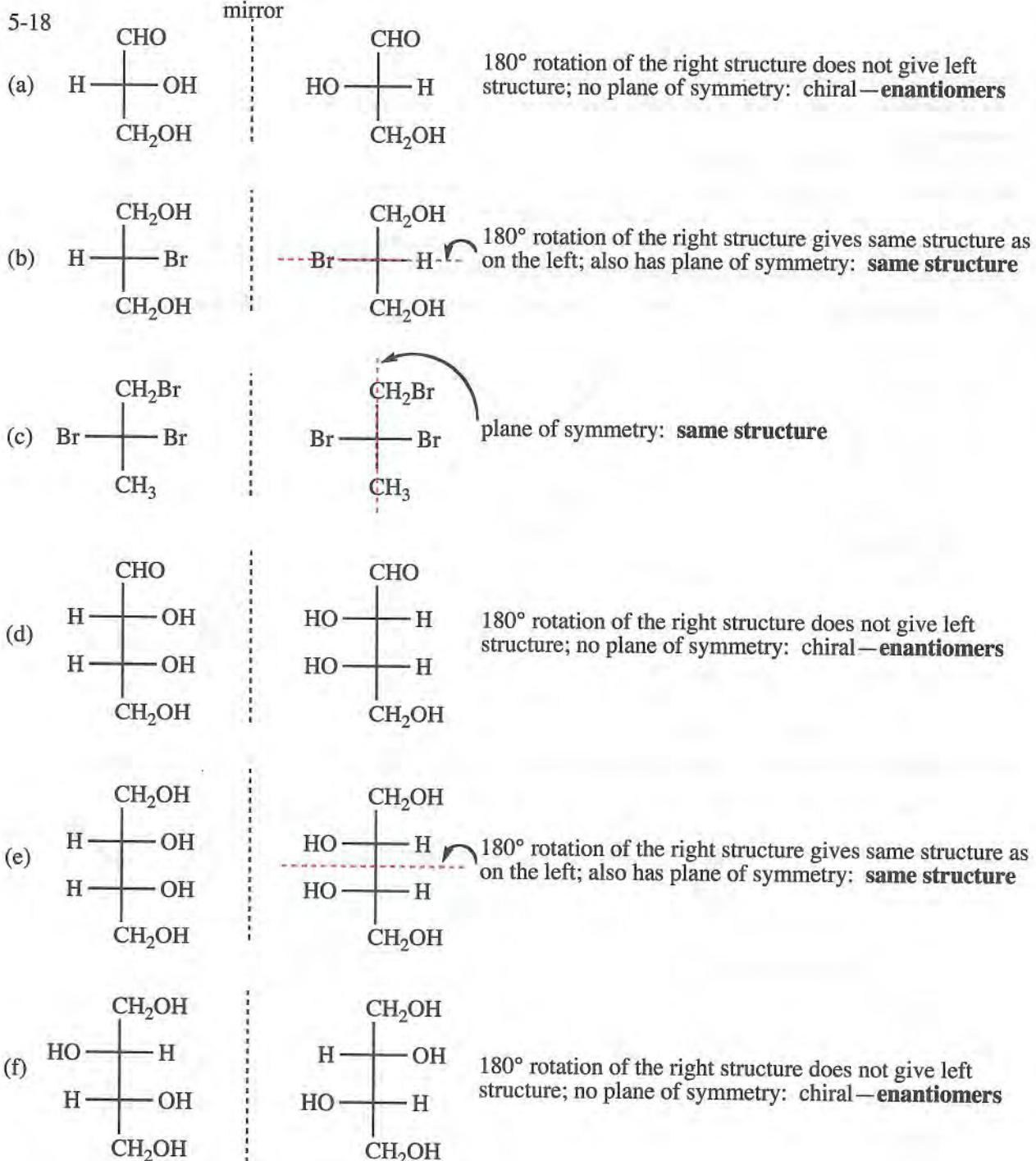
Interchanging any two groups an even number of times (e.g. twice) returns to the original stereoisomer.

2. Rotating the structure by 90° makes the enantiomer.
Rotating by 180° returns to the original stereoisomer.
(The second rule is an application of the first.
Prove this to yourself.)



5-17





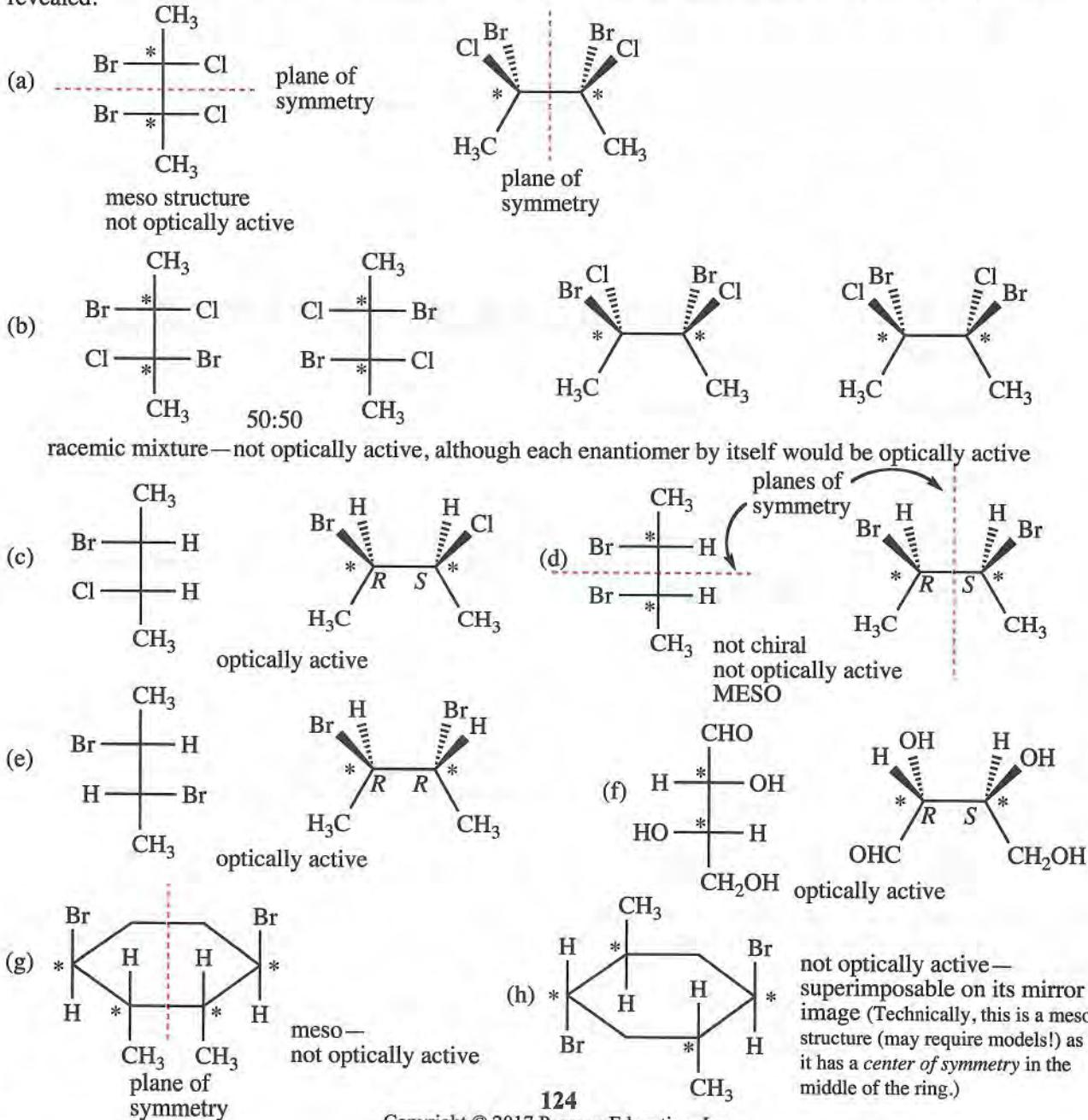
5-19 If the Fischer projection is drawn correctly, the most oxidized carbon (most bonds to oxygen) will be at the top; this is the carbon with the greatest number of bonds to oxygen. Then the numbering goes from the top down.

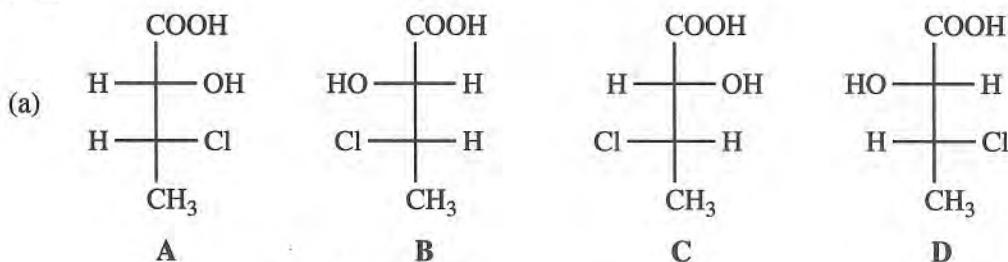
- | | | |
|-----------|----------------------------|----------------------|
| (a) R | (b) no chiral center | (c) no chiral center |
| (d) 2R,3R | (e) 2S,3R (numbering down) | (f) 2R, 3R |
| (g) R | (h) S | (i) S |

5-20

- enantiomers—configurations at both asymmetric carbons inverted
- diastereomers—configuration at only one asymmetric carbon inverted
- diastereomers—configuration at only one asymmetric carbon inverted (the left carbon)
- constitutional isomers—C=C shifted position
- enantiomers—chiral, mirror images
- diastereomers—configuration at only one asymmetric carbon inverted (the top one)
- enantiomers—configuration at all asymmetric carbons inverted
- enantiomers—the front C is an asymmetric carbon atom; the two Newmans are mirror images
- diastereomers—configuration at only one chiral center (the nitrogen) inverted

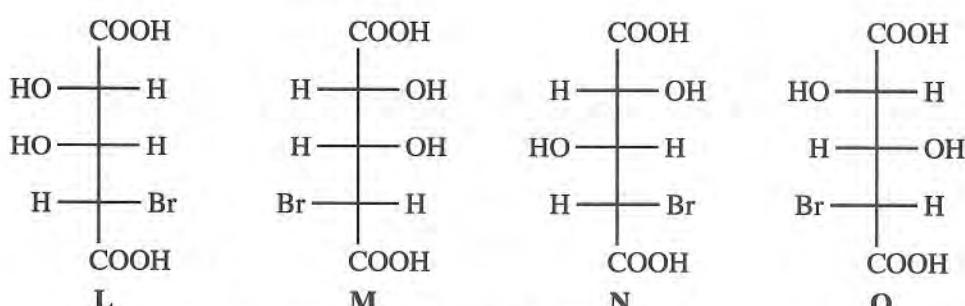
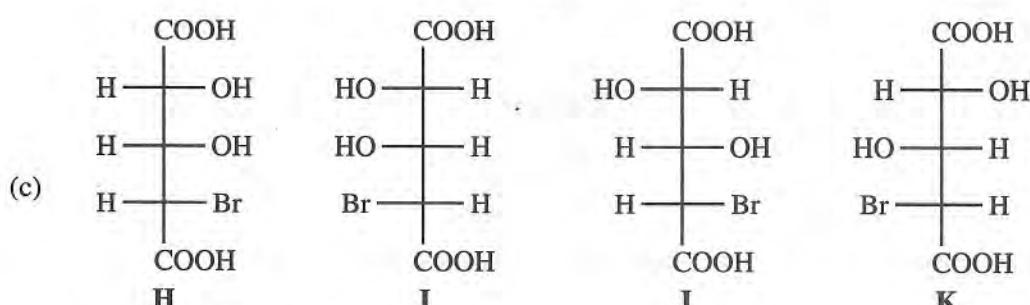
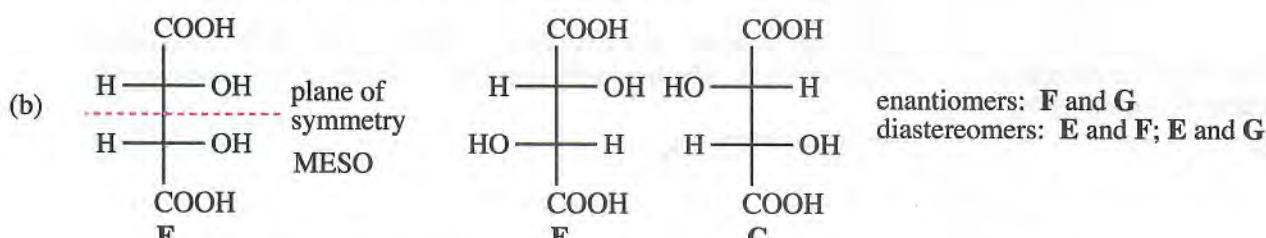
5-21 It would be excellent practice to draw Newman projections of each structure! Symmetry is quickly revealed.



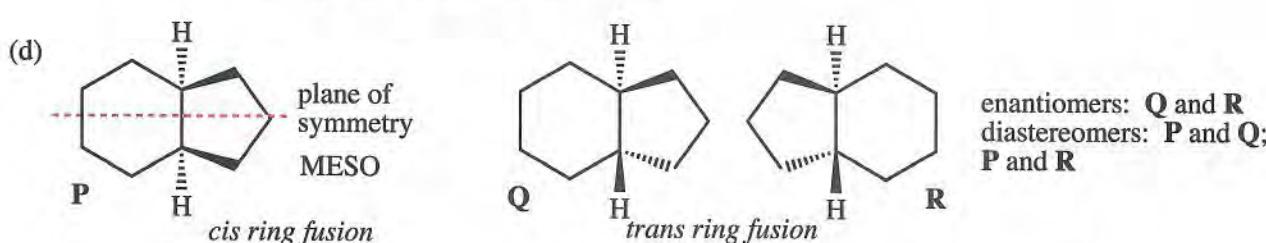


enantiomers: **A** and **B**; **C** and **D**

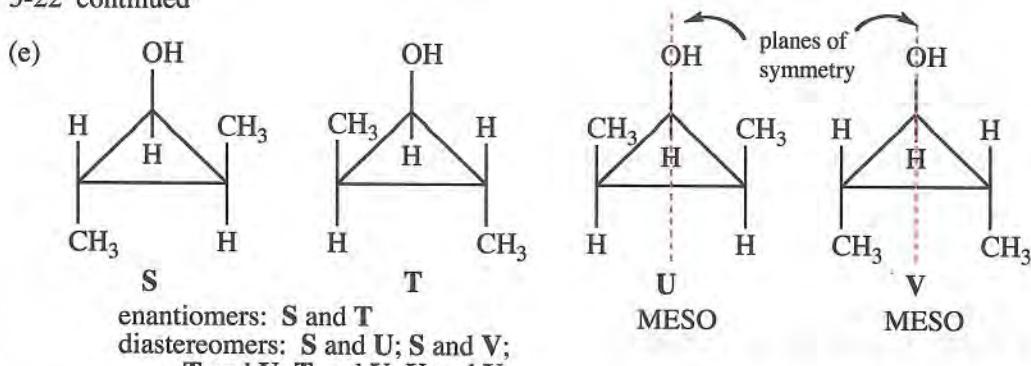
diastereomers: A and C; A and D; B and C; B and D



enantiomers: H and I; J and K; L and M; N and O
 diastereomers: any pair that is not enantiomeric

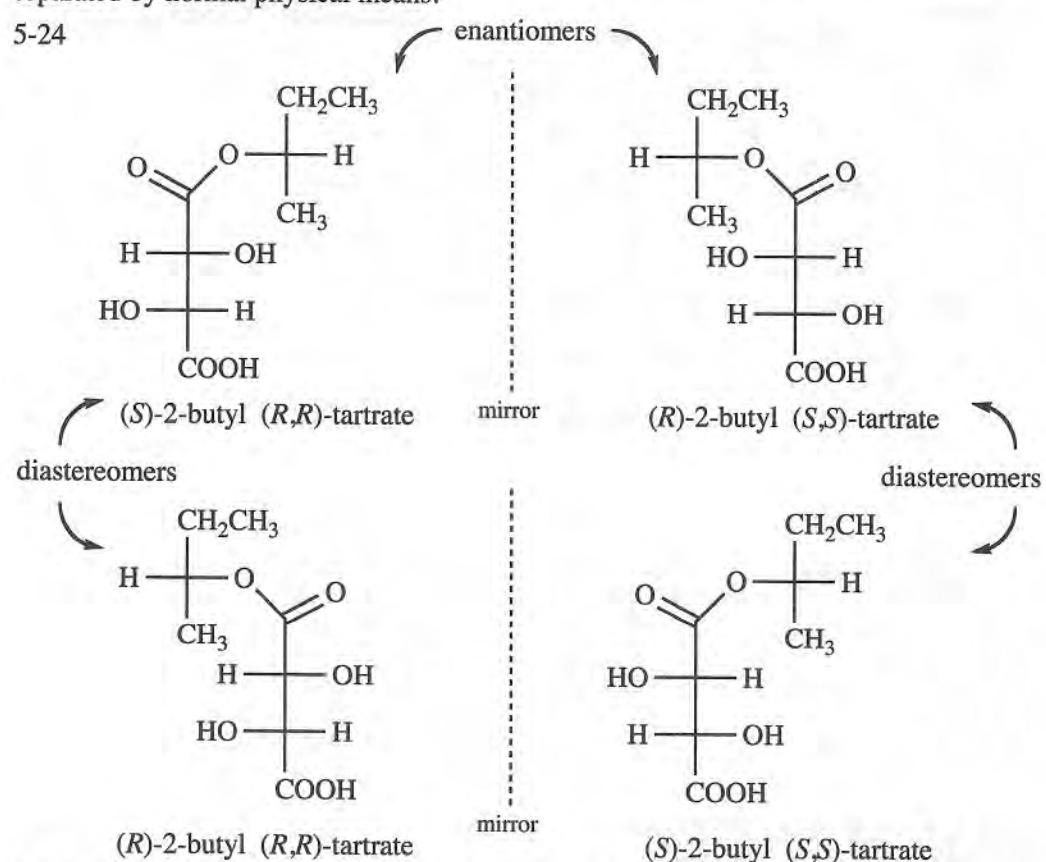


5-22 continued

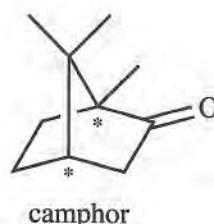
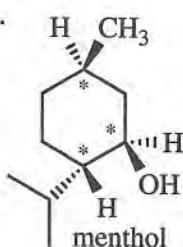
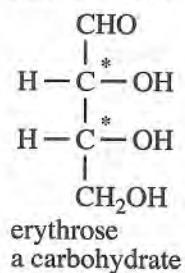
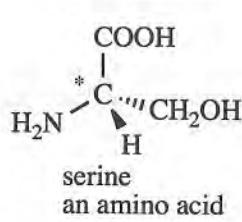


5-23 Any diastereomeric pair could be separated by a physical process like distillation or crystallization. Diastereomers are found in parts (a), (b), and (d). The structures in (c) are enantiomers; they could not be separated by normal physical means.

5-24

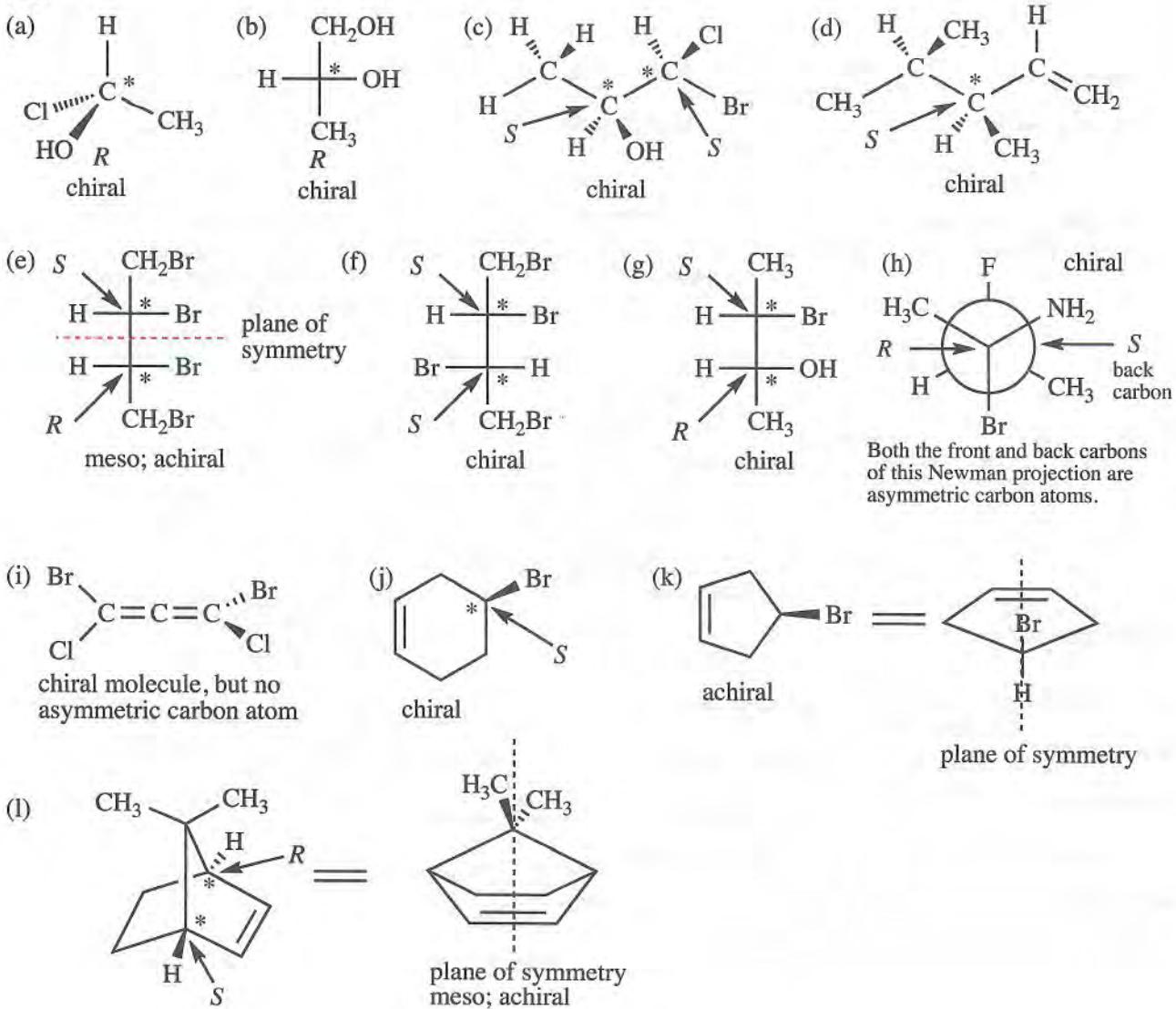


5-25 The asymmetric carbon atoms are indicated by asterisks.

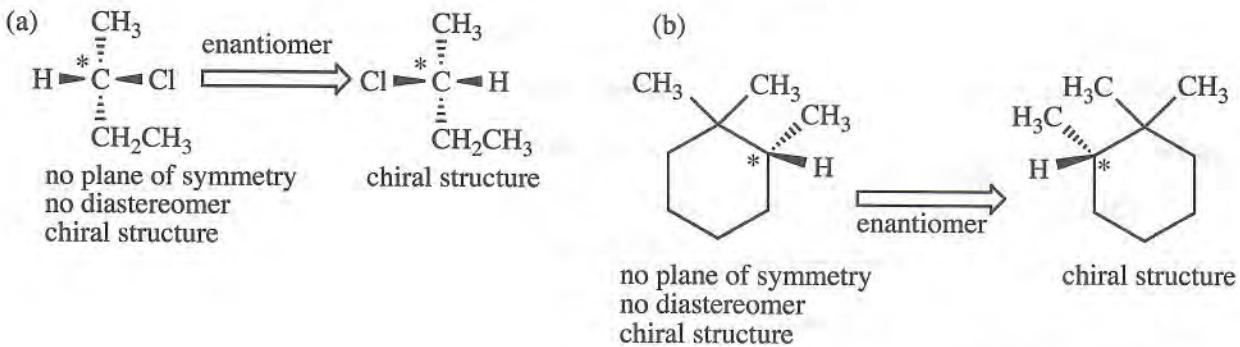


Both of these are monoterpenes.

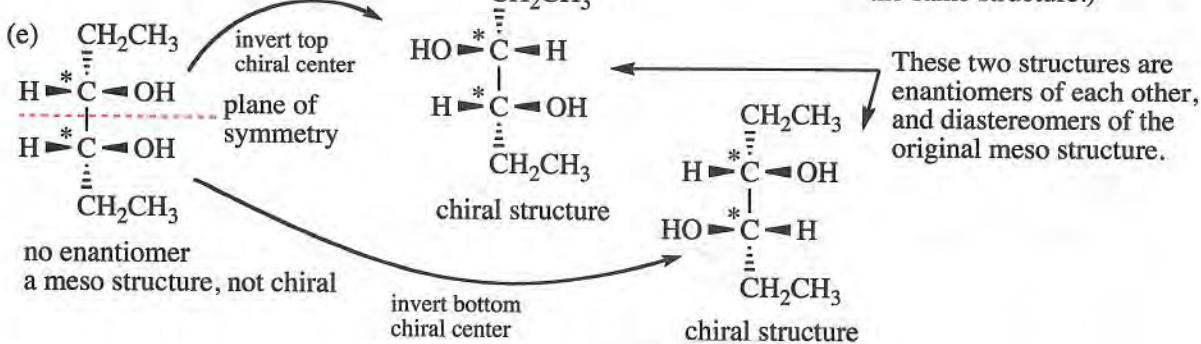
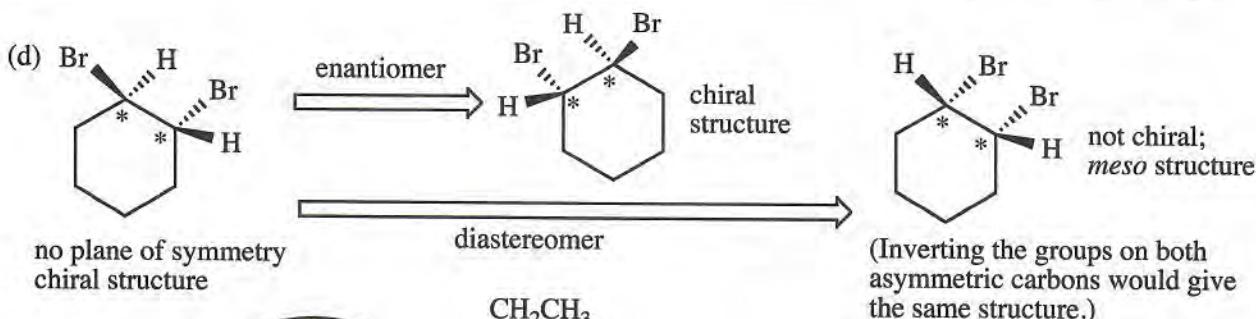
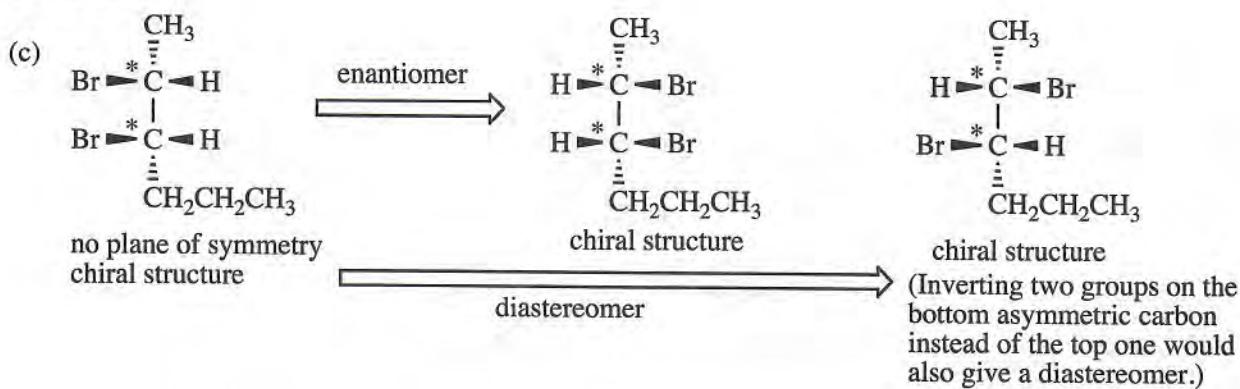
5-26



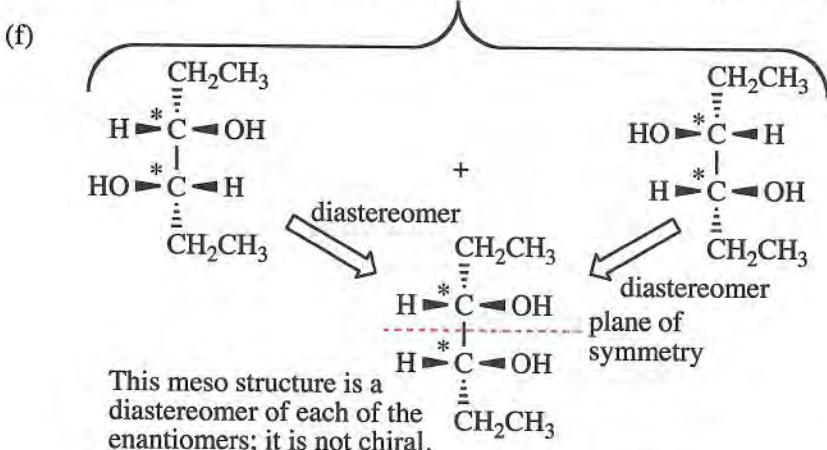
5-27



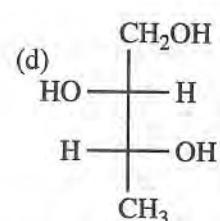
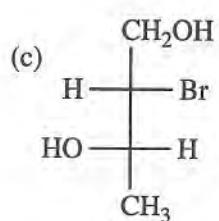
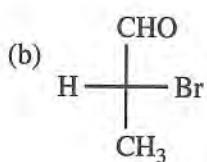
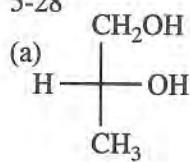
5-27 continued



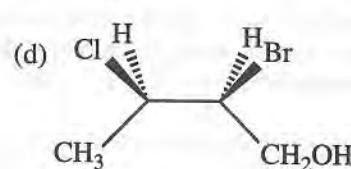
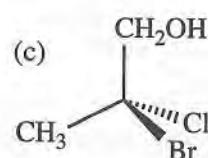
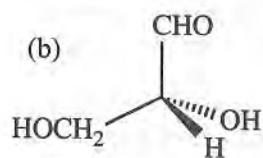
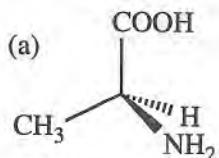
racemic mixture of enantiomers; each is chiral with no plane of symmetry



5-28



5-29 Your drawings may look different from these and still be correct. Check configuration by assigning *R* and *S* to be sure.

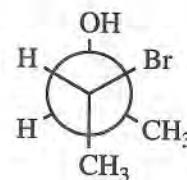
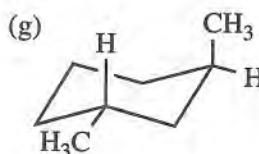
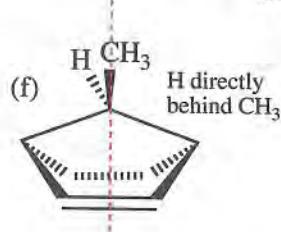
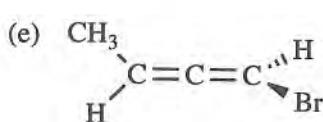
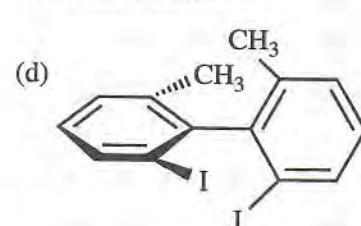
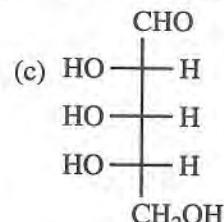
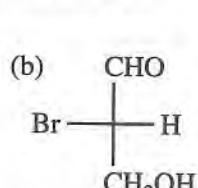
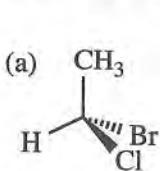


5-30

- (a) same (meso)—plane of symmetry, superimposable
- (b) enantiomers—configuration inverted at both asymmetric carbon atoms
- (c) enantiomers—configuration inverted at both asymmetric carbon atoms
- (d) enantiomers—Solve this problem by switching two groups at a time to put the groups in the same positions as in the first structure; it takes three switches to make the identical compound, so they are enantiomers; an even number of switches would prove they are the same structure.
- (e) diastereomers—Front carbon has same configuration (rotate Br down), back carbon is mirror image
- (f) diastereomers—configuration inverted at only one asymmetric carbon
- (g) enantiomers—configuration inverted at both asymmetric carbon atoms
- (h) same compound—Rotate the right structure 180° around a horizontal axis and it becomes the left structure; it might help to assign *R* and *S* to the C—Br groups: one is *R* and the other is *S*, and this makes it easier to see how they are superimposable.
- (i) enantiomers—nonsuperimposable mirror images

Enantiomers have identical chemical and physical properties and cannot be separated by normal methods like distillation or crystallization. Diastereomers, however, have different properties and are therefore separable: the structures in parts (e) and (f) could be separated by normal physical methods.

5-31 Drawing the enantiomer of a chiral structure is as easy as drawing its mirror image.



plane of symmetry—
no enantiomer

5-32

(a) $1.00 \text{ g} / 20.0 \text{ mL} = 0.0500 \text{ g/mL}$; $20.0 \text{ cm} = 2.00 \text{ dm}$

$$[\alpha]_D^{25} = \frac{-1.25^\circ}{(0.0500)(2.00)} = -12.5^\circ$$

(b) $0.050 \text{ g} / 2.0 \text{ mL} = 0.025 \text{ g/mL}$; $2.0 \text{ cm} = 0.20 \text{ dm}$

$$[\alpha]_D^{25} = \frac{+0.043^\circ}{(0.025)(0.20)} = +8.6^\circ$$

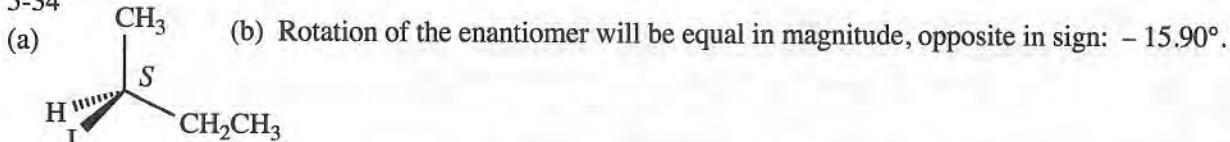
5-33 The 32% of the mixture that is (-)-tartaric acid will cancel the optical rotation of the 32% of the mixture that is (+)-tartaric acid, leaving only $(68 - 32) = 36\%$ of the mixture as excess (+)-tartaric acid to give measurable optical rotation. The specific rotation will therefore be only 36% of the rotation of pure (+)-tartaric acid: $(+12.0^\circ) \times 36\% = +4.3^\circ$

(This algebraic approach has been suggested by Editorial Adviser Richard King.)

$$\text{e.e.} = \frac{d-l}{d+l} \times 100\% = \frac{68-32}{68+32} \times 100\% = 36\%$$

The optical rotation of this mixture is: $36\% \times (+12.0^\circ) = +4.3^\circ$

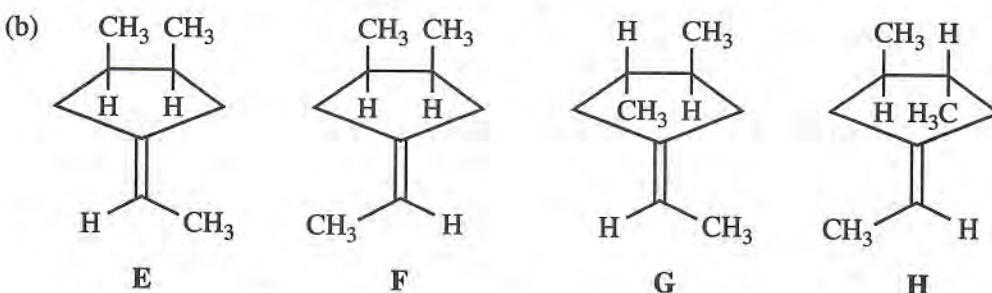
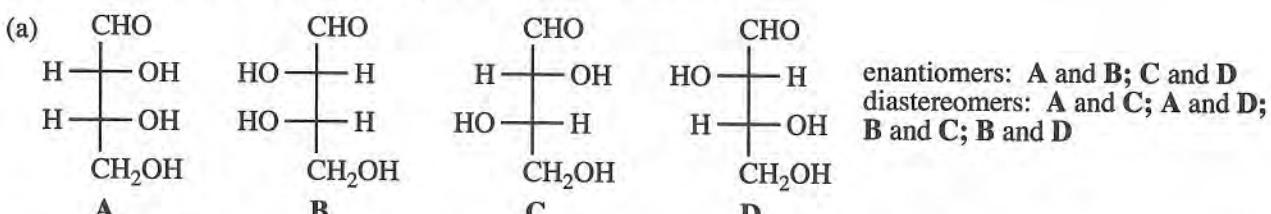
5-34



(c) The rotation -7.95° is what percent of -15.90° ? There is 50% excess of (R)-2-iodobutane over the racemic mixture; that is, another 25% must be R and 25% must be S. The total composition is 75% (R)-(-)-2-iodobutane and 25% (S)-(+)2-iodobutane.

$$\frac{-7.95^\circ}{-15.90^\circ} \times 100\% = 50\% \text{ e.e.}$$

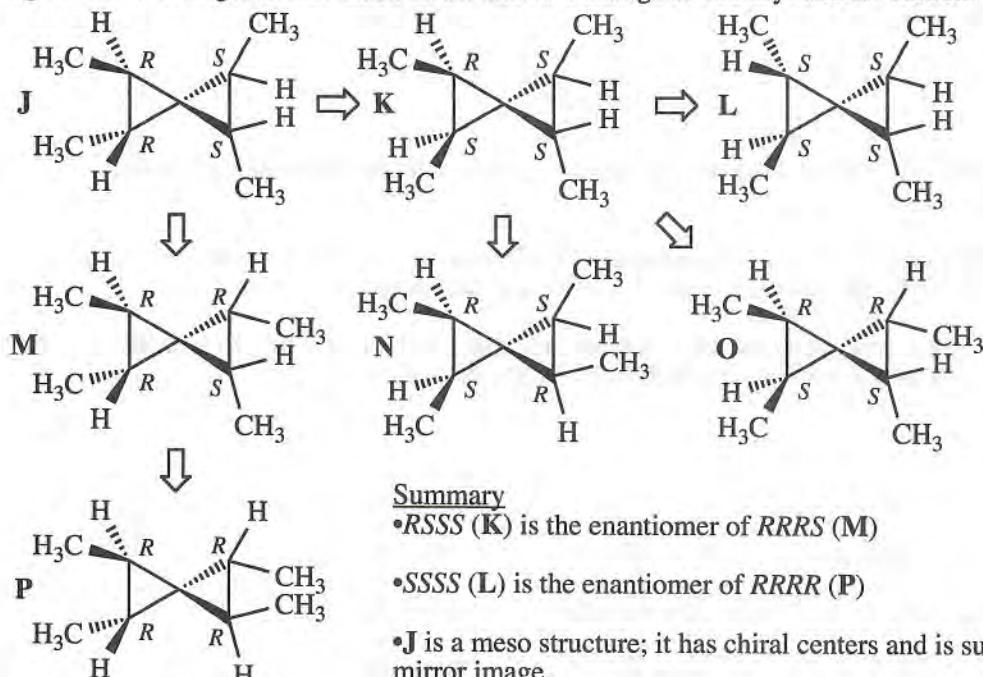
5-35 All structures in parts (a) and (b) of this problem are chiral.



enantiomers: E and F; G and H
diastereomers: E and G; E and H; F and G; F and H

5-35 continued

(c) This structure is a challenge to visualize. A model helps. One way to approach this problem is to assign R and S configurations. Each arrow shows a change at one asymmetric carbon.



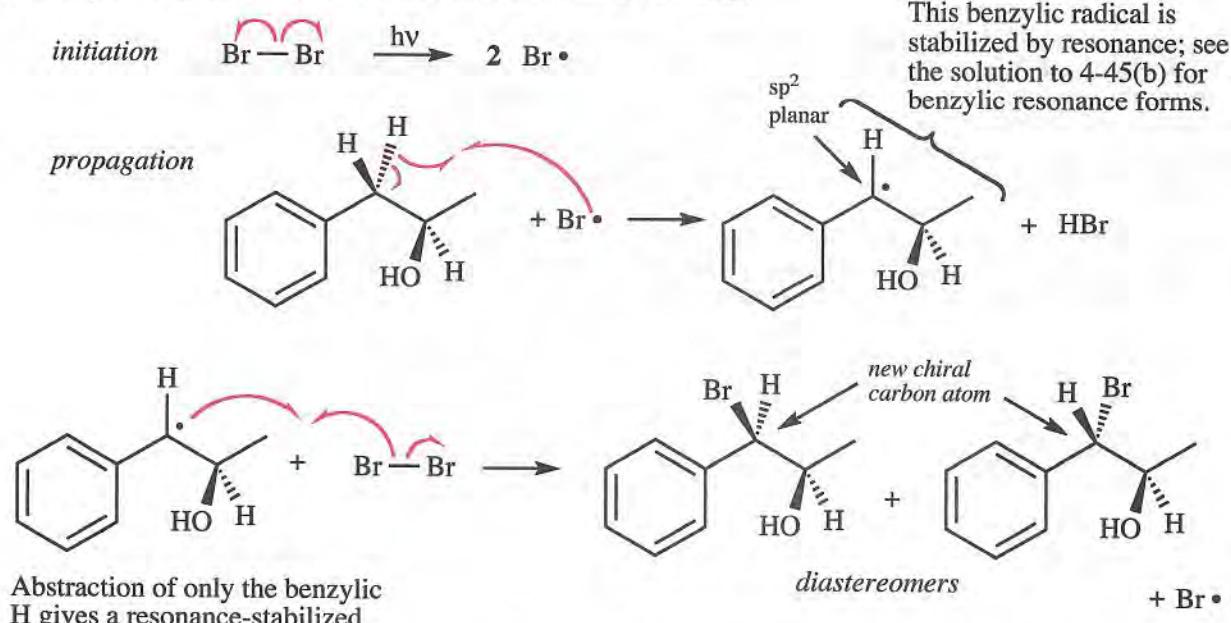
Summary

- RSSS (**K**) is the enantiomer of RRRR (**M**)
- SSSS (**L**) is the enantiomer of RRRR (**P**)
- **J** is a meso structure; it has chiral centers and is superimposable on its mirror image.
- **N** and **O** are enantiomers, and are diastereomers of all of the other structures.

Give yourself a gold star if you got this correct!

5-36

(a) Benzylic bromination follows a free-radical chain mechanism.



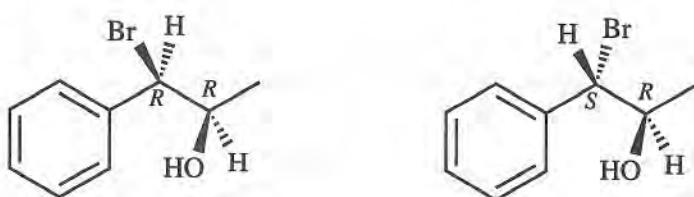
Abstraction of only the benzylic H gives a resonance-stabilized intermediate.

diastereomers

+ Br •

5-36 continued

(b) and (c)



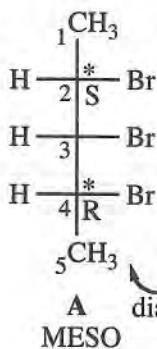
(d) These are diastereomers. *R,R* and *S,R* have one asymmetric carbon with the same configuration and one of opposite configuration.

(e) It is possible but unlikely that they will be produced in a 50:50 mixture. Unlike racemic mixtures of enantiomers that must be 50:50, diastereomers can be and usually are unequal mixtures.

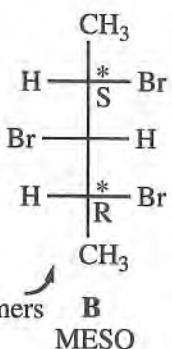
(f) Diastereomers have different physical properties like melting point and boiling point, so in theory, they could be separated by a physical method like distillation or crystallization.

5-37

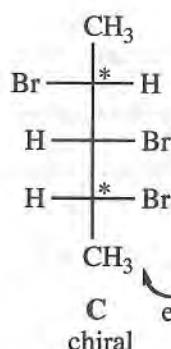
(a)



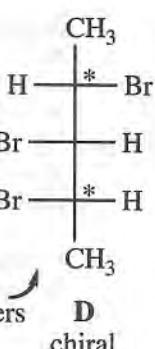
2S,4R
equivalent
to *2R,4S*



2S,4R
equivalent
to *2R,4S*



2R,4R



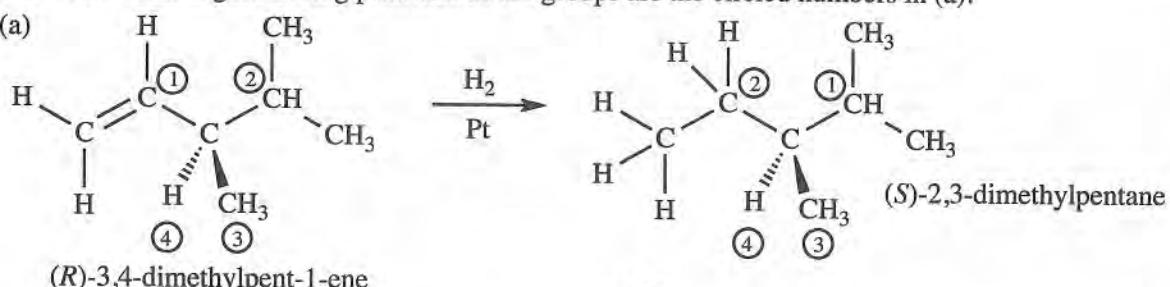
2S,4S

(c) According to the IUPAC designation described in text Section 5-2B, a chiral center is "any atom holding a set of ligands in a spatial arrangement which is not superimposable on its mirror image." An asymmetric carbon must have four different groups on it, but in **A** and **B**, C-3 has two groups that are identical (except for their stereochemistry). C-3 holds its groups in a spatial arrangement that is superimposable on its mirror image, so it is not a chiral center. But it is a stereocenter: in structure **A**, interchanging the H and Br at C-3 gives structure **B**, a diastereomer of **A**; therefore, C-3 is a stereocenter.

(d) In structure **C** or **D**, C-3 is not a stereocenter. Inverting the H and the Br, then rotating the structure 180°, shows that the same structure is formed. Therefore, interchanging two atoms at C-3 does *not* give a stereoisomer, so C-3 does not fit the definition of a stereocenter.

5-38 The Cahn-Ingold-Prelog priorities of the groups are the circled numbers in (a).

(a)

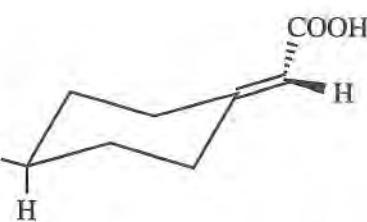


5-38 continued

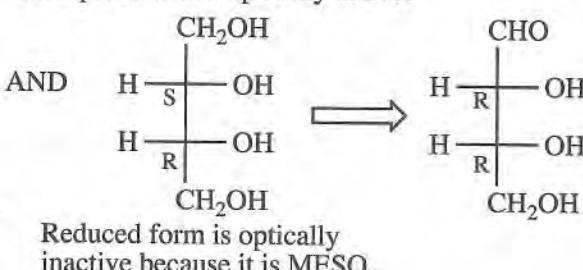
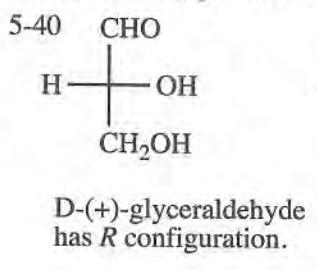
- (b) The reaction did not occur at the asymmetric carbon atom, so the configuration has not changed—the reaction went with retention of configuration at the asymmetric carbon.
- (c) The name changed because the priority of groups in the Cahn-Ingold-Prelog system of nomenclature changed. When the alkene became an ethyl group, its priority changed from the highest priority group to priority 2. (We will revisit this anomaly in problem 6-21(c).)
- (d) There is no general correlation between R and S designation and the physical property of optical rotation. Professor Wade's poetic couplet makes an important point: do not confuse an object and its properties with the name for that object. (Scholars of Shakespeare have come to believe that this quote from Juliet is a veiled reference to designation of R,S configuration versus optical rotation of a chiral molecule. Shakespeare was way ahead of his time.)

5-39

- (a) The product has no asymmetric carbon atoms but it has three stereocenters: the carbon with the OH, plus both carbons of the double bond. Interchange of two bonds on any of these makes the enantiomer.
- (b) The product is an example of a chiral compound with no asymmetric carbons. Like the allenes, it is classified as an "extended tetrahedron"; that is, it has four groups that extend from the rigid molecule in four different directions. (A model will help.) In this structure, the plane containing the COOH and carbons of the double bond is perpendicular to the plane bisecting the OH and H and carbon that they are on. Since the compound is chiral, it is capable of being optically active.



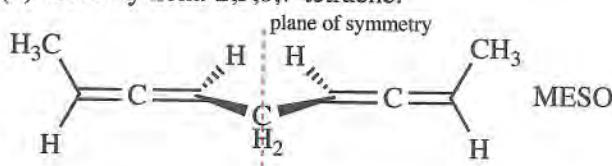
- (c) As shown in text Figure 5-17, Section 5-6, catalytic hydrogenation that creates a new chiral center creates a racemic mixture (both enantiomers in a 1:1 ratio). A racemic mixture is not optically active. In contrast, by using a chiral enzyme to reduce the ketone to the alcohol (as in part (b)), an excess of one enantiomer was produced, so the product was optically active.



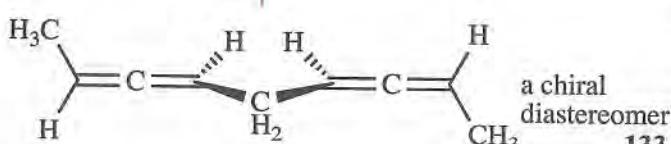
The Cahn-Ingold-Prelog priorities change! The OH = #1, but the CHO = #2, so C-2 is now R!
 D-(−)-erythrose must have the (2R,3R) configuration.

- 5-41 (a) The key to this problem is shown in Figure 5-19: *trans*-cyclooctene is chiral because of the twist created by the strained ring (called a chirality helix). Therefore, *cis*-cyclooctene has a chiral diastereomer (*cis* and *trans* are diastereomers) and it fits the original definition, but neither *cis* nor *trans* has chiral centers, so the *cis* isomer does not fit the working definition. (Without the information in Figure 5-19, or a model, this could not have been deduced from principles.)

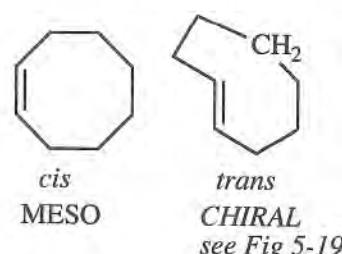
- (b) Let's try nona-2,3,6,7-tetraene:



MESO
 Consider the "twist" of an allene: in the top structure, viewing down C2 to C3, the CH₃ to CH₂ twist is clockwise; from the other end, the CH₃ to CH₂ has a counterclockwise twist.



a chiral diastereomer
 However, in the bottom diastereomer, both ends have a clockwise twist; this is a chiral compound although it has no chiral centers.



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Chlorophyll is a green pigment found in plant cells. It is involved in photosynthesis, which is the process by which plants use light energy to produce glucose. Chlorophyll is a complex molecule containing a central magnesium atom bonded to four nitrogen atoms. It is also bonded to two hydroxyl groups and two side chains. One side chain contains a carbonyl group (C=O) and the other contains a carboxylate group (COO^-). The carboxylate group is negatively charged at pH 7. The side chains are hydrophobic and contain many double bonds, which make them very susceptible to oxidation.

Chlorophyll is found in all green plants and algae, but it is also found in some non-photosynthetic organisms, such as bacteria. It is important to note that chlorophyll is not the only pigment involved in photosynthesis. Other pigments, such as carotenoids, are also present in plants and algae. These pigments absorb light energy and transfer it to the chlorophyll molecule. This process is called energy transfer. The energy transferred to the chlorophyll molecule is used to drive the conversion of carbon dioxide and water into glucose and oxygen.

The diagram shows the structure of chlorophyll. It consists of a central magnesium atom bonded to four nitrogen atoms. It is also bonded to two hydroxyl groups and two side chains. One side chain contains a carbonyl group (C=O) and the other contains a carboxylate group (COO^-). The carboxylate group is negatively charged at pH 7. The side chains are hydrophobic and contain many double bonds, which make them very susceptible to oxidation.



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