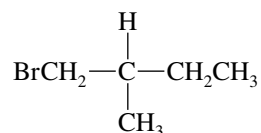


CHAPTER 7

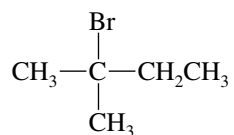
STEREOCHEMISTRY

SOLUTIONS TO TEXT PROBLEMS

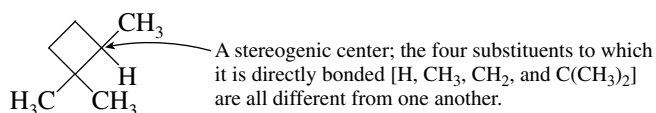
- 7.1 (c) Carbon-2 is a stereogenic center in 1-bromo-2-methylbutane, as it has four different substituents: H, CH₃, CH₃CH₂, and BrCH₂.



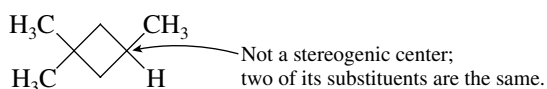
- (d) There are no stereogenic centers in 2-bromo-2-methylbutane.



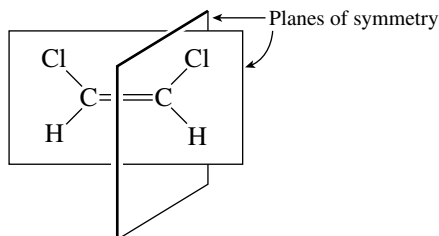
- 7.2 (b) Carbon-2 is a stereogenic center in 1,1,2-trimethylcyclobutane.



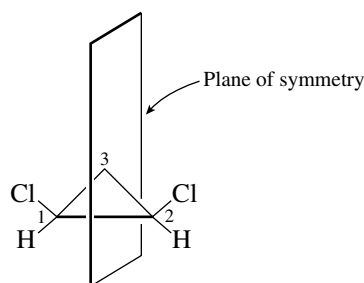
1,1,3-Trimethylcyclobutane however, has no stereogenic centers.



- 7.3 (b) There are *two* planes of symmetry in (*Z*)-1,2-dichloroethene, of which one is the plane of the molecule and the second bisects the carbon–carbon bond. There is no center of symmetry. The molecule is achiral.



- (c) There is a plane of symmetry in *cis*-1,2-dichlorocyclopropane that bisects the C-1—C-2 bond and passes through C-3. The molecule is achiral.



- (d) *trans*-1,2-Dichlorocyclopropane has neither a plane of symmetry nor a center of symmetry. Its two mirror images cannot be superposed on each other. The molecule is chiral.



- 7.4 The equation relating specific rotation $[\alpha]$ to observed rotation α is

$$[\alpha] = \frac{100\alpha}{cl}$$

The concentration c is expressed in grams per 100 mL and the length l of the polarimeter tube in decimeters. Since the problem specifies the concentration as 0.3 g/15 mL and the path length as 10 cm, the specific rotation $[\alpha]$ is:

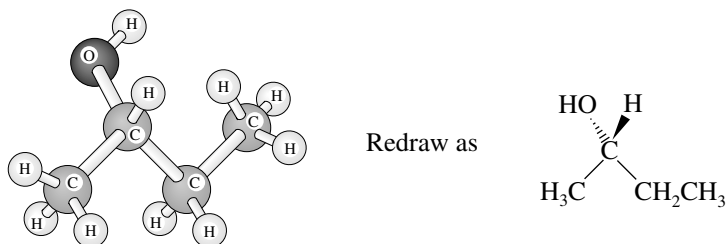
$$\begin{aligned} [\alpha] &= \frac{100(-0.78^\circ)}{100(0.3 \text{ g}/15 \text{ mL})(10 \text{ cm}/10 \text{ cm/dm})} \\ &= -39^\circ \end{aligned}$$

- 7.5 From the previous problem, the specific rotation of natural cholesterol is $[\alpha] = -39^\circ$. The mixture of natural (–)-cholesterol and synthetic (+)-cholesterol specified in this problem has a specific rotation $[\alpha]$ of -13° .

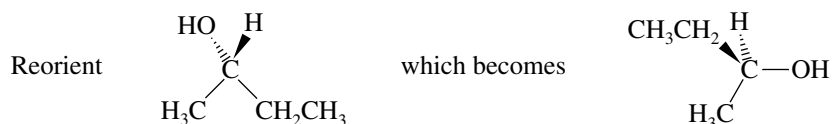
$$\begin{aligned} \text{Optical purity} &= \%(-)\text{-cholesterol} - \%(+)\text{-cholesterol} \\ 33.3\% &= \%(-)\text{-cholesterol} - [100 - \%(-)\text{-cholesterol}] \\ 133.3\% &= 2 [\%(-)\text{-cholesterol}] \\ 66.7\% &= \%(-)\text{-cholesterol} \end{aligned}$$

The mixture is two thirds natural (–)-cholesterol and one third synthetic (+)-cholesterol.

- 7.6 Draw the molecular model so that it is in the same format as the drawings of (+) and (-)-2-butanol in the text.

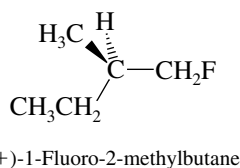


Reorient the molecule so that it can be compared with the drawings of (+) and (-)-2-butanol.



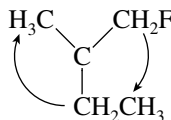
The molecular model when redrawn matches the text's drawing of (+)-2-butanol.

- 7.7 (b) The solution to this problem is exactly analogous to the sample solution given in the text to part (a).



Order of precedence: $\text{CH}_2\text{F} > \text{CH}_3\text{CH}_2 > \text{CH}_3 > \text{H}$

The lowest ranked substituent (H) at the stereogenic center points away from us in the drawing. The three higher ranked substituents trace a clockwise path from CH_2F to CH_2CH_3 to CH_3 .

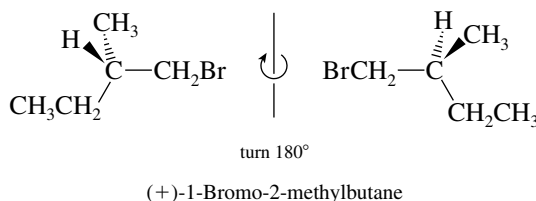


The absolute configuration is *R*; the compound is (*R*)-(+)-1-fluoro-2-methylbutane.

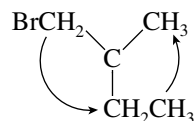
- (c) The highest ranked substituent at the stereogenic center of 1-bromo-2-methylbutane is CH_2Br , and the lowest ranked substituent is H. Of the remaining two, ethyl outranks methyl.

Order of precedence: $\text{CH}_2\text{Br} > \text{CH}_2\text{CH}_3 > \text{CH}_3 > \text{H}$

The lowest ranking substituent (H) is directed toward you in the drawing, and therefore the molecule needs to be reoriented so that H points in the opposite direction.



The three highest ranking substituents trace a counterclockwise path when the lowest ranked substituent is held away from you.

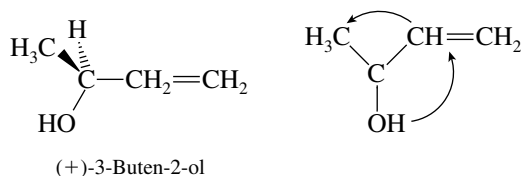


The absolute configuration is *S*, and thus the compound is (*S*)-(+)-1-bromo-2-methylbutane.

- (d) The highest ranked substituent at the stereogenic center of 3-buten-2-ol is the hydroxyl group, and the lowest ranked substituent is H. Of the remaining two, vinyl outranks methyl.

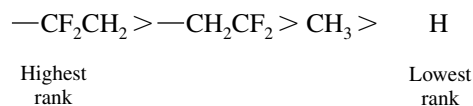
Order of precedence: HO > CH₂=CH > CH₃ > H

The lowest ranking substituent (H) is directed away from you in the drawing. We see that the order of decreasing precedence appears in a counterclockwise manner.

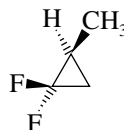


The absolute configuration is *S*, and the compound is (*S*)-(+)-3-buten-2-ol.

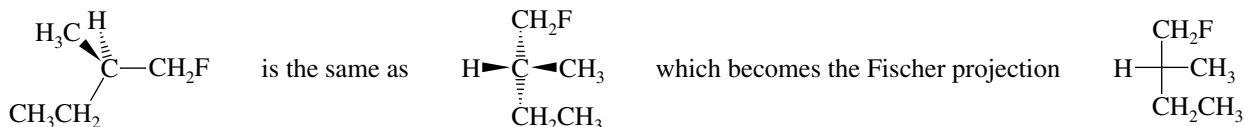
- 7.8 (b) The stereogenic center is the carbon that bears the methyl group. Its substituents are:



When the lowest ranked substituent points away from you, the remaining three must appear in descending order of precedence in a counterclockwise fashion in the *S* enantiomer. (*S*)-1,1-difluoro-2-methylcyclopropane is therefore

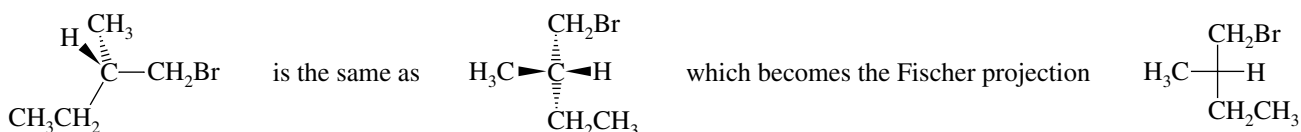


- 7.9 (b) The Fischer projection of (*R*)-(+)-1-fluoro-2-methylbutane is analogous to that of the alcohol in part (a). The only difference in the two is that fluorine has replaced hydroxyl as a substituent at C-1.

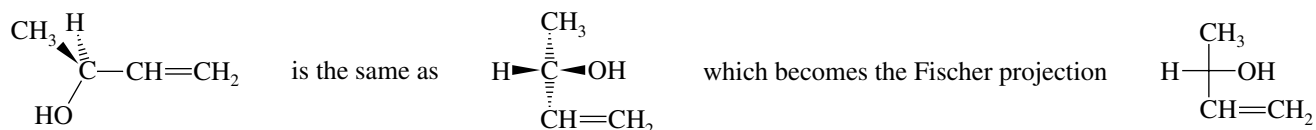


Although other Fischer projections may be drawn by rotating the perspective view in other directions, the one shown is preferred because it has the longest chain of carbon atoms oriented on the vertical axis with the lowest numbered carbon at the top.

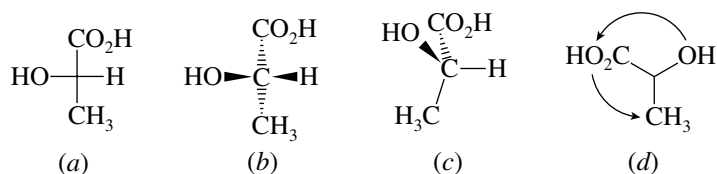
- (c) As in the previous parts of this problem, orient the structural formula of (*S*)-(+)-1-bromo-2-methylbutane so the segment BrCH₂—C—CH₂CH₃ is aligned vertically with the lowest numbered carbon at the top.



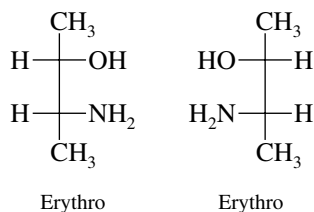
- (d) Here we need to view the molecule from behind the page in order to write the Fischer projection of (*S*)-(+)-3-buten-2-ol.



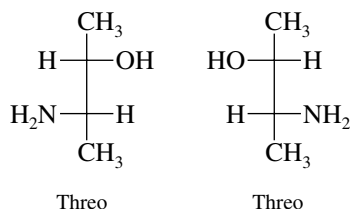
- 7.10** In order of decreasing rank, the substituents attached to the stereogenic center in lactic acid are —OH, —CO₂H, —CH₃, and —H. The Fischer projection given for (+)-lactic acid (*a*) corresponds to the three-dimensional representation (*b*), which can be reoriented as in (*c*). When (*c*) is viewed from the side opposite the lowest ranked substituent (H), the order of decreasing precedence is anti-clockwise, as shown in (*d*). (+)-Lactic acid has the *S* configuration.



- 7.11** The erythro stereoisomers are characterized by Fischer projections in which analogous substituents, in this case OH and NH₂, are on the same side when the carbon chain is vertical. There are two erythro stereoisomers that are enantiomers of each other:



Analogous substituents are on opposite sides in the threo isomer:

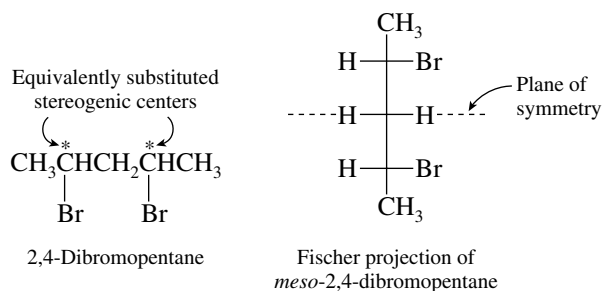


- 7.12** There are four stereoisomeric forms of 3-amino-3-butanol:

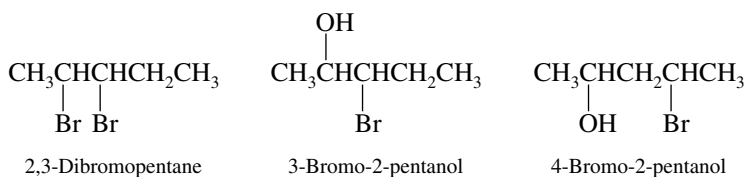
(*2R,3R*) and its enantiomer (*2S,3S*)
 (*2R,3S*) and its enantiomer (*2S,3R*)

In the text we are told that the (*2R,3R*) stereoisomer is a liquid. Its enantiomer (*2S,3S*) has the same physical properties and so must also be a liquid. The text notes that the (*2R,3S*) stereoisomer is a solid (mp 49°C). Its enantiomer (*2S,3R*) must therefore be the other stereoisomer that is a crystalline solid.

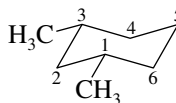
- 7.13 Examine the structural formula of each compound for equivalently substituted stereogenic centers. The only one capable of existing in a meso form is 2,4-dibromopentane.



None of the other compounds has equivalently substituted stereogenic centers. No meso forms are possible for:



- 7.14 There is a plane of symmetry in the *cis* stereoisomer of 1,3-dimethylcyclohexane, and so it is an achiral substance—it is a meso form.



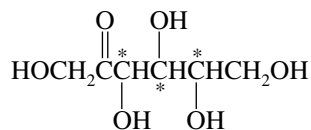
Plane of symmetry passes through C-2 and C-5 and bisects the ring.

The *trans* stereoisomer is chiral. It is not a meso form.

- 7.15 A molecule with three stereogenic centers has 2^3 , or 8, stereoisomers. The eight combinations of *R* and *S* stereogenic centers are:

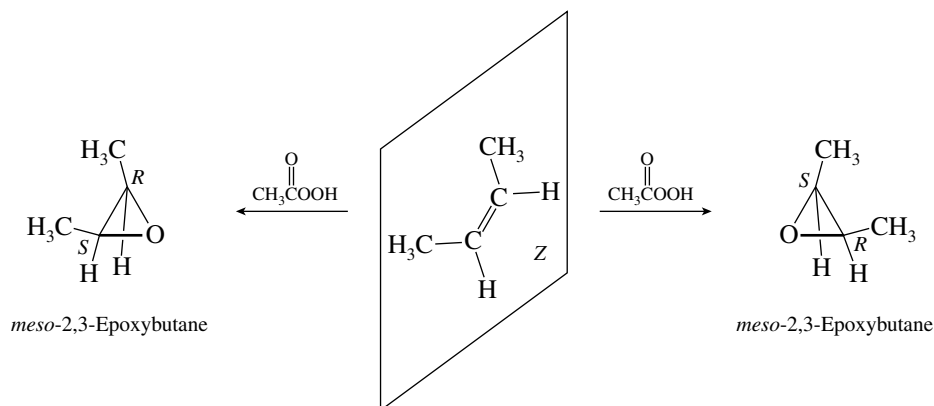
	<i>Stereogenic center</i>			<i>Stereogenic center</i>		
	1	2	3	1	2	3
Isomer 1	<i>R</i>	<i>R</i>	<i>R</i>	Isomer 5	<i>S</i>	<i>S</i>
Isomer 2	<i>R</i>	<i>R</i>	<i>S</i>	Isomer 6	<i>S</i>	<i>S</i>
Isomer 3	<i>R</i>	<i>S</i>	<i>R</i>	Isomer 7	<i>S</i>	<i>R</i>
Isomer 4	<i>S</i>	<i>R</i>	<i>R</i>	Isomer 8	<i>R</i>	<i>S</i>

- 7.16 2-Hexuloses have three stereogenic centers. They are marked with asterisks in the structural formula.

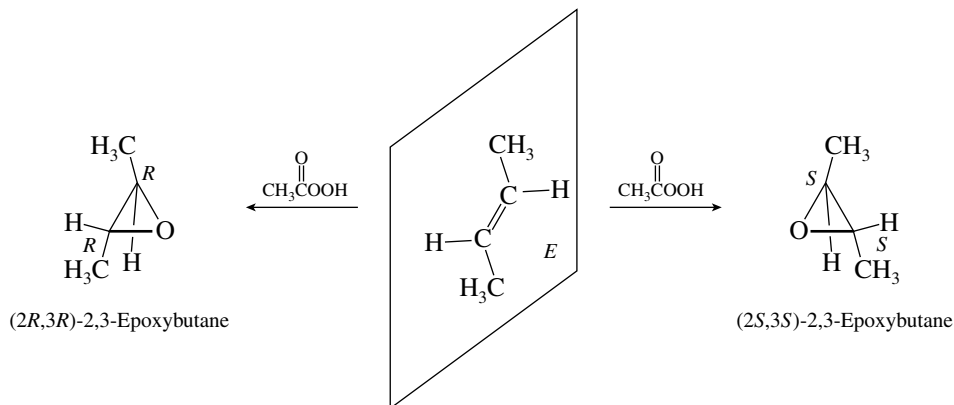


No meso forms are possible, and so there are a total of 2^3 , or 8, stereoisomeric 2-hexuloses.

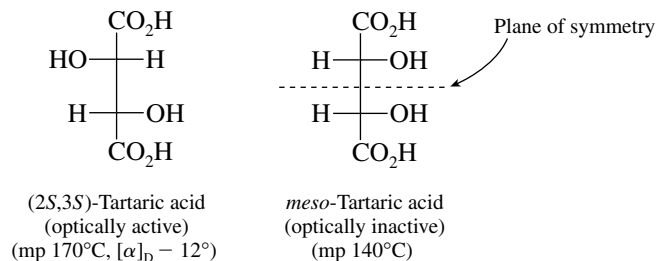
- 7.17 Epoxidation of (*Z*)-2-butene gives the meso (achiral) epoxide. Oxygen transfer from the peroxy acid can occur at either face of the double bond, but the product formed is the same because the two mirror-image forms of the epoxide are superposable.



Epoxidation of (*E*)-2-butene gives a racemic mixture of two enantiomeric epoxides.

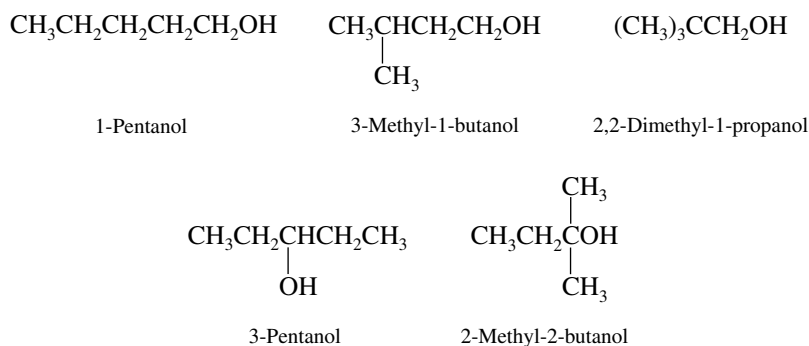


- 7.18 The observed product mixture (68% *cis*-1,2-dimethylcyclohexane: 32% *trans*-1,2-dimethylcyclohexane) contains more of the less stable *cis* stereoisomer than the *trans*. The relative stabilities of the products therefore play no role in determining the stereoselectivity of this reaction.
- 7.19 The tartaric acids incorporate two equivalently substituted stereogenic centers. (+)-Tartaric acid, as noted in the text, is the *2R,3R* stereoisomer. There will be two additional stereoisomers, the enantiomeric (–)-tartaric acid (*2S,3S*) and an optically inactive meso form.

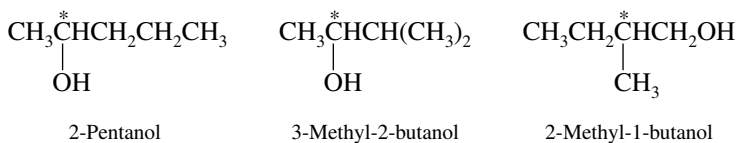


- 7.20 No. Pasteur separated an optically inactive racemic mixture into two optically active enantiomers. A meso form is achiral, is identical to its mirror image, and is incapable of being separated into optically active forms.

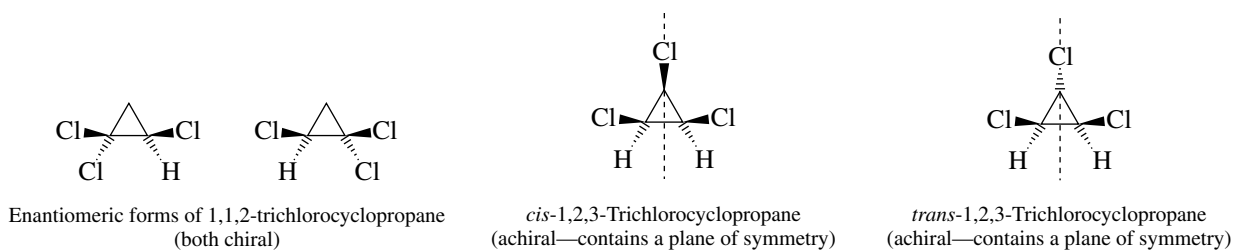
- 7.21** The more soluble salt must have the opposite configuration at the stereogenic center of 1-phenylethylamine, that is, the *S* configuration. The malic acid used in the resolution is a single enantiomer, *S*. In this particular case the more soluble salt is therefore (*S*)-1-phenylethylammonium (*S*)-malate.
- 7.22** In an earlier exercise (Problem 4.23) the structures of all the isomeric $C_5H_{12}O$ alcohols were presented. Those that lack a stereogenic center and thus are *achiral* are



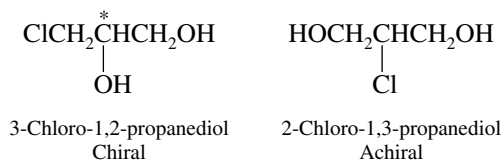
The chiral isomers are characterized by carbons that bear four different groups. These are:



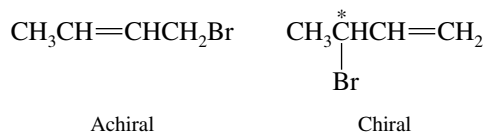
- 7.23** The isomers of trichlorocyclopropane are



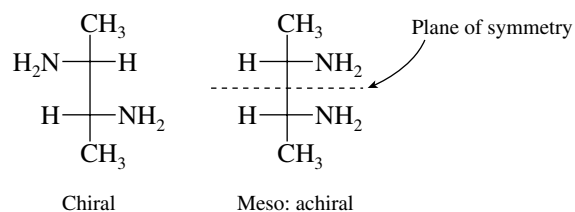
- 7.24** (a) Carbon-2 is a stereogenic center in 3-chloro-1,2-propanediol. Carbon-2 has two equivalent substituents in 2-chloro-1,3-propanediol, and is not a stereogenic center.



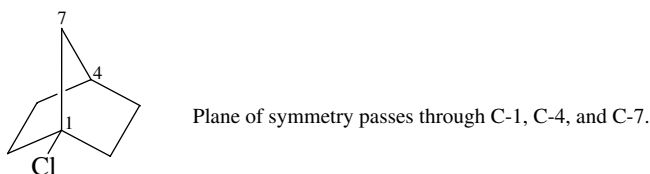
- (b) The primary bromide is achiral; the secondary bromide contains a stereogenic center and is chiral.



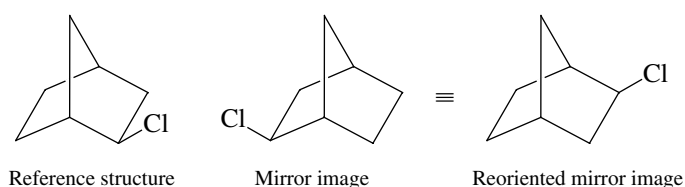
- (c) Both stereoisomers have two equivalently substituted stereogenic centers, and so we must be alert for the possibility of a meso stereoisomer. The structure at the left is chiral. The one at the right has a plane of symmetry and is the achiral meso stereoisomer.



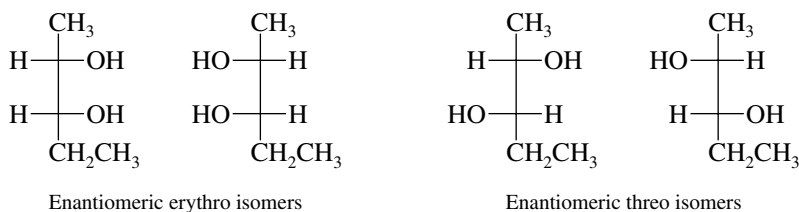
- (d) The first structure is achiral; it has a plane of symmetry.



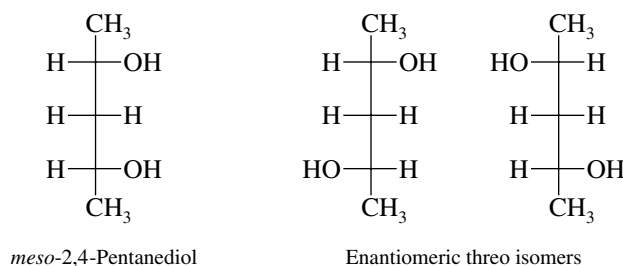
The second structure cannot be superposed on its mirror image; it is chiral.



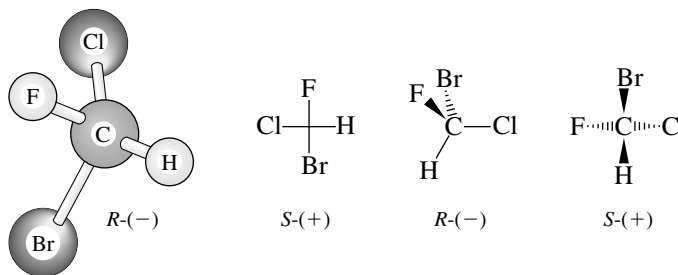
- 7.25** There are four stereoisomers of 2,3-pentanediol, represented by the Fischer projections shown. All are chiral.



There are three stereoisomers of 2,4-pentanediol. The meso form is achiral; both threo forms are chiral.



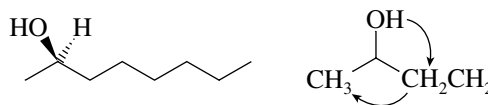
- 7.26 Among the atoms attached to the stereogenic center, the order of decreasing precedence is $\text{Br} > \text{Cl} > \text{F} > \text{H}$. When the molecule is viewed with the hydrogen pointing away from us, the order $\text{Br} \rightarrow \text{Cl} \rightarrow \text{F}$ appears clockwise in the *R* enantiomer, anticlockwise in the *S* enantiomer.



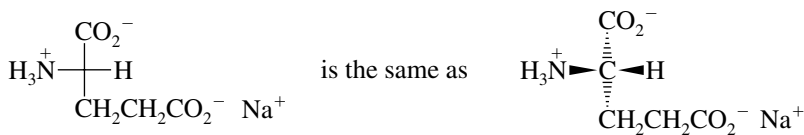
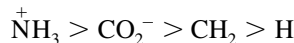
- 7.27 (a) (-)-2-Octanol has the *R* configuration at C-2. The order of substituent precedence is



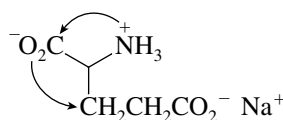
The molecule is oriented so that the lowest ranking substituent is directed away from you and the order of decreasing precedence is clockwise.



- (b) In order of decreasing sequence rule precedence, the four substituents at the stereogenic center of monosodium L-glutamate are

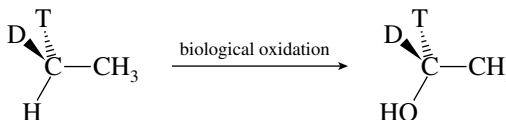


When the molecule is oriented so that the lowest ranking substituent (hydrogen) is directed away from you, the other three substituents are arranged as shown.



The order of decreasing rank is counterclockwise; the absolute configuration is *S*.

- 7.28 (a) Among the isotopes of hydrogen, T has the highest mass number (3), D next (2), and H lowest (1). Thus, the order of rank at the stereogenic center in the reactant is $\text{CH}_3 > \text{T} > \text{D} > \text{H}$. The order of rank in the product is $\text{HO} > \text{CH}_3 > \text{T} > \text{D}$.



Orient with lowest ranked substituent away from you.

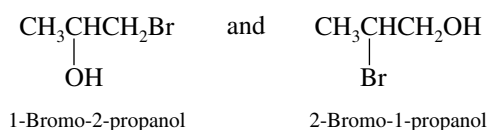


The order of decreasing rank in the reactant is anticlockwise; the configuration is *S*. The order of decreasing rank in the product is clockwise; the configuration is *R*.

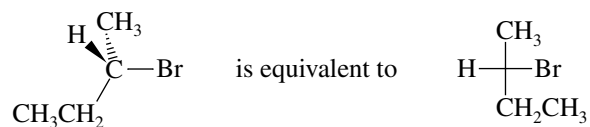
- (b) Retention of configuration means that the three-dimensional arrangement of bonds at the stereogenic center is the same in the reactant and the product. The *R* and *S* descriptors change because the order of precedence changes in going from reactant to product; for example, CH_3 is the highest ranked substituent in the reactant, but becomes the second-highest ranked in the product.

7.29 Two compounds can be stereoisomers only if they have the *same* constitution. Thus, you should compare first the constitution of the two structures and then their stereochemistry. The best way to compare constitutions is to assign a systematic (IUPAC) name to each molecule. Also remember that enantiomers are nonsuperposable mirror images, and diastereomers are stereoisomers that are not enantiomers.

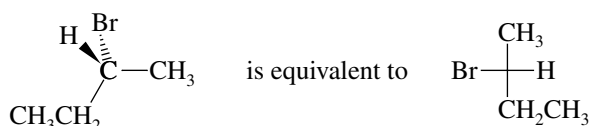
- (a) The two compounds are constitutional isomers. Their IUPAC names clearly reflect this difference.



- (b) The two structures have the same constitution. Test them for superposability. To do this we need to place them in comparable orientations.

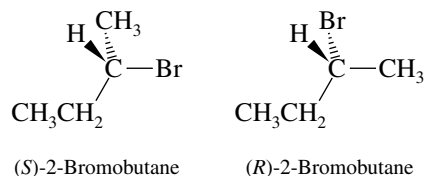


and

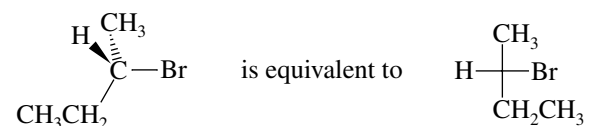


The two are nonsuperposable mirror images of each other. They are enantiomers.

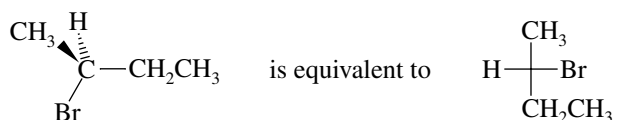
To check this conclusion, work out the absolute configuration of each using the Cahn–Ingold–Prelog system.



- (c) Again, place the structures in comparable orientations, and examine them for superposability.

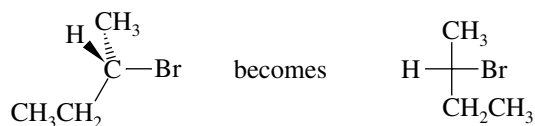


and

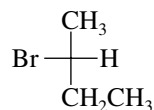


The two structures represent the same compound, since they are superposable. (As a check, notice that both have the *S* configuration.)

- (d) If we reorient the first structure,

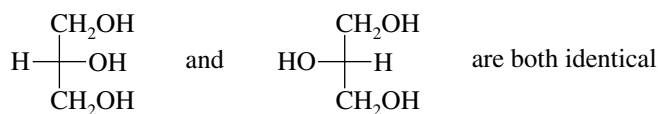


which is the enantiomer of

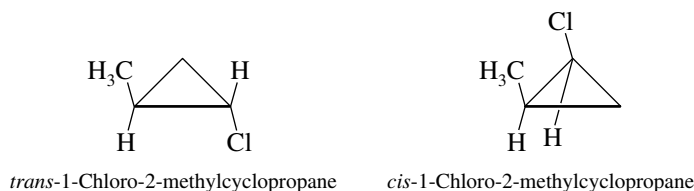


As a check, the first structure is seen to have the *S* configuration, and the second has the *R* configuration.

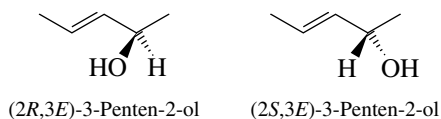
- (e) As drawn, the two structures are mirror images of each other; however, they represent an achiral molecule. The two structures are superposable mirror images and are not stereoisomers but identical.



- (f) The two structures—one *cis*, the other *trans*—are stereoisomers that are not mirror images; they are diastereomers.

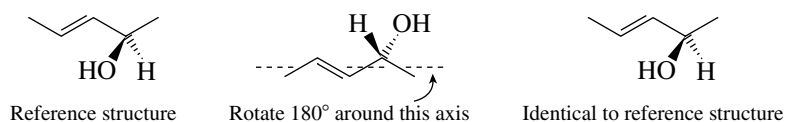


- (g) The two structures are enantiomers, since they are nonsuperposable mirror images. Checking their absolute configurations reveals one to be *R*, the other *S*. Both have the *E* configuration at the double bond.



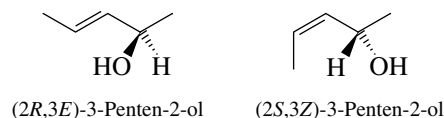
- (h) These two structures are identical; both have the *E* configuration at the double bond and the *R* configuration at the stereogenic center.

Alternatively, we can show their superposability by rotating the second structure 180° about an axis passing through the doubly bonded carbons.

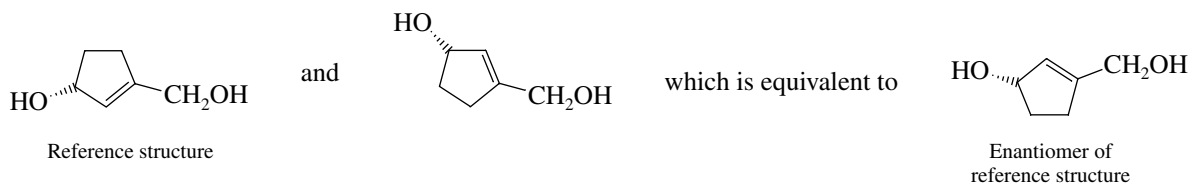


- (i) One structure has a *cis* double bond, the other a *trans* double bond; therefore, the two are diastereomers. Even though one stereogenic center is *R* and the other is *S*, the two structures are

not enantiomers. The mirror image of a cis (or *Z*) double bond is cis, and that of a trans (or *E*) double bond is trans.

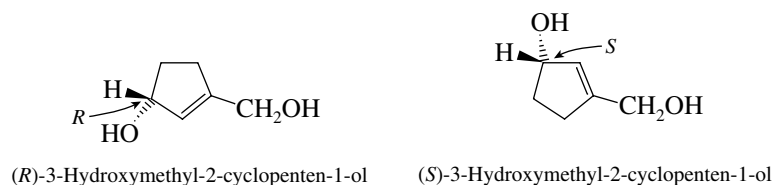


- (j) Here it will be helpful to reorient the second structure so that it may be more readily compared with the first.

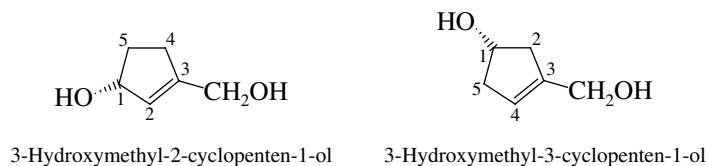


The two compounds are enantiomers.

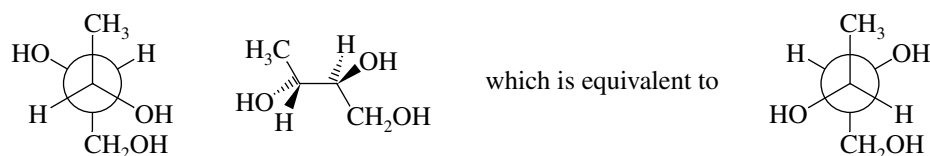
Examining their absolute configurations confirms the enantiomeric nature of the two compounds.



- (k) These two compounds differ in the order in which their atoms are joined together; they are constitutional isomers.

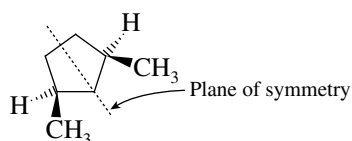


- (l) To better compare these two structures, place them both in the same format.

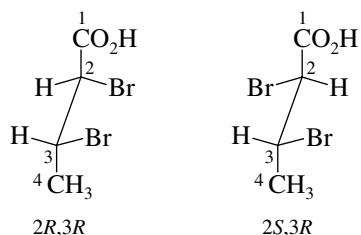


The two are enantiomers.

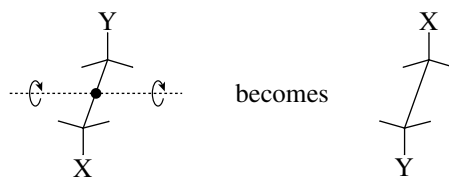
- (m) Since *cis*-1,3-dimethylcyclopentane has a plane of symmetry, it is achiral and cannot have an enantiomer. The two structures given in the problem are identical.



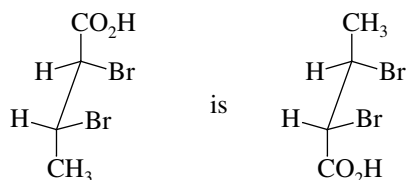
- (n) These structures are diastereomers, that is, stereoisomers that are not mirror images. They have the same configuration at C-3 but opposite configurations at C-2.



- (o) To compare these compounds, reorient the first structure so that it may be drawn as a Fischer projection. The first step in the reorientation consists of a 180° rotation about an axis passing through the midpoint of the C-2—C-3 bond.

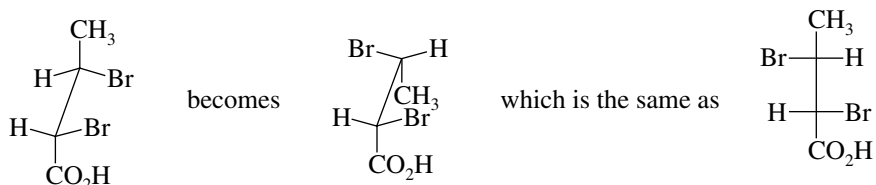


Thus



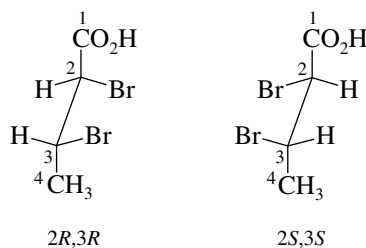
Reference structure

Now rotate the “back” carbon of the reoriented structure to give the necessary alignment for a Fischer projection.

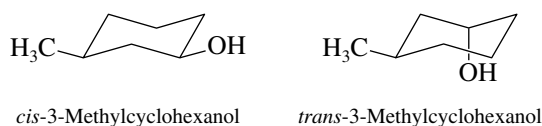


This reveals that the original two structures in the problem are equivalent.

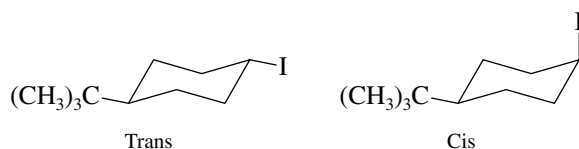
- (p) These two structures are nonsuperposable mirror images of a molecule with two nonequivalent stereogenic centers; they are enantiomers.



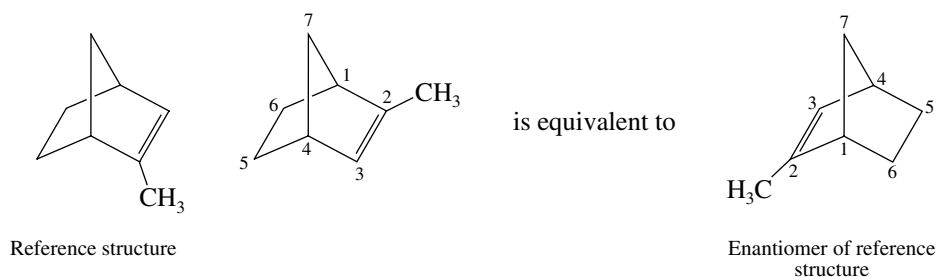
- (q) The two structures are stereoisomers that are not enantiomers; they are diastereomers.



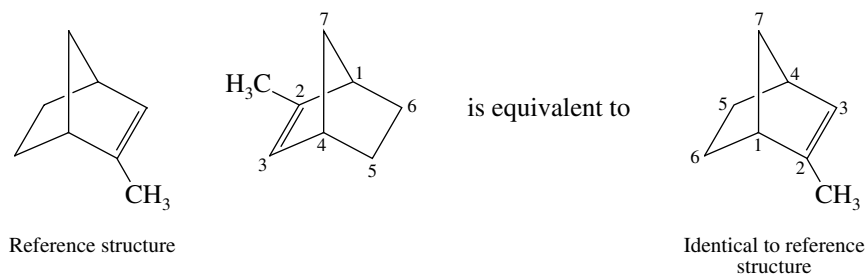
- (r) These two structures, *cis*- and *trans*-4-*tert*-butylcyclohexyl iodide, are diastereomers.



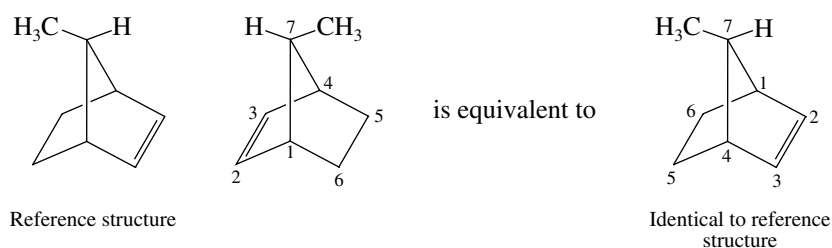
- (s) The two structures are nonsuperposable mirror images; they are enantiomers.



- (t) The two structures are identical.

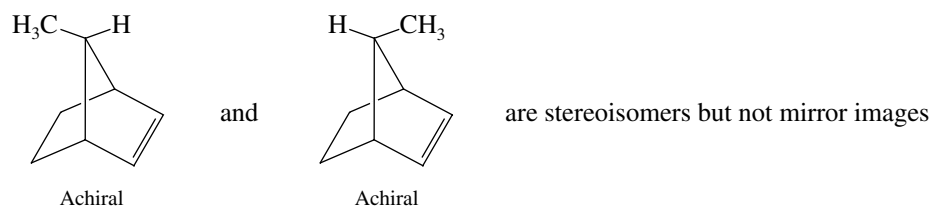


- (u) As represented, the two structures are mirror images of each other, but because the molecule is achiral (it has a plane of symmetry), the two must be superposable. They represent the same compound.



The plane of symmetry passes through C-7 and bisects the C-2—C-3 bond and the C-5—C-6 bond.

- (v) The structures are stereoisomers but not enantiomers; they are diastereomers. (Both are achiral and so cannot have enantiomers.)



- 7.30 Write a structural formula for phytol and count the number of structural units capable of stereochemical variation.



3,7,11,15-Tetramethyl-2-hexadecen-1-ol

Phytol has two stereogenic centers (C-7 and C-11) and one double bond. The stereogenic centers may be either *R* or *S*, and the double bond may be either *E* or *Z*. Eight stereoisomers are possible.

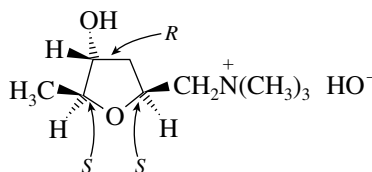
	Isomer							
	1	2	3	4	5	6	7	8
Double bond	<i>E</i>	<i>E</i>	<i>E</i>	<i>E</i>	<i>Z</i>	<i>Z</i>	<i>Z</i>	<i>Z</i>
Carbon-7	<i>R</i>	<i>S</i>	<i>R</i>	<i>S</i>	<i>R</i>	<i>S</i>	<i>R</i>	<i>S</i>
Carbon-11	<i>R</i>	<i>S</i>	<i>S</i>	<i>R</i>	<i>R</i>	<i>S</i>	<i>S</i>	<i>R</i>

- 7.31 (a) Muscarine has three stereogenic centers, and so *eight* stereoisomers have this constitution.
 (b) The three substituents on the ring (at C-2, C-3, and C-5) can be thought of as being either up (U) or down (D) in a perspective drawing. Thus the eight possibilities are:

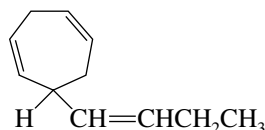


Of these, *six* have one substituent trans to the other two.

- (c) Muscarine is

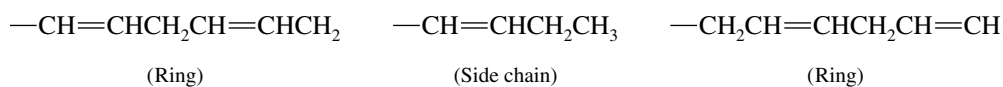


- 7.32 To write a stereochemically accurate representation of ectocarpene, it is best to begin with the configuration of the stereogenic center, which we are told is *S*.

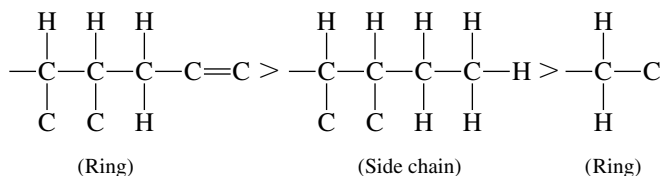


Clearly, hydrogen is the lowest ranking substituent; among the other three substituents, two are part of the ring and the third is the four-carbon side chain. The priority rankings of these groups are determined by systematically working along the chain.

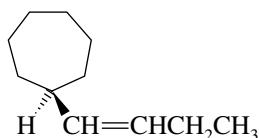
The substituents



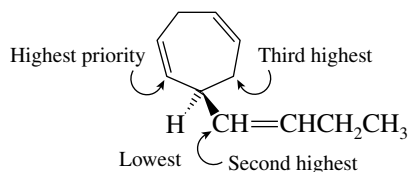
are considered as if they were



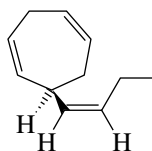
Orienting the molecule with the hydrogen away from you



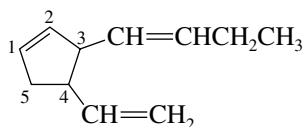
we place the double bonds in the ring so that the order of decreasing sequence rule precedence is counterclockwise:



Finally, since all the double bonds are *cis*, the complete structure becomes:

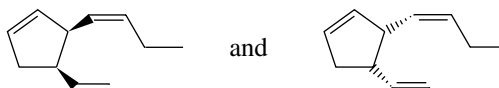


- 7.33 (a) Multifidene has two stereogenic centers and three double bonds. Neither the ring double bond nor the double bond of the vinyl substituent can give rise to stereoisomers, but the butenyl side chain can be either *E* or *Z*. Eight (2^3) stereoisomers are therefore possible. We can rationalize them as

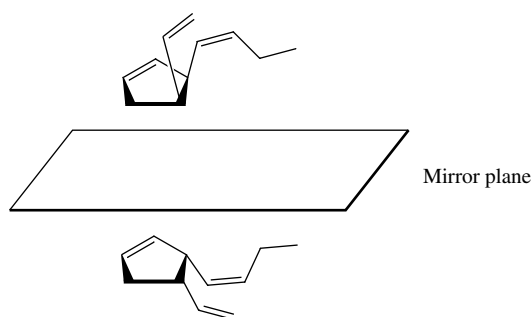


Stereoisomer	C-3	C-4	Butenyl double bond	
1	<i>R</i>	<i>R</i>	<i>E</i>	} enantiomers
2	<i>S</i>	<i>S</i>	<i>E</i>	
3	<i>R</i>	<i>R</i>	<i>Z</i>	} enantiomers
4	<i>S</i>	<i>S</i>	<i>Z</i>	
5	<i>R</i>	<i>S</i>	<i>E</i>	} enantiomers
6	<i>S</i>	<i>R</i>	<i>E</i>	
7	<i>R</i>	<i>S</i>	<i>Z</i>	} enantiomers
8	<i>S</i>	<i>R</i>	<i>Z</i>	

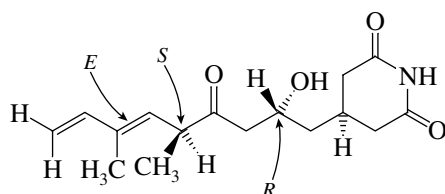
- (b) Given the information that the alkenyl substituents are *cis* to each other, the number of stereoisomers is reduced by half. Four stereoisomers are therefore possible.
 (c) Knowing that the butenyl group has a *Z* double bond reduces the number of possibilities by half. Two stereoisomers are possible.
 (d) The two stereoisomers are



- (e) These two stereoisomers are enantiomers. They are nonsuperposable mirror images.

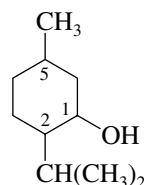


- 7.34** In a substance with more than one stereogenic center, each center is independently specified as *R* or *S*. Streptimidone has two stereogenic centers and two double bonds. Only the internal double bond is capable of stereoisomerism.



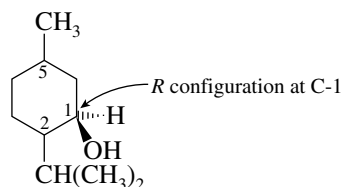
The three stereochemical variables give rise to eight (2^3) stereoisomers, of which one is streptimidone and a second is the enantiomer of streptimidone. The remaining six stereoisomers are diastereomers of streptimidone.

- 7.35** (a) The first step is to set out the constitution of menthol, which we are told is 2-isopropyl-5-methylcyclohexanol.

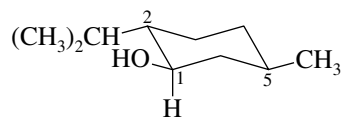


2-Isopropyl-5-methylcyclohexanol

Since the configuration at C-1 is *R* in (–)-menthol, the hydroxyl group must be “up” in our drawing.

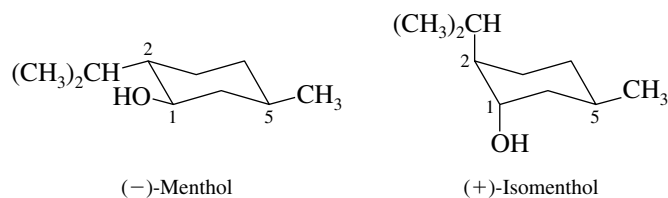


Because menthol is the most stable stereoisomer of this constitution, all three of its substituents must be equatorial. We therefore draw the chair form of the preceding structure, which has the hydroxyl group equatorial and up, placing isopropyl and methyl groups so as to preserve the *R* configuration at C-1.

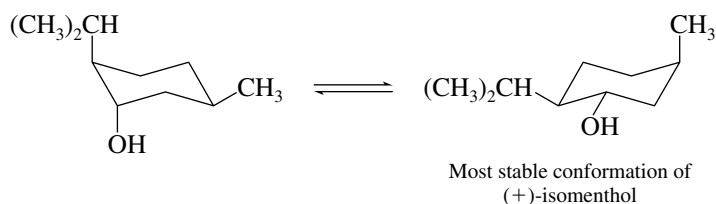


(–)-Menthol

- (b) To transform the structure of (–)-menthol to that of (+)-isomenthol, the configuration at C-5 must remain the same, whereas those at C-1 and C-2 are inverted.

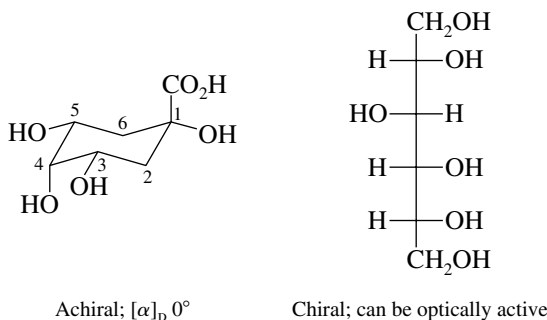


(+)-Isomenthol is represented here in its correct configuration, but the conformation with two axial substituents is not the most stable one. The ring-flipped form will be the preferred conformation of (+)-isomenthol:



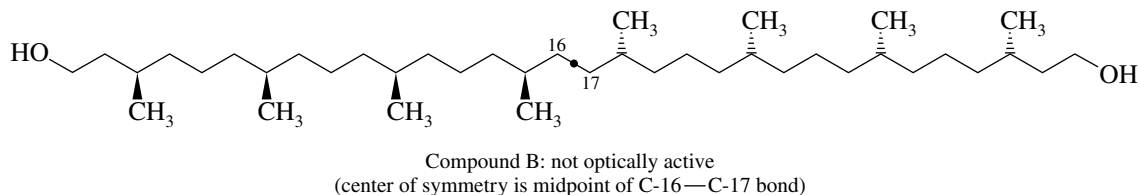
- 7.36** Since the only information available about the compound is its optical activity, examine the two structures for chirality, recalling that only chiral substances can be optically active.

The structure with the six-membered ring has a plane of symmetry passing through C-1 and C-4. It is achiral and cannot be optically active.



The open-chain structure has neither a plane of symmetry nor a center of symmetry; it is not superposable on its mirror image and so is chiral. It can be optically active and is more likely to be the correct choice.

- 7.37** Compound B has a center of symmetry, is achiral, and thus cannot be optically active.



The diol in the problem is optically active, and so it must be chiral. Compound A is the naturally occurring diol.

- 7.38** (a) The equation that relates specific rotation $[\alpha]_D$ to observed rotation α is

$$[\alpha]_D = \frac{100\alpha}{cl}$$

where c is concentration in grams per 100 mL and l is path length in decimeters.

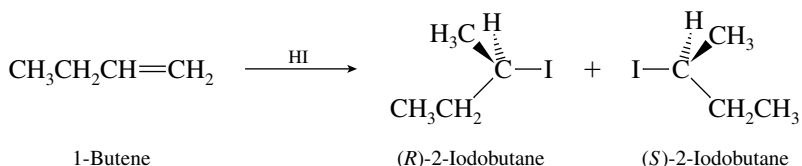
$$[\alpha]_D = \frac{100(-5.20^\circ)}{(2.0 \text{ g}/100 \text{ mL})(2 \text{ dm})}$$

$$= -130^\circ$$

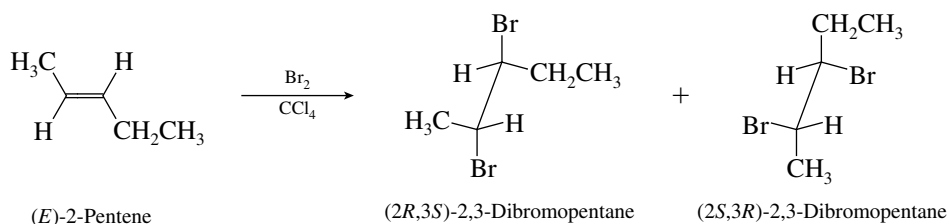
- (b) The optical purity of the resulting solution is 10/15, or 66.7%, since 10 g of optically pure fructose has been mixed with 5 g of racemic fructose. The specific rotation will therefore be two thirds (10/15) of the specific rotation of optically pure fructose:

$$[\alpha]_D = \frac{2}{3}(-130^\circ) = -87^\circ$$

- 7.39 (a) The reaction of 1-butene with hydrogen iodide is one of electrophilic addition. It follows Markovnikov's rule and yields a racemic mixture of (*R*)- and (*S*)-2-iodobutane.

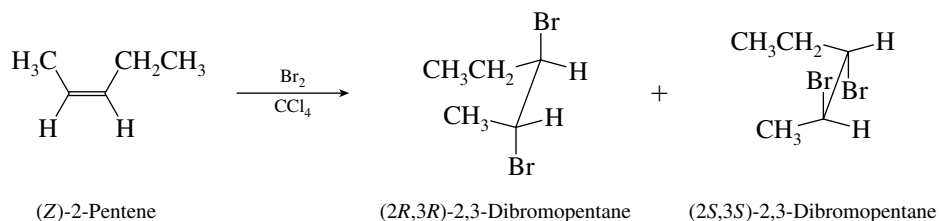


- (b) Bromine adds anti to carbon-carbon double bonds to give vicinal dibromides.

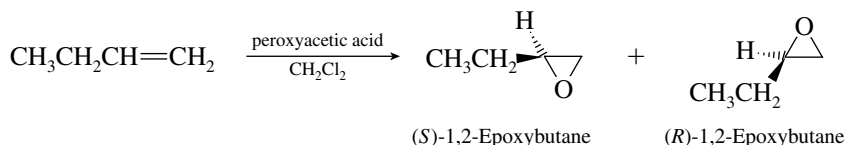


The two stereoisomers are enantiomers and are formed in equal amounts.

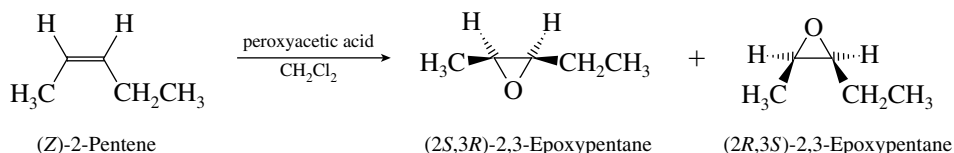
- (c) Two enantiomers are formed in equal amounts in this reaction, involving electrophilic addition of bromine to (*Z*)-2-pentene. These two are diastereomeric with those formed in part (b).



- (d) Epoxidation of 1-butene yields a racemic epoxide mixture.

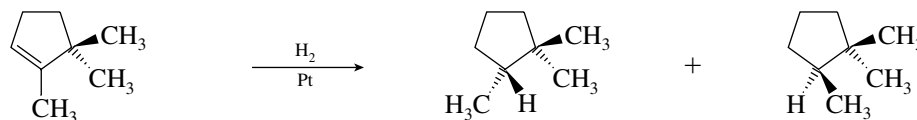


- (e) Two enantiomeric epoxides are formed in equal amounts on epoxidation of (*Z*)-2-pentene.



The reaction is a stereospecific syn addition. The cis alkyl groups in the starting alkene remain cis in the product epoxide.

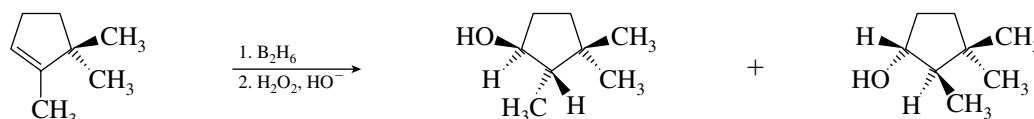
- (f) The starting material is achiral, so even though a chiral product is formed, it is a racemic mixture of enantiomers and is optically inactive.



1,5-Trimethylcyclopentene

(R)-1,1,2-Trimethylcyclopentane*(S)*-1,1,2-Trimethylcyclopentane

- (g) Recall that hydroboration–oxidation leads to anti-Markovnikov hydration of the double bond.

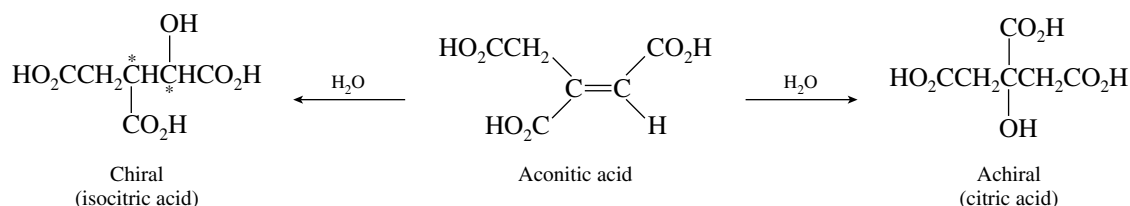


1,5,5-Trimethylcyclopentene

(1S,2S)-2,3,3-Trimethylcyclopentanol*(1R,2R)*-2,3,3-Trimethylcyclopentanol

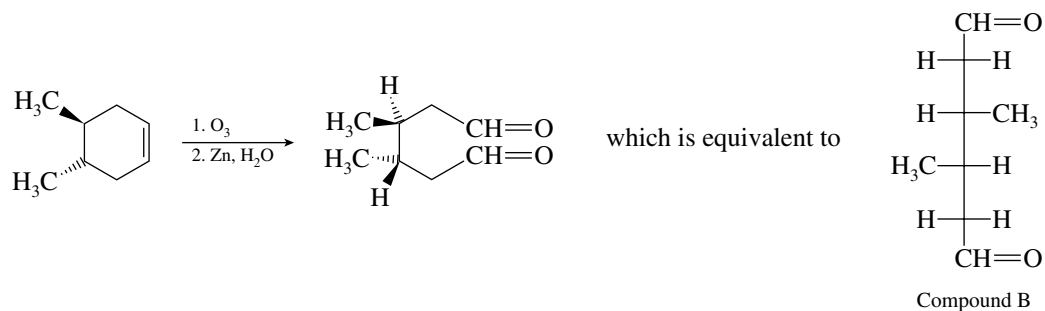
The product has two stereogenic centers. It is formed as a racemic mixture of enantiomers.

- 7.40** Hydration of the double bond of aconitic acid (shown in the center) can occur in two regiochemically distinct ways:



One of the hydration products lacks a stereogenic center. It must be citric acid, the achiral, optically inactive isomer. The other one has two different stereogenic centers and must be isocitric acid, the optically active isomer.

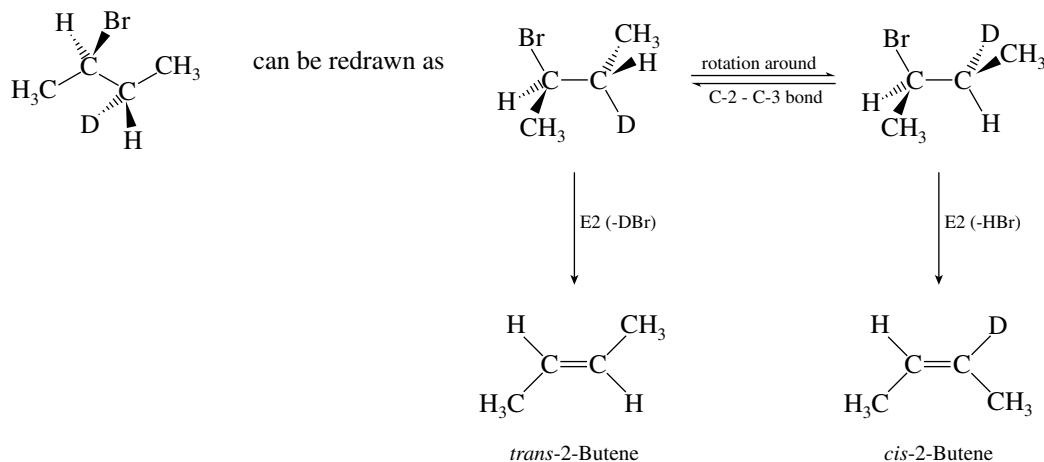
- 7.41** (a) Structures A and B are chiral. Structure C has a plane of symmetry and is an achiral meso form.
 (b) Ozonolysis of the starting material proceeds with the stereochemistry shown. Compound B is the product of the reaction.



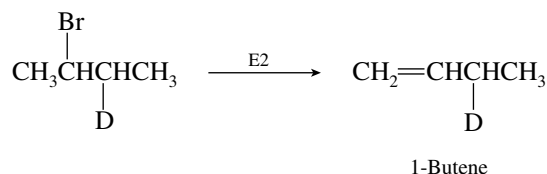
- (c) If the methyl groups were cis to each other in the cycloalkene, they would be on the same side of the Fischer projection in the product. Compound C would be formed.

- 7.42** (a) The E2 transition state requires that the bromine and the hydrogen that is lost be antiperiplanar to each other. Examination of the compound given in the problem reveals that loss of

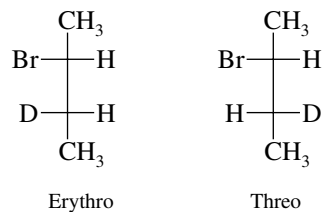
bromine and the deuterium will yield *trans*-2-butene, whereas loss of the bromine and the hydrogen on C-3 will yield *cis*-2-butene.



The *trans*-2-butene that forms does not contain deuterium, but *cis*-2-butene does. 1-Butene also contains deuterium.

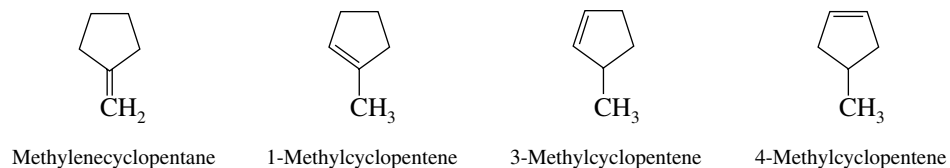


- (b) The starting material in part (a) is the erythro isomer. The relative positions of the H and C at C-3 are reversed in the threo isomer. The erythro and threo isomers can be drawn using Fischer projections:

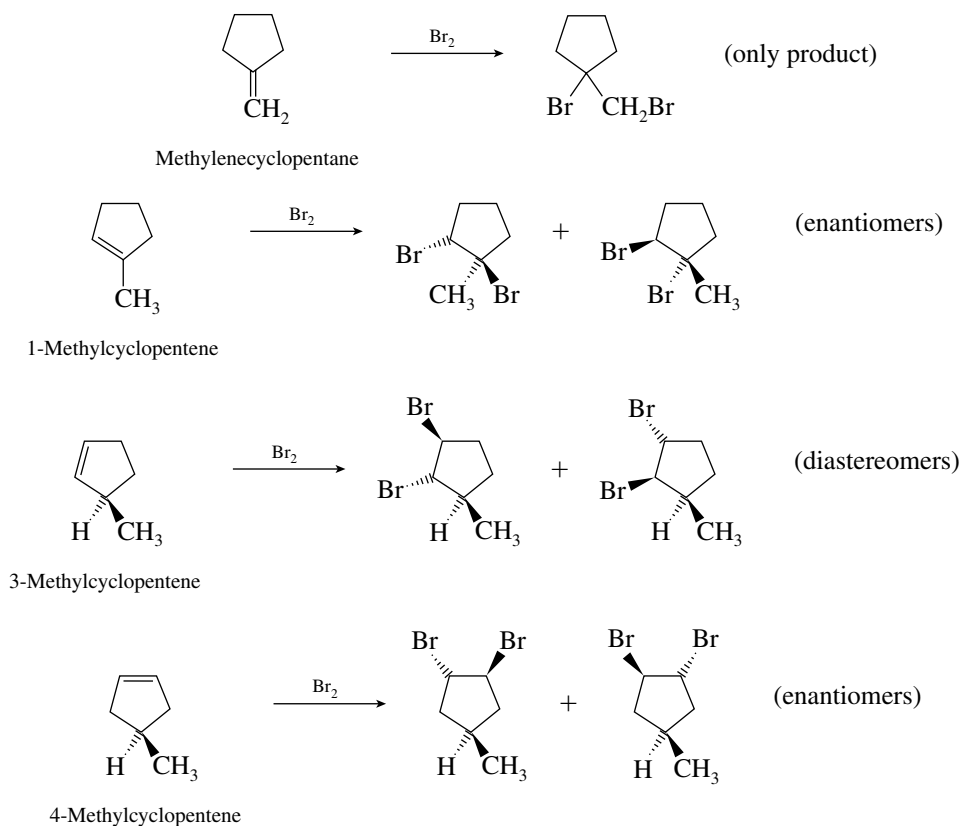


Because the positions of the H and D on C-3 in the threo isomer are opposite that in the erythro, the deuterium content of *cis*- and *trans*-2-butene would be reversed. *trans*-2-Butene obtained from the threo isomer would contain deuterium, and *cis*-2-butene would not. 1-Butene obtained from the threo isomer would also contain deuterium.

- 7.43** Bromine adds to the unknown compound, suggesting the presence of a double bond in addition to the five-membered ring. The following are possible structures for the unknown:

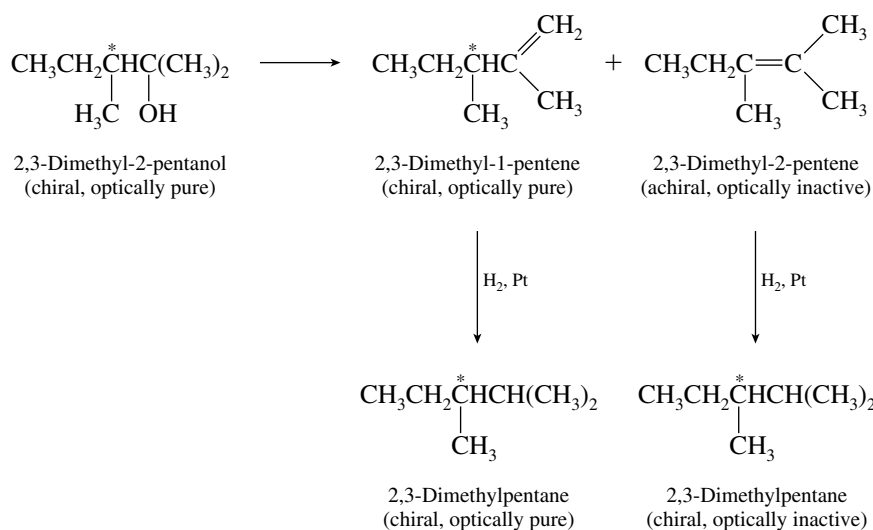


Which of these form diastereomeric dibromides on anti addition of bromine?



We are told in the problem that two diastereomeric bromides were formed, thus the compound must be 3-methylcyclopentene.

- 7.44** Dehydration of this tertiary alcohol can yield 2,3-dimethyl-1-pentene or 2,3-dimethyl-2-pentene. Only the terminal alkene in this case is chiral.

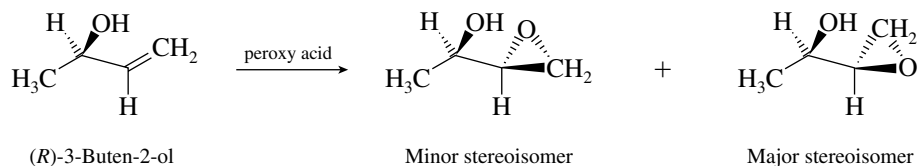


The 2,3-dimethyl-1-pentene formed in the dehydration reaction must be optically pure because it arises from optically pure alcohol by a reaction that does not involve any of the bonds to the stereogenic center. When optically pure 2,3-dimethyl-1-pentene is hydrogenated, it must yield optically pure 2,3-dimethylpentane—again, no bonds to the stereogenic center are involved in this step.

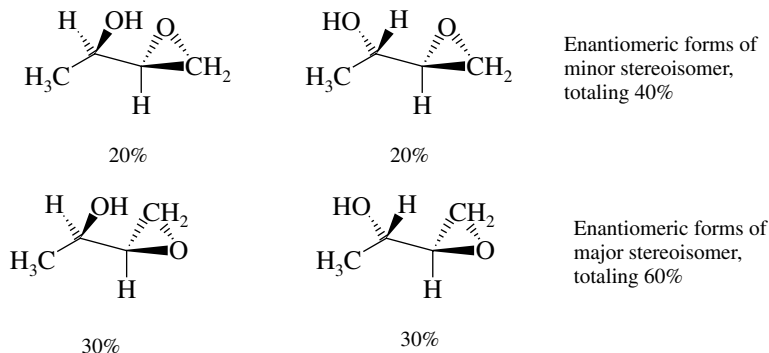
The 2,3-dimethyl-2-pentene formed in the dehydration reaction is achiral and must yield racemic 2,3-dimethylpentane on hydrogenation.

Because the alkane is 50% optically pure, the alkene fraction must have contained equal amounts of optically pure 2,3-dimethyl-1-pentene and its achiral isomer 2,3-dimethyl-2-pentene.

- 7.45 (a) Oxygen may be transferred to either the front face or the back face of the double bond when (*R*)-3-buten-2-ol reacts with a peroxy acid. The structure of the minor stereoisomer was given in the problem. The major stereoisomer results from addition to the opposite face of the double bond.



- (b) The two epoxides have the same configuration (*R*) at the secondary alcohol carbon, but opposite configurations at the stereogenic center of the epoxide ring. They are diastereomers.
 (c) In addition to the two diastereomeric epoxides whose structures are shown in the solution to part (a), the enantiomers of each will be formed when racemic 3-buten-2-ol is epoxidized. The relative amounts of the four products will be:

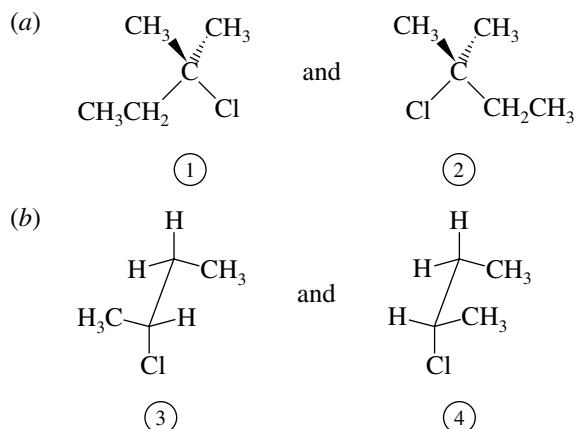


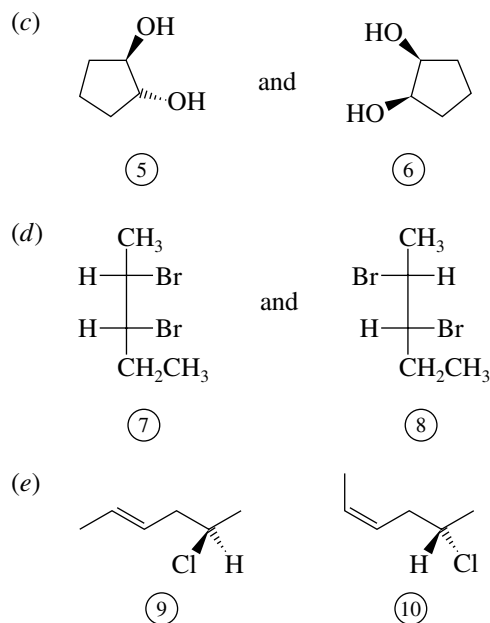
- 7.46–7.49 Solutions to molecular modeling exercises are not provided in this *Study Guide and Solutions Manual*. You should use *Learning By Modeling* for these exercises.

SELF-TEST

PART A

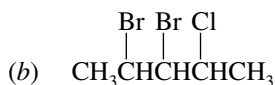
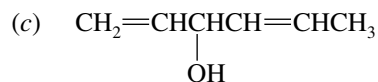
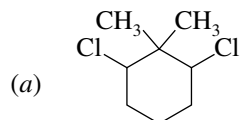
- A-1. For each of the following pairs of drawings, identify the molecules as chiral or achiral and tell whether each pair represents molecules that are enantiomers, diastereomers, or identical.



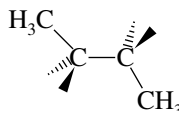


A-2. Specify the configuration of each stereogenic carbon in the preceding problem, using the Cahn–Ingold–Prelog *R*–*S* system.

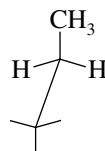
A-3. Predict the number of stereoisomers possible for each of the following constitutions. For which of these will meso forms be possible?



A-4. Using the skeletons provided as a guide,
 (a) Draw a perspective view of (*2R,3R*)-3-chloro-2-butanol.



(b) Draw a sawhorse diagram of (*R*)-2-bromobutane.



(c) Draw Fischer projections of both these compounds.

A-5. Draw Fischer projections of each stereoisomer of 2,3-dichlorobutane. Identify each stereogenic center as *R* or *S*. Which stereoisomers are chiral? Which are not? Why?

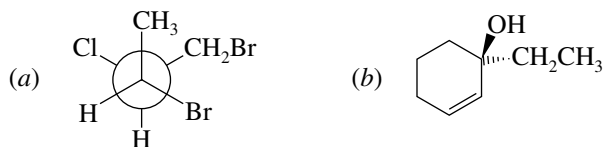
A-6. (a) The specific rotation of pure (–)-cholesterol is -39° . What is the specific rotation of a sample of cholesterol containing 10% (+)-cholesterol and 90% (–)-cholesterol.

(b) If the rotation of optically pure (*R*)-2-octanol is -10° , what is the percentage of the *S* enantiomer in a sample of 2-octanol that has a rotation of -4° ?

A-7. Write the organic product(s) expected from each of the following reactions. Show each stereoisomer if more than one forms.

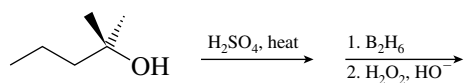
- (a) 1,5,5-Trimethylcyclopentene and hydrogen bromide
 (b) (*E*)-2-Butene and chlorine (Cl₂)
 (c) (*Z*)-2-Pentene and peroxyacetic acid

A-8. Give the IUPAC name, including stereochemistry, for the following:



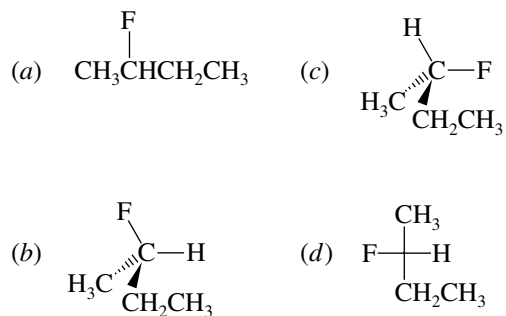
A-9. How many stereoisomeric products are obtained from the reaction of (*S*)-3-chloro-1-butene with hydrogen bromide? What is their relationship (enantiomers, diastereomers)?

A-10. Write the final product of the following reaction sequence, clearly showing its stereochemistry. Is the product achiral, a meso compound, optically active, or a racemic mixture?



PART B

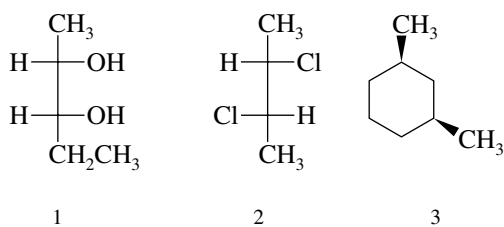
B-1. The structure of (*S*)-2-fluorobutane is best represented by



B-2. Which one of the following is chiral?

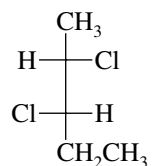
- (a) 1,1-Dibromo-1-chloropropane
 (b) 1,1-Dibromo-3-chloropropane
 (c) 1,3-Dibromo-1-chloropropane
 (d) 1,3-Dibromo-2-chloropropane

B-3. Which of the following compounds are meso forms?



- (a) 1 only (c) 1 and 2
 (b) 3 only (d) 2 and 3

B-4. The 2,3-dichloropentane whose structure is shown is

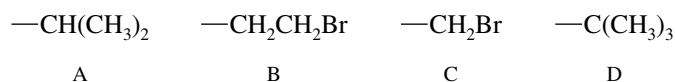


- (a) 2*R*,3*R* (b) 2*R*,3*S* (c) 2*S*,3*R* (d) 2*S*,3*S*

B-5. The separation of a racemic mixture into the pure enantiomers is termed

- (a) Racemization (c) Isomerization
 (b) Resolution (d) Equilibration

B-6. Order the following groups in order of *R-S* ranking (4 is highest):

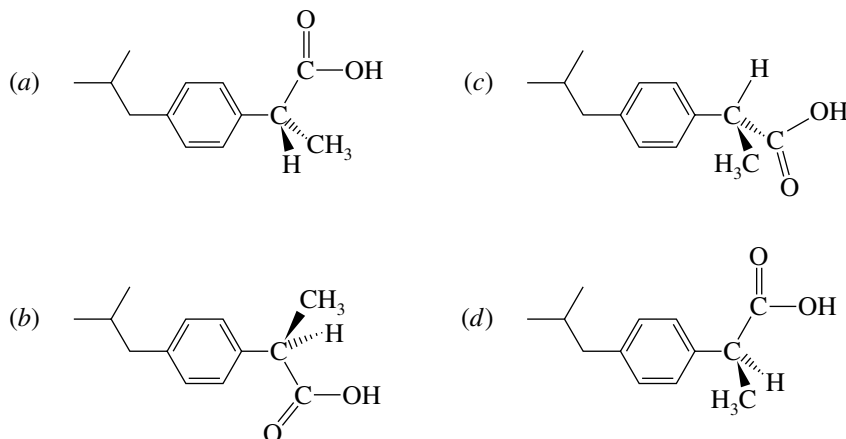


	4	3	2	1
(a)	C	B	D	A
(b)	A	D	B	C
(c)	C	D	A	B
(d)	C	D	B	A

B-7. A meso compound

- (a) Is an achiral molecule that contains stereogenic centers.
 (b) Contains a plane of symmetry or a center of symmetry.
 (c) Is optically inactive.
 (d) Is characterized by all of these.

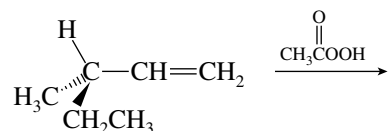
B-8. The *S* enantiomer of ibuprofen is responsible for its pain-relieving properties. Which one of the structures shown is (*S*)-ibuprofen?



B-9. Which one of the following is a diastereomer of (*R*)-4-bromo-*cis*-2-hexene?

- (a) (*S*)-4-bromo-*cis*-2-hexene (d) (*S*)-5-bromo-*trans*-2-hexene
 (b) (*R*)-4-bromo-*trans*-2-hexene (e) (*R*)-5-bromo-*trans*-2-hexene
 (c) (*R*)-5-bromo-*cis*-2-hexene

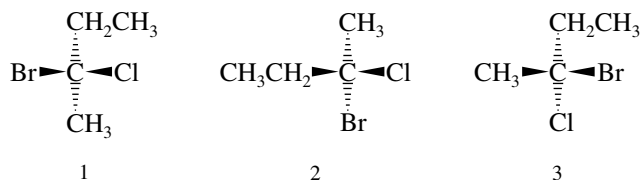
B-10. The reaction sequence



will yield:

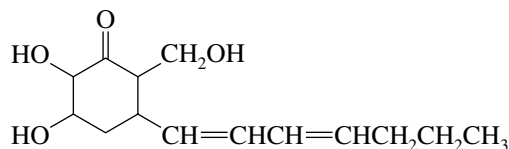
- (a) A pair of products that are enantiomers
- (b) A single product that is optically active
- (c) A pair of products that are diastereomers
- (d) A pair of products one of which is meso

B-11. Which of the following depict the same stereoisomer?



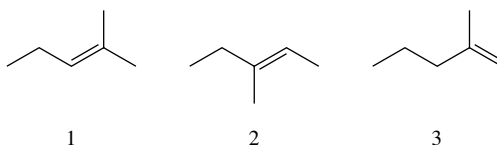
- (a) 1 and 2
- (b) 1 and 3
- (c) 2 and 3
- (d) 1, 2, and 3

B-12. A naturally occurring substance has the constitution shown. How many stereoisomers may have this constitution?



- (a) 2
- (b) 8
- (c) 16
- (d) 64
- (e) 128

B-13. Acid-catalyzed hydration of an unknown compound X, C_6H_{12} , yielded as the major product a racemic mixture Y, $C_6H_{14}O$. Which (if any) of the following is (are) likely candidate(s) for X?



- (a) 3 only
- (b) 2 only
- (c) 1 and 3
- (d) 2 and 3
- (e) None of these

B-14. The major product(s) from the reaction of Br_2 with (Z)-3-hexene is (are)

- (a) Optically pure
- (b) A racemic mixture of enantiomers
- (c) The meso form
- (d) Both the racemic mixture and the meso form