

## Chapter 9 – Stereochemistry

### Chapter Outline

#### I. Handedness (Sections 9.1 – 9.4).

##### A. Enantiomers and tetrahedral carbon (Section 9.1).

When four different groups are bonded to a carbon atom, two different arrangements are possible.

- These arrangements are mirror images.
- The two mirror-image molecules are enantiomers.

##### B. The reason for handedness in molecules: Chirality (Section 9.2).

- Molecules that are not superimposable on their mirror-images are chiral.
  - A molecule is not chiral if it contains a plane of symmetry.
  - A molecule with no plane of symmetry is chiral.
- A carbon bonded to four different groups is a chirality center.
- Any  $-\text{CH}_2-$  or  $-\text{CH}_3$  carbon is achiral.

##### C. Optical activity (Section 9.3).

- Solutions of certain substances rotate the plane of plane-polarized light.

These substances are said to be optically active.
- The amount of rotation can be measured with a polarimeter.
- The direction of rotation can also be measured.
  - A compound whose solution rotates plane-polarized light to the right is dextrorotatory.
  - A compound whose solution rotates plane-polarized light to the left is levorotatory.
- Specific rotation.
  - The amount of rotation depends on concentration, path length and wavelength.
  - Specific rotation is the observed rotation of a sample with concentration = 1 g/mL, sample path length of 1 dm, and light of wavelength = 589 nm.
  - Specific rotation is a physical constant characteristic of a given optically active compound.

##### D. Pasteur's discovery of enantiomerism (Section 9.4).

- Pasteur discovered two different types of crystals in a solution that he was evaporating.
- The crystals were mirror images.
- Solutions of each of the two types of crystals were optically active, and their specific rotations were equal in magnitude but opposite in sign.
- Pasteur postulated that some molecules are handed and thus discovered the phenomenon of enantiomerism.

#### II. Stereoisomers and configurations (Sections 9.5 – 9.8).

##### A. Specification of configurations of stereoisomers (Section 9.5).

- Rules for assigning configurations at a chirality center:
  - Assign priorities to each group bonded to the carbon by using Cahn-Ingold-Prelog rules (Section 6.5).
  - Orient the molecule so that the group of lowest priority is pointing to the rear.
  - Draw a curved arrow from group 1 to group 2 to group 3.
  - If the arrow rotates clockwise, the chirality center is *R*, and if the arrow rotates counterclockwise, the chirality center is *S*.
- The sign of rotation is not related to *R,S* designation.
- X-ray experiments have proven *R,S* conventions to be correct.

## B. Diastereomers (Section 9.6).

1. A molecule with two chirality centers can have four possible stereoisomers.
  - a. The stereoisomers group into two pairs of enantiomers.
  - b. A stereoisomer from one pair is the diastereomer of a stereoisomer from the other pair.
2. Diastereomers are stereoisomers that are not mirror images.
3. Epimers are diastereomers whose configuration differs at only one chirality center.

## C. Meso compounds (Section 9.7).

1. A meso compound occurs when a compound with two chirality centers possesses a plane of symmetry.
2. A meso compound is achiral despite having two chirality centers.
3. The physical properties of meso compounds, diastereomers and racemic mixtures differ from each other and from the properties of enantiomers.

## F. Racemic mixtures and their resolution (Section 9.8).

1. A racemic mixture is a 50:50 mixture of two enantiomers.

Racemic mixtures show zero optical rotation.
2. Some racemic mixtures can be resolved into their component enantiomers.
  - a. If a racemic mixture of a carboxylic acid reacts with a chiral amine, the product ammonium salts are diastereomers.
  - b. The diastereomeric salts differ in chemical and physical properties and can be separated.
  - c. The original enantiomers can be recovered by acidification.

## III. A review of isomerism (Section 9.9).

## A. Constitutional isomers differ in connections between atoms.

1. Skeletal isomers have different carbon skeletons.
2. Functional isomers contain different functional groups.
3. Positional isomers have functional groups in different positions.

## B. Stereoisomers have the same connections between atoms, but different geometry.

1. Enantiomers have a mirror-image relationship.
2. Diastereomers are non-mirror-image stereoisomers.
  - a. Configurational diastereomers.
  - b. Cis-trans isomers differ in the arrangement of substituents in a double bond or ring.

## IV. Stereochemistry of reactions (Sections 9.10 – 9.11).

A. Addition of  $\text{H}_2\text{O}$  to an achiral alkene (Section 9.10).

1. When  $\text{H}_2\text{O}$  adds to an achiral alkene, a racemic mixture of products is formed.
2. The achiral cationic intermediate can react from either side to produce a racemic mixture.
3. Alternatively, the transition states for top side reaction and bottom side reaction are enantiomers and have the same energy.
4. Enzyme-catalyzed reactions give a single enantiomer, even when the substrate is achiral.

B. Addition of  $\text{H}_2\text{O}$  to a chiral alkene (Section 9.11).

1. When  $\text{H}^+$  adds to a chiral alkene, the intermediate carbocation is chiral.
2. The original chirality center is unaffected by the reaction.
3. Reaction of  $\text{H}_2\text{O}$  with the carbocation doesn't occur with equal probability from either side, and the resulting product is an optically active mixture of diastereomeric alcohols.
4. Reaction of a chiral reactant with an achiral reactant leads to unequal amounts of diastereomeric products.

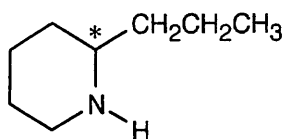
- V. Chirality at atoms other than carbon (Section 9.12).
- Other elements with tetrahedral atoms can be chirality centers.
  - Trivalent nitrogen can, theoretically, be chiral, but rapid inversion of the nitrogen lone pair interconverts the enantiomers.
  - Chiral phosphines can be isolated because their rate of inversion is slower.
- VI. Prochirality (Section 9.13).
- A molecule is prochiral if it can be converted from achiral to chiral in a single chemical step.
  - Identifying prochirality.
    - For  $sp^2$  carbon, draw the plane that includes the atoms bonded to the  $sp^2$  carbon.
      - Assign priorities to the groups bonded to the carbon.
      - Draw an curved arrow from group 1 to group 2 to group 3.
      - The face of the plane on which the curved arrow rotates clockwise is the *re* face.
      - The face on which the arrow rotates counterclockwise is the *si* face.
    - An atom that is  $sp^3$ -hybridized may have a prochirality center if, when one of its attached groups is replaced, it becomes a chirality center.
      - For  $-CH_2X$ , imagine a replacement of one hydrogen with deuterium.
      - Rank the groups, including the deuterium.
      - If the replacement leads to *R* chirality, the atom is *pro-R*.
      - If the replacement leads to *S* chirality, the atom is *pro-S*.
  - Many biochemical reactions involve prochiral compounds.
- VII. Chirality in nature (Section 9.14).
- Different enantiomers of a chiral molecule have different properties in nature.
    - (+)-Limonene has the odor of oranges, and (–)-limonene has the odor of lemons.
    - Racemic fluoxetine is an antidepressant, but the *S* enantiomer is effective against migraine.
  - In nature, a molecule must fit into a chiral receptor, and only one enantiomer usually fits.
  - Enantioselective synthesis allows for the synthesis of one enantiomer of a compound, rather than a racemic mixture.

## Solutions to Problems

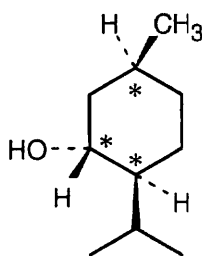
- 9.1** Objects having a plane of symmetry are achiral.  
 Chiral: screw, beanstalk, shoe.  
 Achiral: screwdriver.
- 9.2 Strategy:** Use the following rules to locate centers that are *not* chirality centers.
- All  $-CH_3$  and  $-CX_3$  carbons are not chirality centers.
  - All  $-CH_2-$  and  $-CX_2-$  carbons are not chirality centers.
  - All  $\begin{array}{c} | \quad | \\ -C=C- \end{array}$  and  $-C\equiv C-$  carbons are not chirality centers  
 By rule 3, all aromatic ring carbons are not chirality centers.

**Solution:**

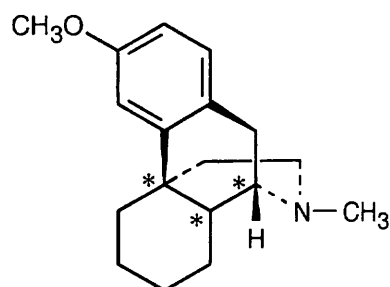
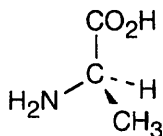
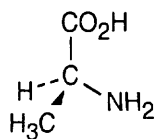
(a)

**Coniine**

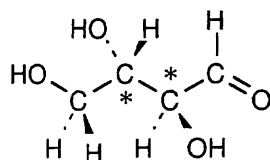
(b)

**Menthol**

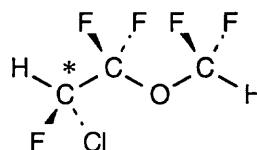
(c)

**Dextromethorphan****9.3****Alanine****9.4**

(a)

**Threose**

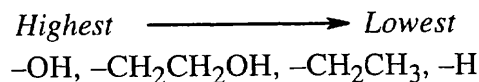
(b)

**Enflurane****9.5** By convention, a (–) rotation indicates rotation to the left, and thus cocaine is levorotatory.**9.6****Strategy:**Use the formula  $[\alpha]_D = \frac{\alpha}{l \times C}$ , where $[\alpha]_D$  = specific rotation $\alpha$  = observed rotation $l$  = path length of cell (in dm) $C$  = concentration (in g/mL)In this problem:  $\alpha = 1.21^\circ$  $l = 5.00 \text{ cm} = 0.500 \text{ dm}$  $C = 1.50 \text{ g}/10.0 \text{ mL} = 0.150 \text{ g/mL}$ 

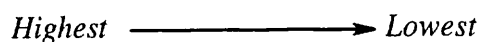
**Solution:**  $[\alpha]_D = \frac{+1.21^\circ}{0.500 \text{ dm} \times 0.150 \text{ g/mL}} = +16.1^\circ$

**9.7** Use the sequence rules in Section 9.5.

(a) By Rule 1,  $-\text{H}$  is of lowest priority, and  $-\text{OH}$  is of highest priority. By Rule 2,  $-\text{CH}_2\text{CH}_2\text{OH}$  is of higher priority than  $-\text{CH}_2\text{CH}_3$ .



(b) By Rule 3,  $-\text{CO}_2\text{H}$  is considered as  $\begin{array}{c} \text{---O} \quad \text{O---} \\ \diagdown \quad \diagup \\ \text{---C---OH} \end{array}$ . Because 3 oxygens are attached to a  $-\text{CO}_2\text{H}$  carbon and only one oxygen is attached to  $-\text{CH}_2\text{OH}$ ,  $-\text{CO}_2\text{H}$  is of higher priority than  $-\text{CH}_2\text{OH}$ .  $-\text{CO}_2\text{CH}_3$  is of higher priority than  $-\text{CO}_2\text{H}$  by Rule 2, and  $-\text{OH}$  is of highest priority by Rule 1.



(b)  $-\text{OH}$ ,  $-\text{CO}_2\text{CH}_3$ ,  $-\text{CO}_2\text{H}$ ,  $-\text{CH}_2\text{OH}$

(c)  $-\text{NH}_2$ ,  $-\text{CN}$ ,  $-\text{CH}_2\text{NHCH}_3$ ,  $-\text{CH}_2\text{NH}_2$

(d)  $-\text{SSCH}_3$ ,  $-\text{SH}$ ,  $-\text{CH}_2\text{SCH}_3$ ,  $-\text{CH}_3$

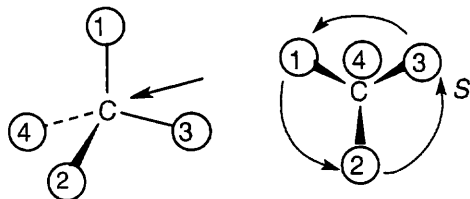
**9.8 Strategy:** All stereochemistry problems are easier if you use models. Part (a) will be solved by two methods – with models and without models.

(a) *With models:* Build a model of (a). Orient the model so that group 4 is pointing to the rear. Note the direction of rotation of arrows that go from group 1 to group 2 to group 3. The arrows point counterclockwise, and the configuration is *S*.

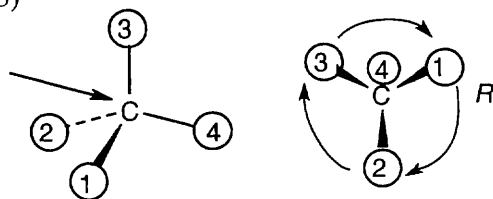
*Without models:* Imagine yourself looking at the molecule, with the group of lowest priority pointing to the back. Your viewpoint would be at the upper right of the molecule, and you would see group 1 on the left, group 3 on the right and group 2 at the bottom. The arrow of rotation travels counterclockwise, and the configuration is *S*.

**Solution:**

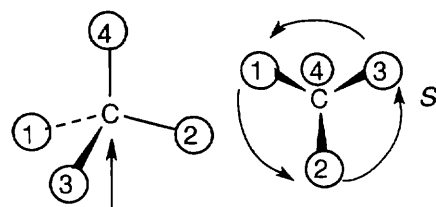
(a)



(b)



(c)



## 9.9 Strategy:

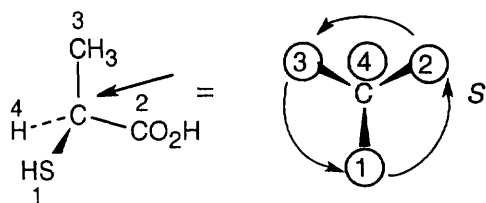
*Step 1.* For each chirality center, rank substituents by the Cahn–Ingold–Prelog system; give the number 4 to the lowest priority substituent. For part (a):

Substituent	Priority
–SH	1
–CO <sub>2</sub> H	2
–CH <sub>3</sub>	3
–H	4

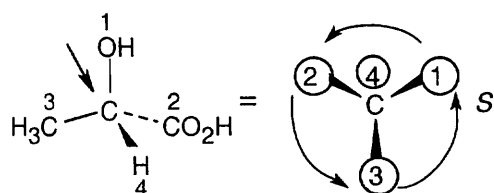
*Step 2.* As in the previous problem, orient yourself so that you are 180° from the lowest priority group (indicated by the arrow in the drawing). From that viewpoint, draw the molecule as it looks when you face it. Draw the arrow that travels from group 1 to group 2 to group 3, and note its direction of rotation. The molecule in (a) has *S* configuration.

## Solution:

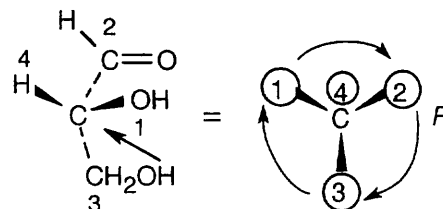
(a)



(b)

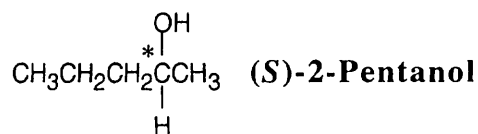


(c)

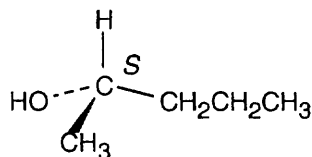
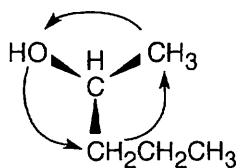


In (b), the observer is behind the page, looking out and down toward the right. In (c), the observer is behind the page looking out and up to the left.

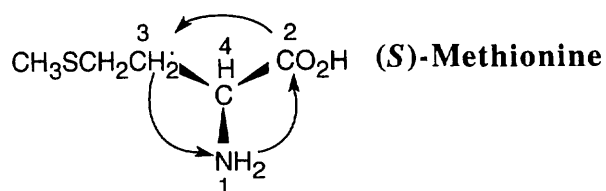
## 9.10



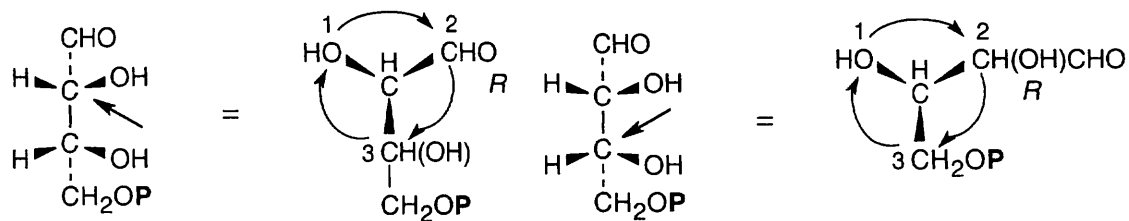
Substituent	Priority
–OH	1
–CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	2
–CH <sub>3</sub>	3
–H	4



9.11 Fortunately, methionine is shown in the correct orientation.



9.12 For (a):

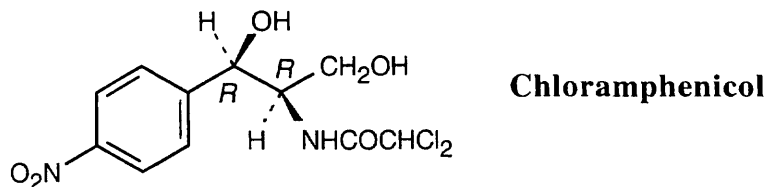


a, d are enantiomers and are diastereomeric with b, c.

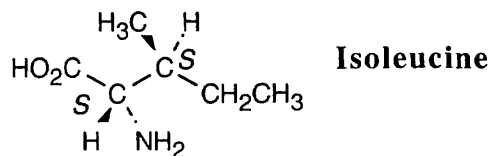
b, c are enantiomers and are diastereomeric with a, d.

Structure (a) is D-erythrose, structure (d) is its enantiomer, and structures (b) and (c) are its diastereomers.

9.13



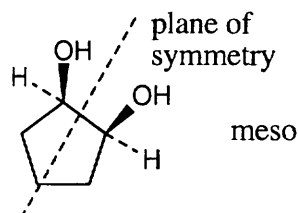
9.14



**9.15 Strategy:** To decide if a structure represents a meso compound, try to locate a plane of symmetry that divides the molecule into two halves that are mirror images. Molecular models are always helpful.

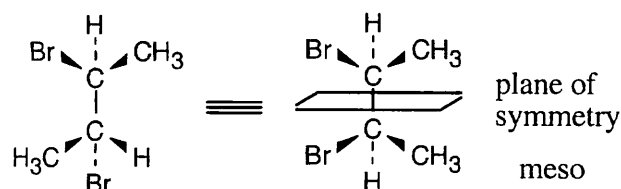
**Solution.**

(a)



(b) and (c) are not meso structures.

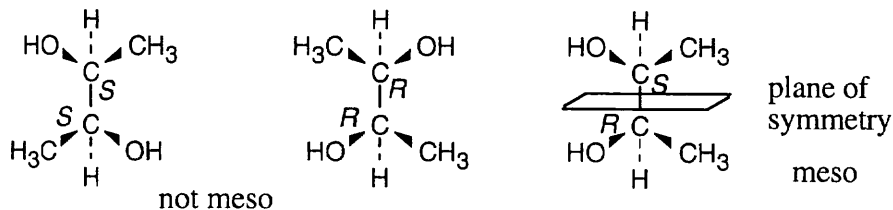
(d)



**9.16 Strategy:** For a molecule to exist as a meso form, it must possess a plane of symmetry. 2,3-Butanediol can exist as a pair of enantiomers *or* as a meso compound, depending on the configurations at carbons 2 and 3.

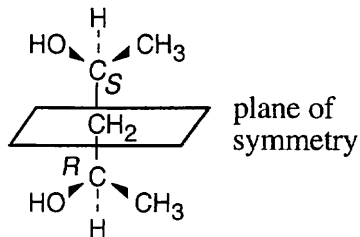
**Solution:**

(a)



(b) 2,3-Pentanediol has no symmetry plane and thus can't exist in a meso form.

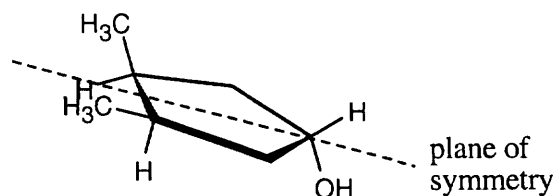
(c) 2,4-Pentanediol can exist in a meso form.



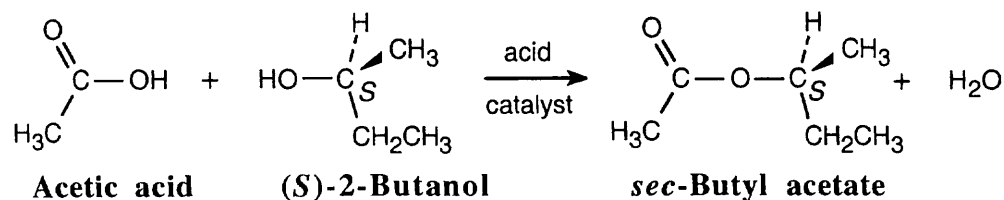
2,4-Pentanediol can also exist as a pair of enantiomers (*2R,4R*) and (*2S,4S*) that are not meso compounds.



- 9.17 The molecule represents a meso compound. The symmetry plane passes through the carbon bearing the  $\text{-OH}$  group and between the two ring carbons that are bonded to methyl groups.

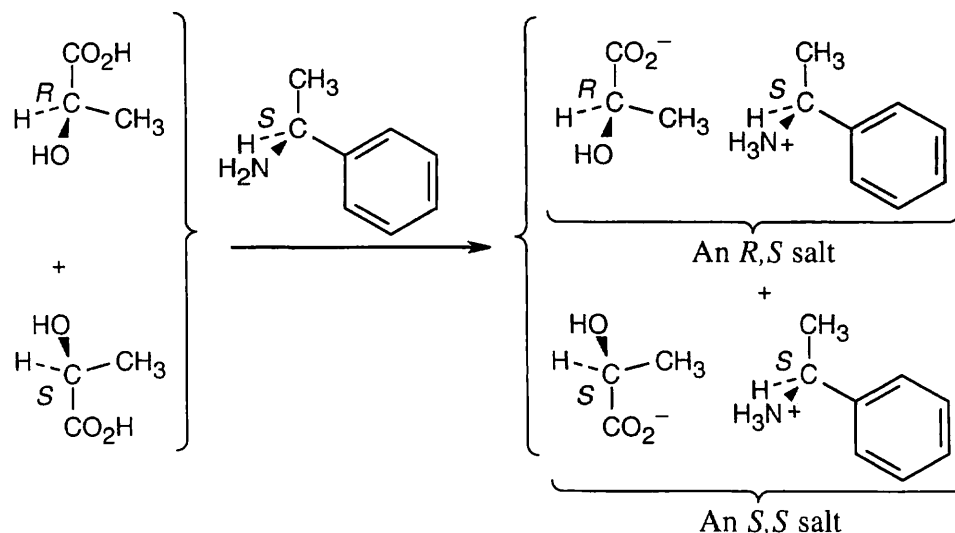


9.18



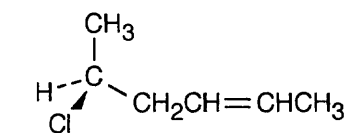
The product is the pure  $S$ -ester. No new chirality centers are formed during the reaction, and the configuration at the chirality center of  $(S)$ -2-butanol is unchanged.

9.19

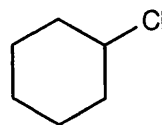


The two product salts have the configurations  $(R,S)$  and  $(S,S)$  and are diastereomers.

9.20 (a)



**(S)-5-Chloro-2-hexene**

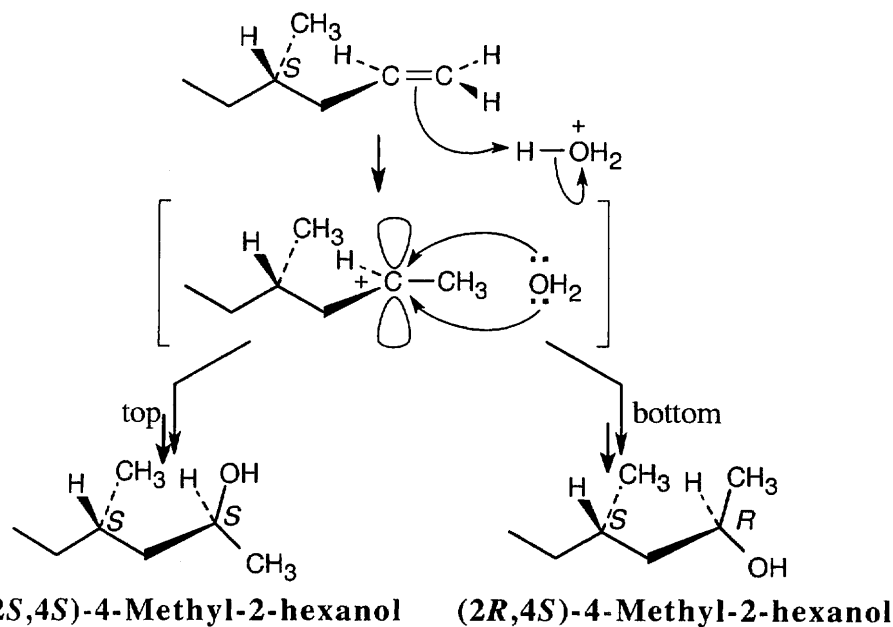


**Chlorocyclohexane**

These two compounds are constitutional isomers (skeletal isomers).

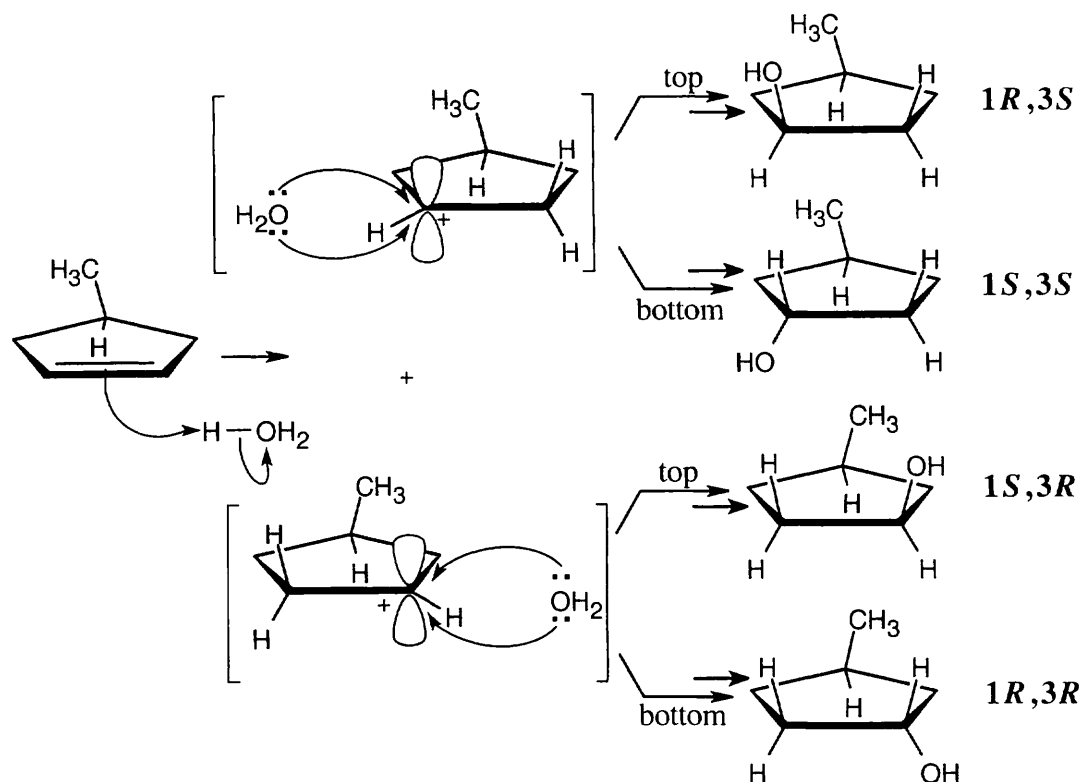
(b) The two dibromopentane stereoisomers are diastereomers.

- 9.21 Look back to Figure 9.16, which shows the reaction of (*R*)-4-methyl-1-hexene with  $\text{H}_3\text{O}^+$ . In a similar way, we can write a reaction mechanism for the reaction of  $\text{H}_3\text{O}^+$  with (*S*)-4-methyl-1-hexene.



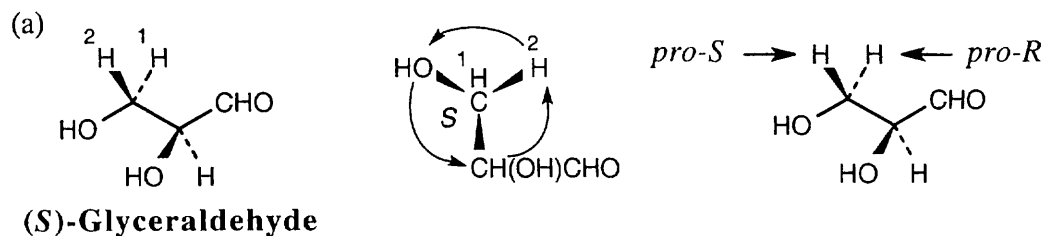
The products shown above are diastereomers and are formed in unequal amounts. The (2*S*,4*S*) stereoisomer is the enantiomer of the (2*R*,4*R*) isomer (shown in Figure 9.16), and the transition states leading to the formation of these two isomers are enantiomeric and of equal energy. Thus, the (2*S*,4*S*) and (2*R*,4*R*) enantiomers are formed in equal amounts. A similar argument can be used to show that the (2*R*,4*S*) and (2*S*,4*R*) isomers are formed in equal amounts.

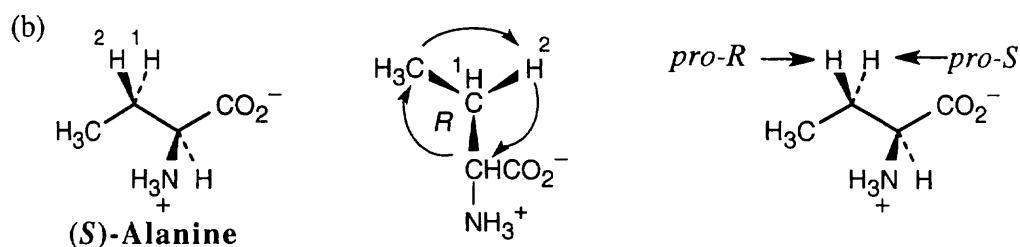
## 9.22



Two enantiomeric carbocations are formed. Each carbocation can react with  $\text{H}_2\text{O}$  from either the top or the bottom to yield a total of four stereoisomers. The same argument used in Problem 9.21 can be used to show that the  $(1S,3R)$  and  $(1R,3S)$  enantiomers are formed in equal amounts, and the  $(1S,3S)$  and  $(1R,3R)$  isomers are formed in equal amounts. The result is a non-50:50 mixture of two racemic pairs.

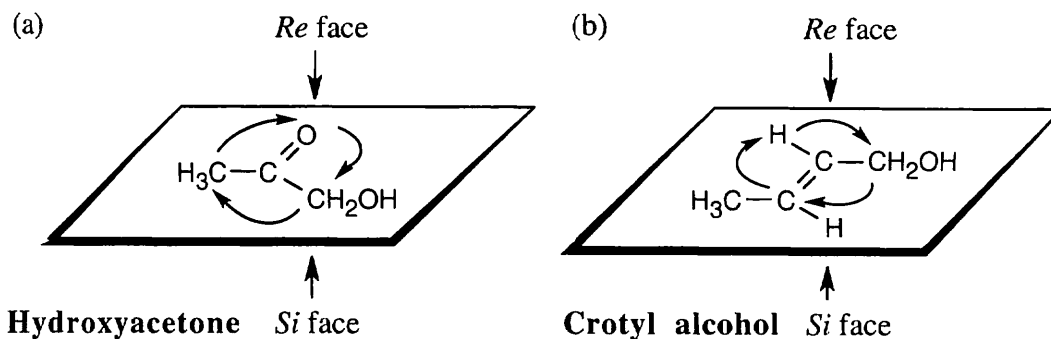
- 9.23 Strategy:** For each molecule, replace the left hydrogen with  $^2\text{H}$ . Give priorities to the groups and assign  $R,S$  configuration to the chirality center. If the configuration is  $R$ , the replaced hydrogen is *pro-R*, and if the configuration is  $S$ , the replaced hydrogen is *pro-S*.

**Solution:**



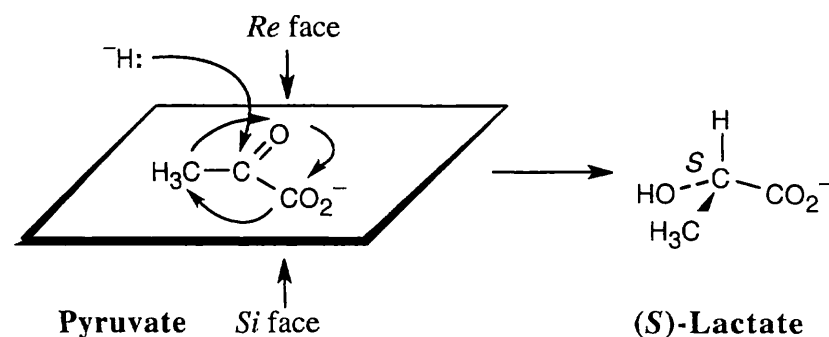
- 9.24 Strategy:** Draw the plane that includes the  $sp^2$  carbon and its substituents, and rank the substituents. For the upper face, draw the arrow that proceeds from group 1 to group 2 to group 3. If the direction of rotation is clockwise, the face is the *Re* face; if rotation is counterclockwise, the face is the *Si* face.

**Solution:**

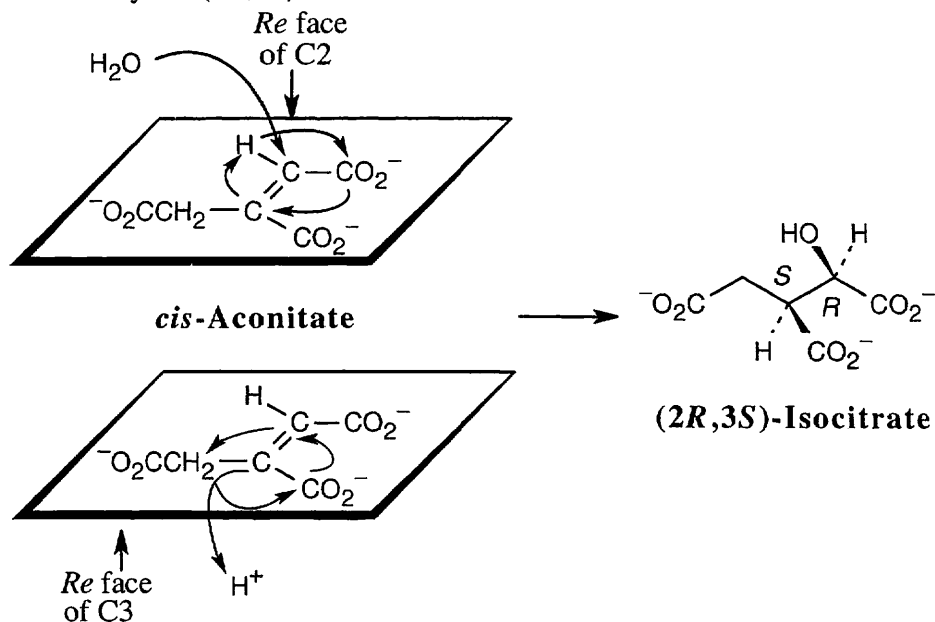


- 9.25 Strategy:** Use the strategy in the previous problem to identify the faces of the plane that contains the  $sp^2$  carbon. Draw the product that results from reaction at the *Re* face, and assign configuration to the chirality center.

**Solution:**



- 9.26** Addition of  $\text{-OH}$  takes place on the *Re* face of aconitate. Addition of  $\text{-H}$  also occurs on the *Re* face to yield (2*R*,3*S*)-isocitrate. The overall result is an anti addition.

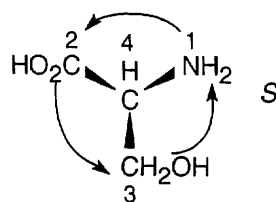
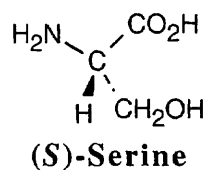


### Visualizing Chemistry

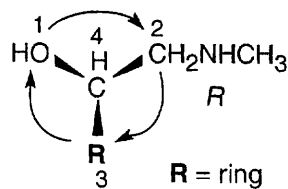
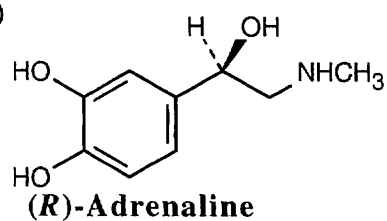
- 9.27** Structures (a), (b), and (d) are identical (*R* enantiomer), and (c) represents the *S* enantiomer.

### 9.28

(a)

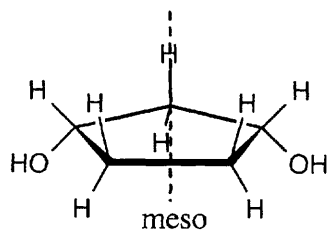


(b)

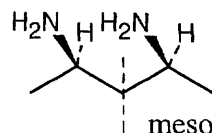


### 9.29

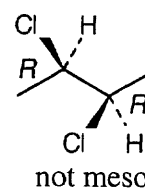
(a)



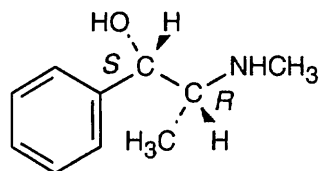
(b)



(c)

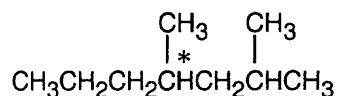


## 9.30

**Pseudoephedrine****Additional Problems**

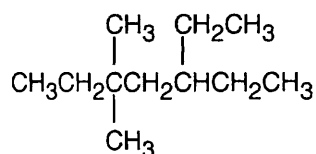
## 9.31

(a)



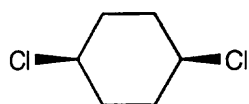
2,4-Dimethylheptane has one chirality center.

(b)

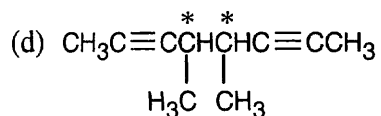


5-Ethyl-3,3-dimethylheptane is achiral.

(c)

*cis*-1,4-Dichlorocyclohexane is achiral. Notice the plane of symmetry that passes through the  $\text{-Cl}$  groups.

(d)

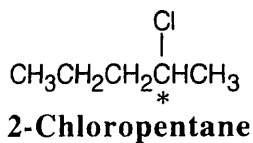


4,5-Dimethyl-2,6-octadiyne has two chirality centers.

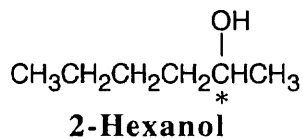
The chirality of (d) depends on the configuration at both of the chirality centers. The (*R,R*) and (*S,S*) isomers are chiral enantiomers; the (*R,S*) isomer is an achiral meso compound.

## 9.32

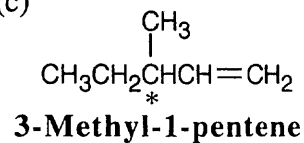
(a)



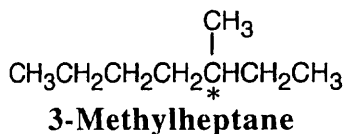
(b)



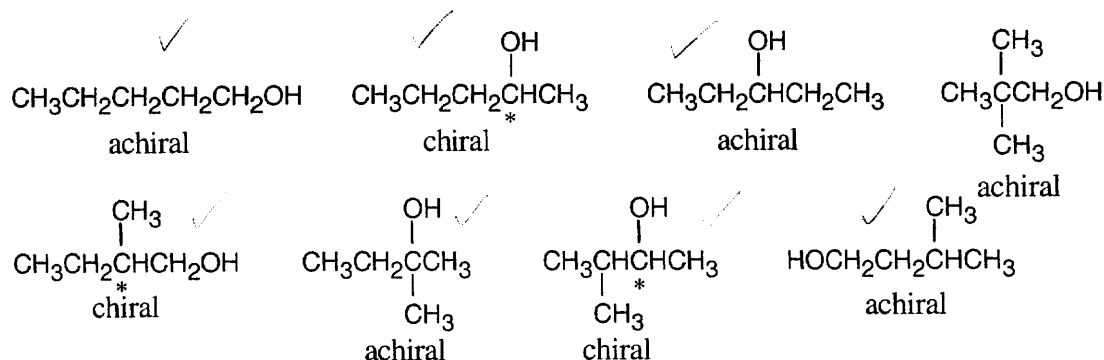
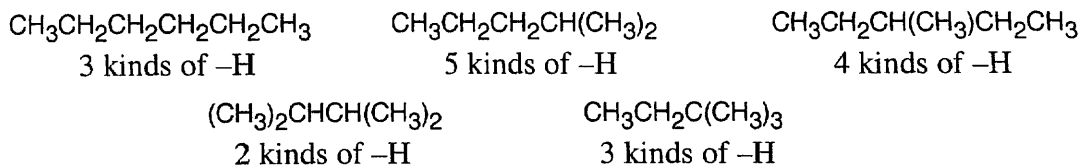
(c)



(d)

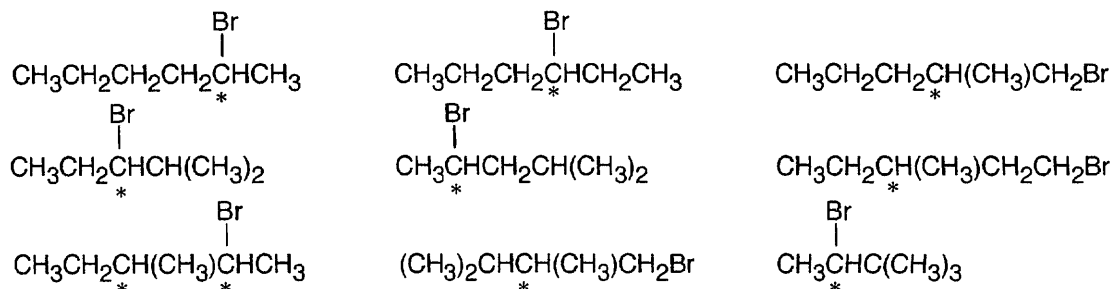


## 9.33

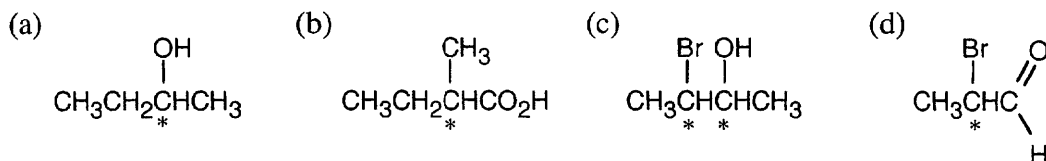
9.34 Strategy: Draw the five  $\text{C}_6\text{H}_{14}$  isomers.

17 different monobromo compounds can be formed from the isomers. You may need to draw all of them to find the nine that are chiral:

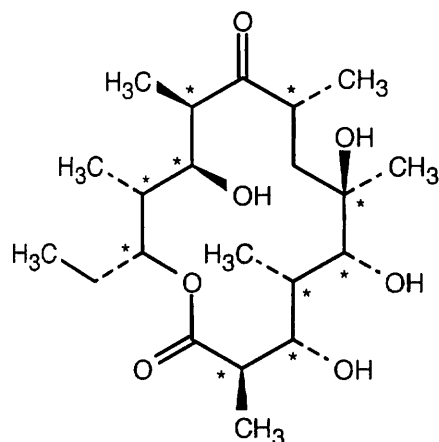
## Solution:



## 9.35

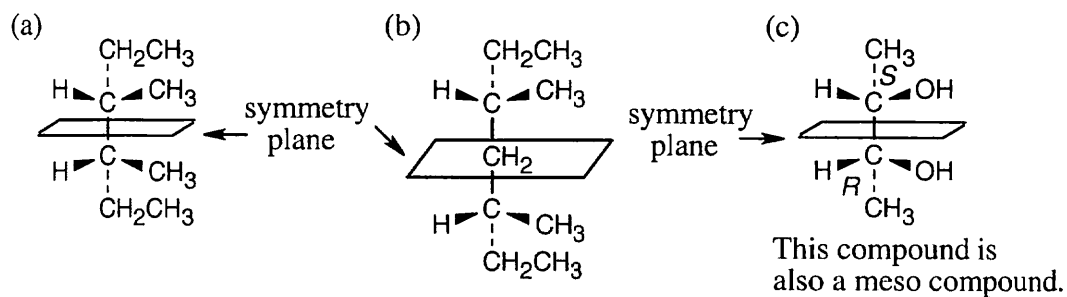
9.36 Chiral: (d) golf club, (e) monkey wrench (because of the threads).  
Achiral: (a) basketball, (b) fork, (c) wine glass, (f) snowflake.

## 9.37

**Erythronolide B**

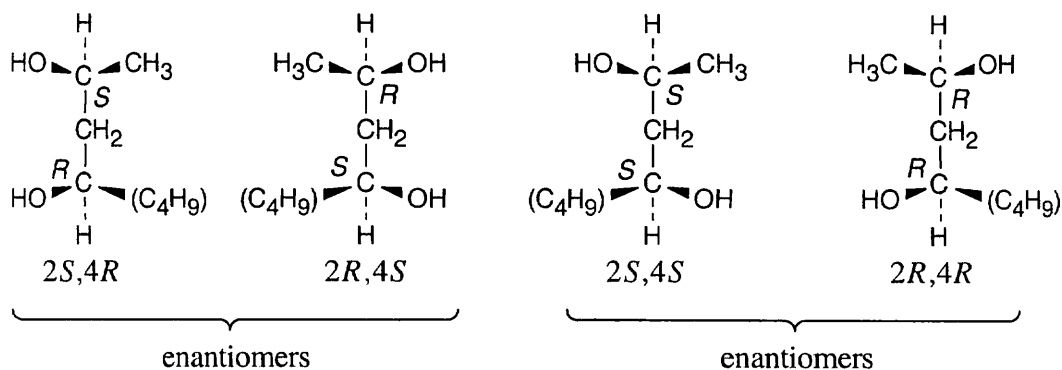
Erythronolide B has ten chirality centers.

## 9.38



**9.39** The specific rotation of (2*R*,3*R*)-dichloropentane is equal in magnitude and opposite in sign to the specific rotation of (2*S*,3*S*)-dichloropentane because the compounds are enantiomers. There is no predictable relationship between the specific rotations of the (2*R*,3*S*) and (2*R*,3*R*) isomers because they are diastereomers.

## 9.40–9.41

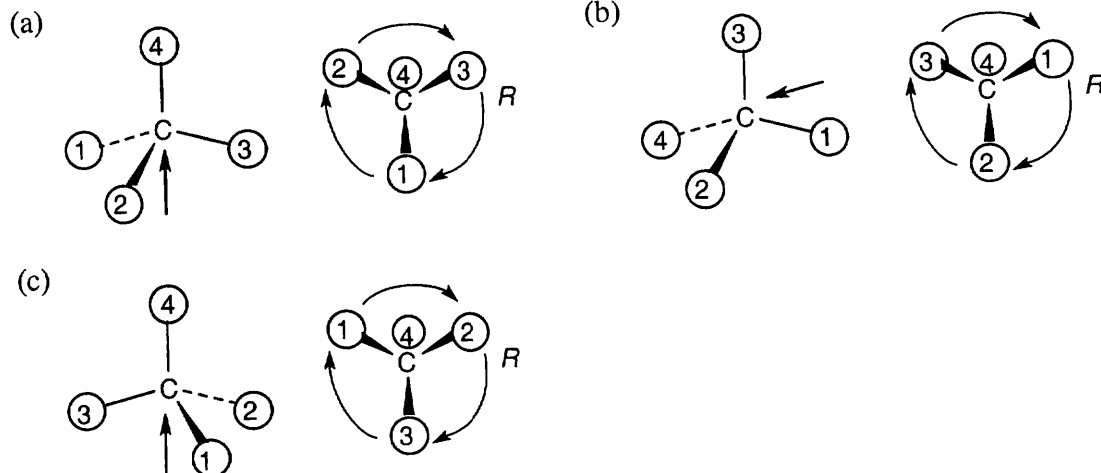


The (2*R*,4*S*) stereoisomer is the enantiomer of the (2*S*,4*R*) stereoisomer.

The (2*S*,4*S*) and (2*R*,4*R*) stereoisomers are diastereomers of the (2*S*,4*R*) stereoisomer.

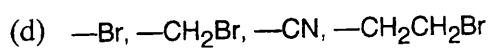
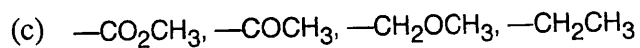
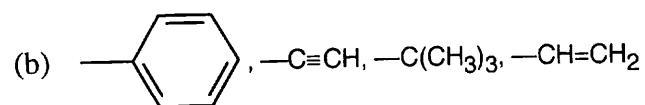
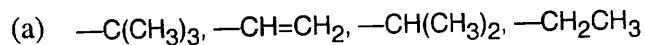


9.42

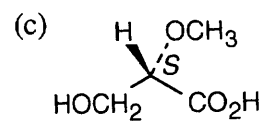
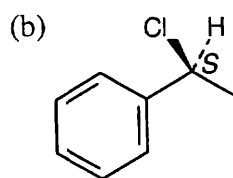
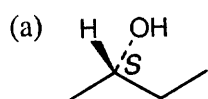


9.43

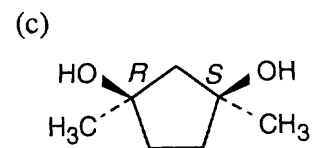
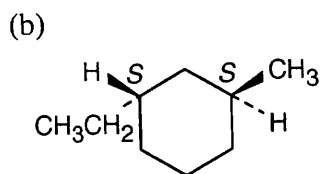
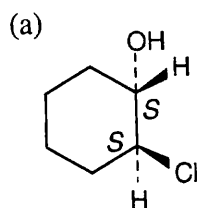
Highest  $\xrightarrow{\hspace{2cm}}$  Lowest



9.44

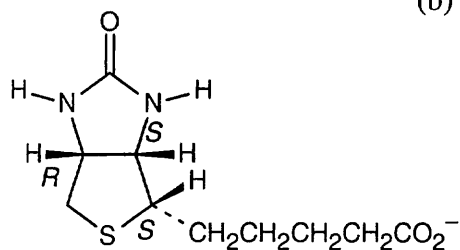


9.45

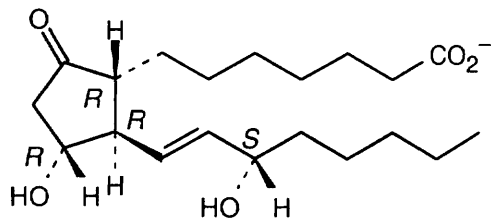


9.46

(a)

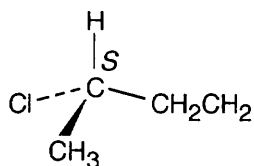
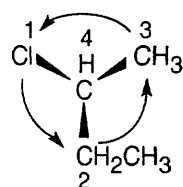
**Biotin**

(b)

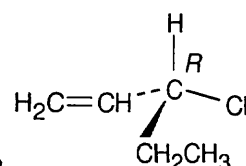
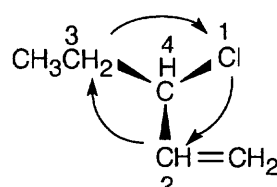
**Prostaglandin E<sub>1</sub>**

9.47

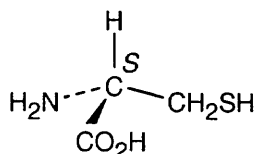
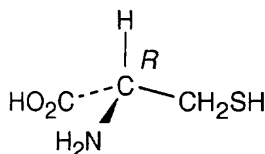
(a)



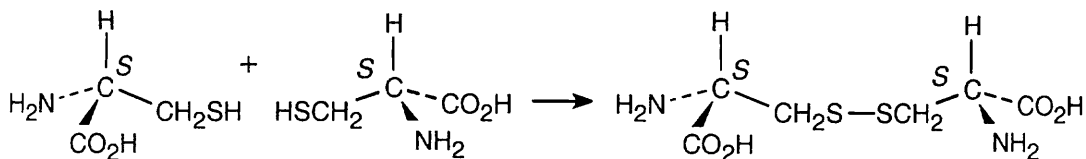
(b)



9.48



9.49

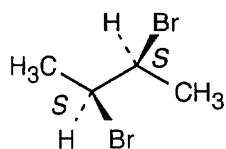


Cystine has the (*S,S*) configuration and is optically active.

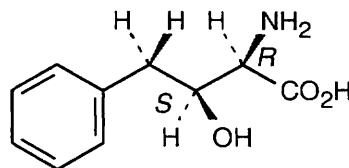
9.50 Identical molecules: b (*S* enantiomer), c (*R* enantiomer), d (*S* enantiomer).  
Pair of enantiomers: a

9.51

(a)

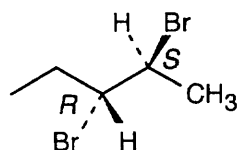


(b)

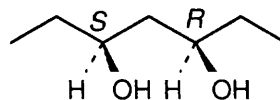


9.52

(a)

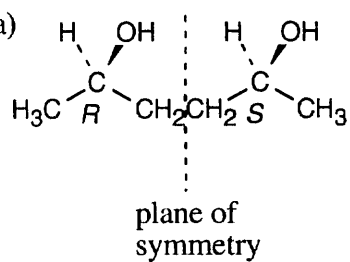
**(2*S*,3*R*)-2,3-Dibromopentane**

(b)

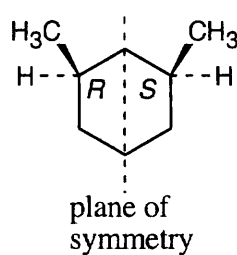
***meso*-3,5-Heptanediol**

9.53

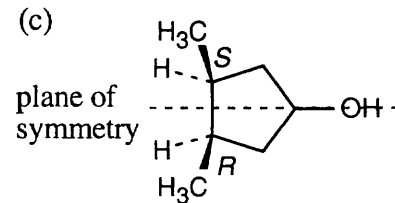
(a)



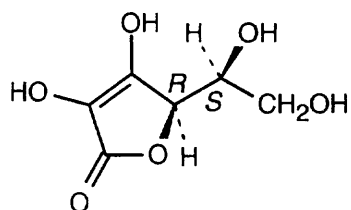
(b)



(c)

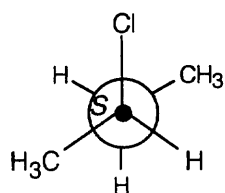


9.54

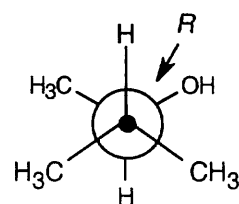
**Ascorbic acid**

9.55

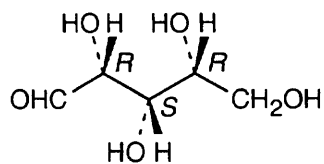
(a)



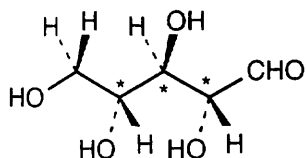
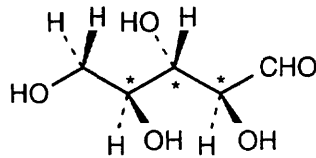
(b)



9.56

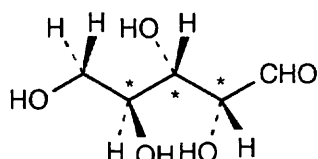
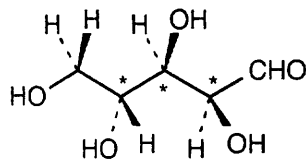
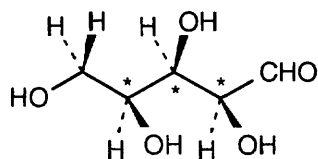
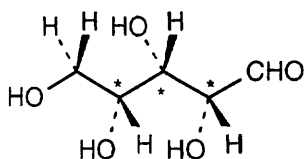
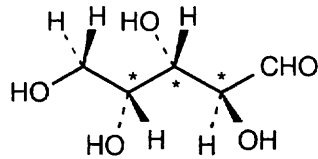
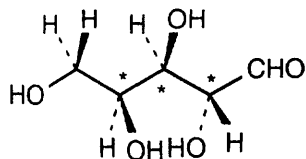
**(+)-Xylose**

## 9.57 (a) - (c)

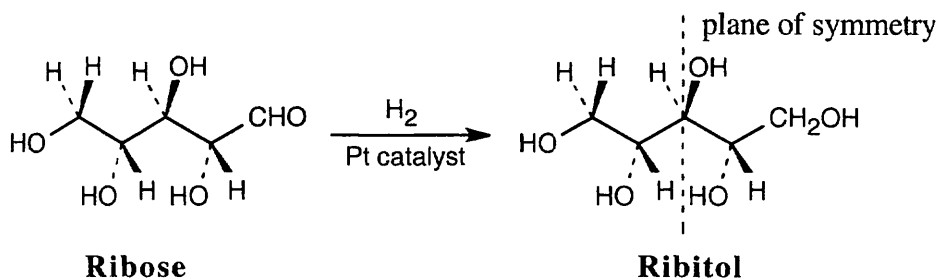
**Ribose****Enantiomer of ribose**

Ribose has three chirality centers, which give rise to eight stereoisomers.

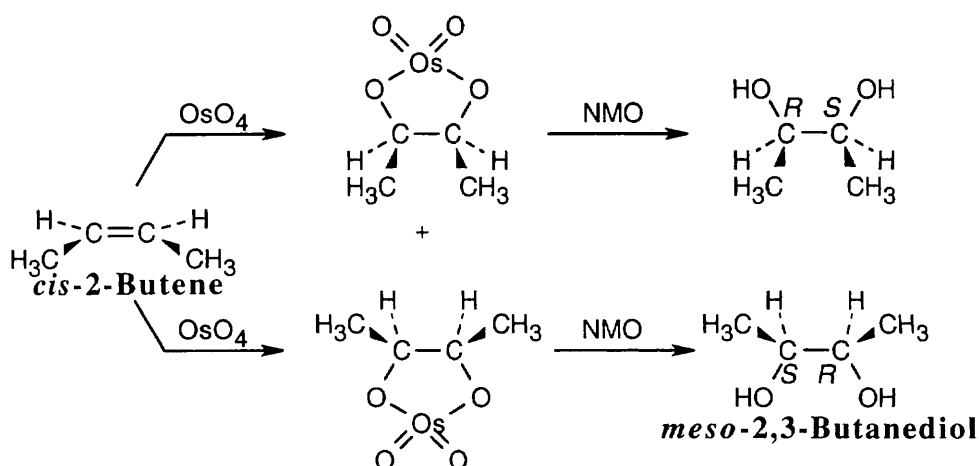
(d) Ribose has six diastereomers.



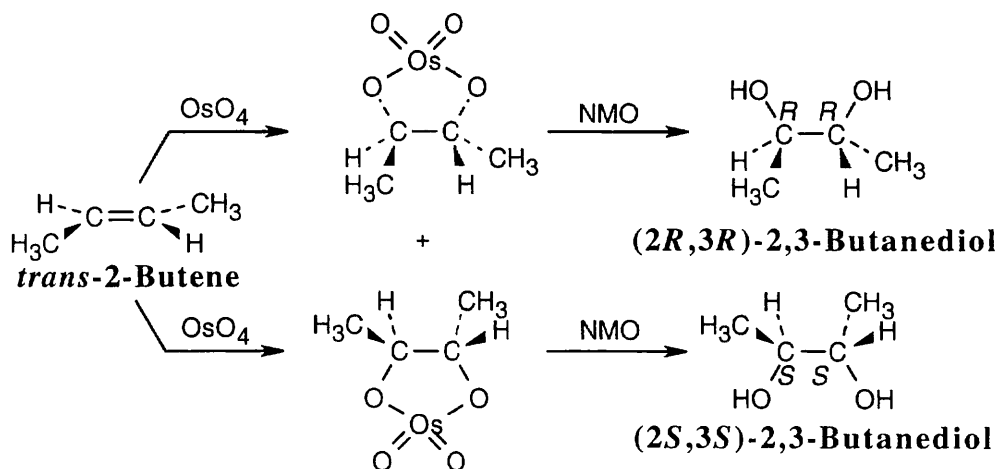
- 9.58** Ribitol is an optically inactive meso compound. Catalytic hydrogenation converts the aldehyde functional group into a hydroxyl group and makes the two halves of ribitol mirror images of each other.



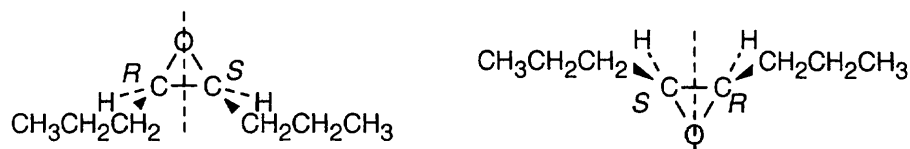
- 9.59** The initial product of hydroxylation of a double bond is a cyclic *osmate*, which is reduced on treatment with NMO to cleave the osmium–oxygen bonds. Since no carbon–oxygen bonds are broken in the cleavage step, the final stereochemistry is the same as that of the initial adduct. The product is *meso*-2,3-butanediol.



- 9.60** The osmates and the diol products of hydroxylation of *trans*-2-butene are shown below. The product is a racemic mixture of the (*R,R*) and (*S,S*) enantiomers.

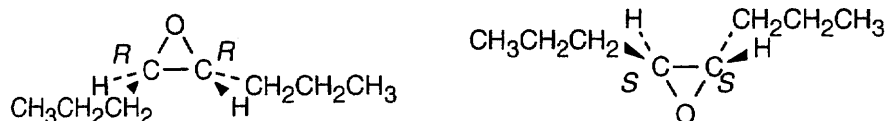


### 9.61



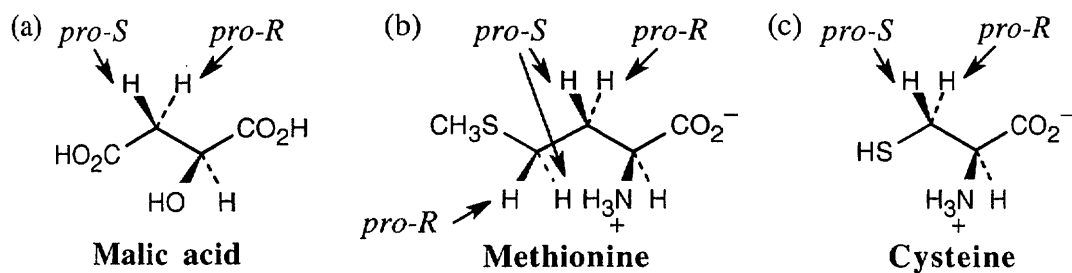
Peroxydicarboxylic acids can attack either the top side or the bottom side of a double bond. The epoxide resulting from top-side attack on *cis*-4-octene has two chirality centers, but because it has a plane of symmetry, it is a meso compound. The two epoxides are identical.

## 9.62

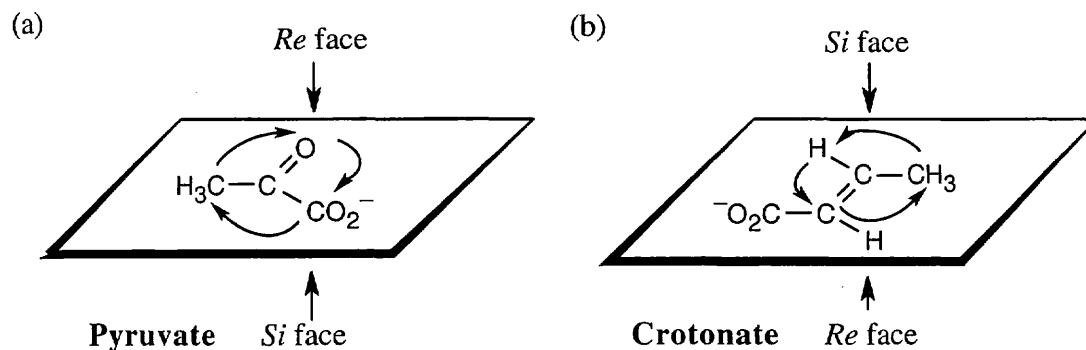


The epoxide formed by top-side attack of a peroxyacid on *trans*-4-octene has two chirality centers of *R* configuration. The epoxide formed by bottom-side attack has (*S,S*) configuration. The two epoxide enantiomers are formed in equal amounts and constitute a racemic mixture.

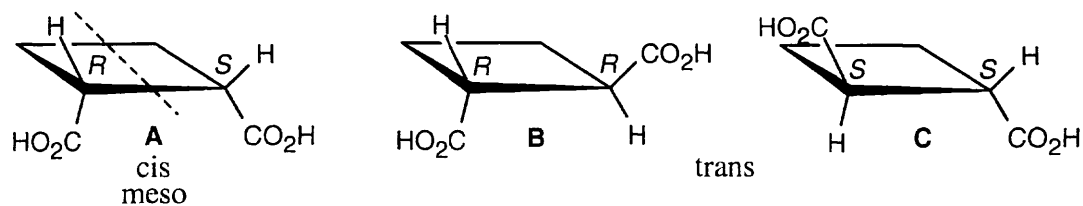
## 9.63



## 9.64

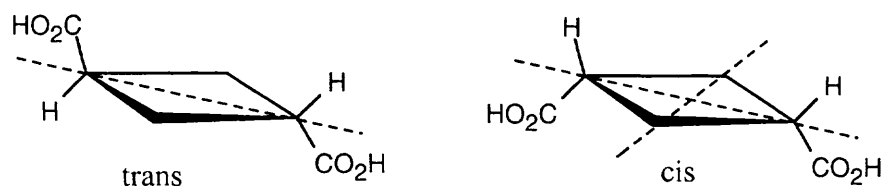


9.65

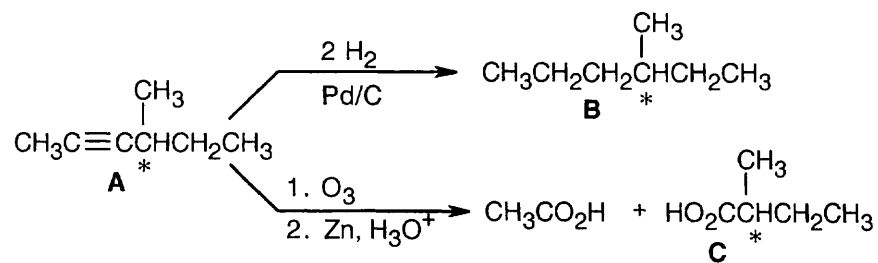


**B** and **C** are enantiomers and are optically active. Compound **A** is their diastereomer and is a *meso* compound, which is not optically active.

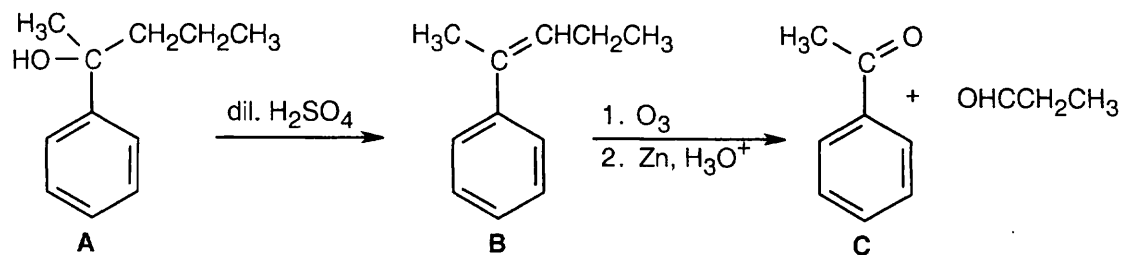
The two isomeric cyclobutane-1,3-dicarboxylic acids are achiral and are optically inactive.



9.66

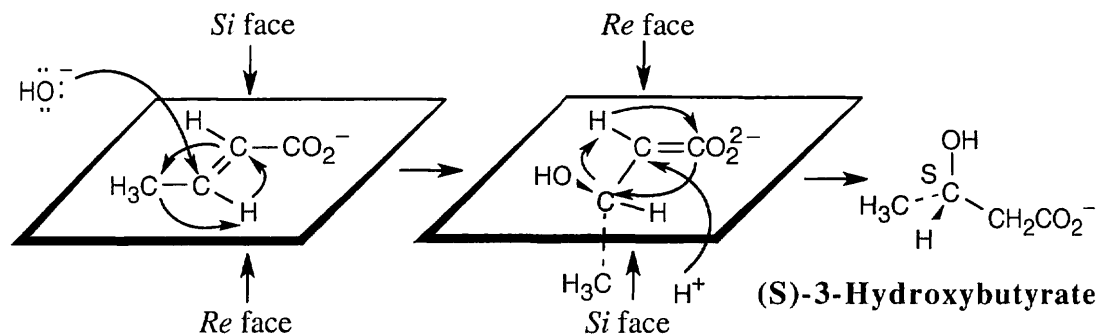


9.67 **A** has four multiple bonds/rings.

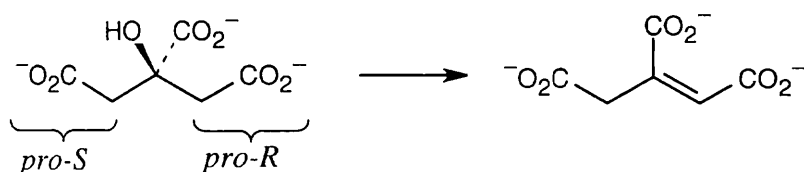


2-Phenyl-3-pentanol is also an acceptable answer.

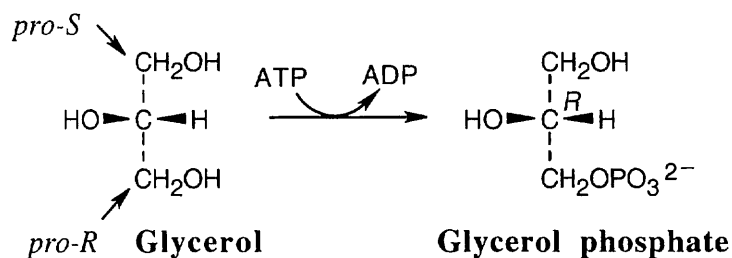
9.68 Remember that *each*  $sp^2$  carbon has a *Re* face and a *Si* face.



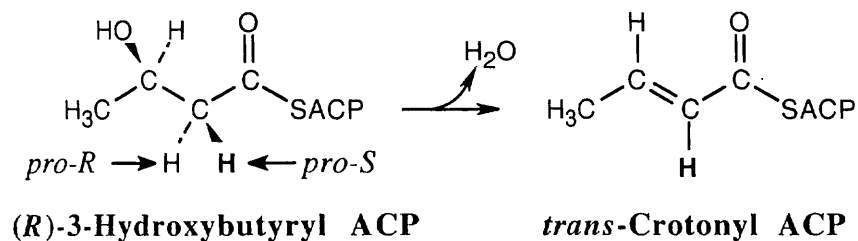
9.69 If you perform the “replacement test” to assign *pro-R/pro-S* prochirality, you will see that the right “arm” of citrate is *pro-R* and the product pictured on the right is formed.



9.70



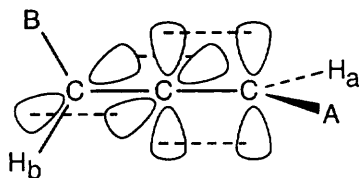
9.71



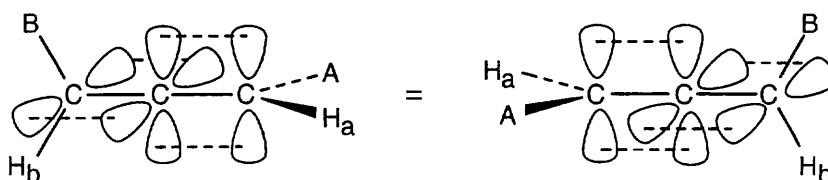
The reaction removes the *pro-R* hydrogen.



- 9.72** Mycomycin contains no chiral carbon atoms, yet is chiral. To see why, make a model of mycomycin. For simplicity, call  $-\text{CH}=\text{CHCH}=\text{CHCH}_2\text{CO}_2\text{H}$  "A" and  $-\text{C}\equiv\text{CC}\equiv\text{CH}$  "B". Remember from Chapter 6 that the carbon atoms of an allene have a linear relationship and that the  $\pi$  bonds formed are perpendicular to each other. Attach substituents at the  $sp^2$  carbons.

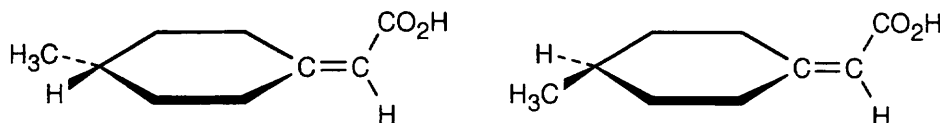


Notice that the substituents A,  $\text{H}_a$ , and all carbon atoms lie in a plane that is perpendicular to the plane that contains B,  $\text{H}_b$ , and all carbon atoms.

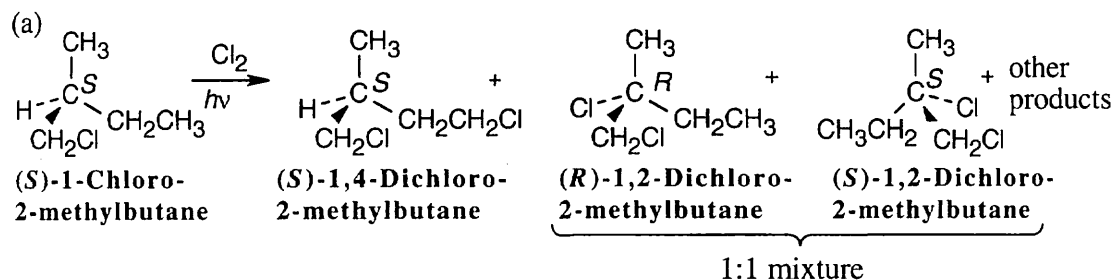


Now, make another model identical to the first, except for an exchange of A and  $\text{H}_a$ . This new allene is not superimposable on the original allene. The two allenes are enantiomers and are chiral because they possess no plane of symmetry.

- 9.73** 4-Methylcyclohexylideneacetic acid is chiral for the same reason that mycomycin (Problem 9.72) is chiral: It possesses no plane of symmetry and is not superimposable on its mirror image. As in the case of allenes, the two groups at one end of the molecule lie in a plane perpendicular to the plane that contains the two groups at the other end.



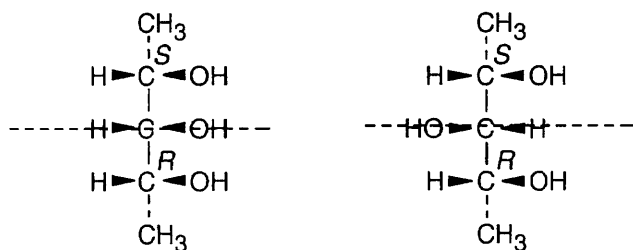
## 9.74



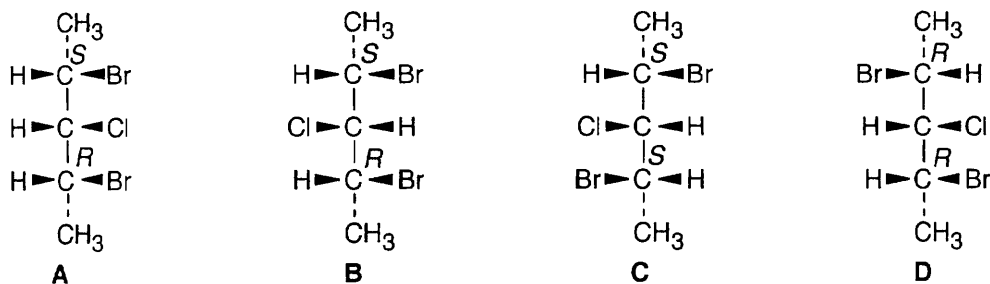
(b) Chlorination at carbon 4 yields an optically active product because the chirality center at C2 is not affected. Chlorination at carbon 2 yields an optically inactive racemic product.

(c) Radical chlorination reactions taking place at a chirality center occur with racemization; radical chlorination reactions at a site other than the chirality center do not affect the stereochemistry of the chirality center.

9.75 Both of the diastereomers shown below are meso compounds with three chirality centers. Each is a meso compound because it has a symmetry plane, and in each structure the central carbon is bonded to four different groups (a group with *R* configuration, a group with *S* configuration,  $-\text{OH}$ , and  $-\text{H}$ ).

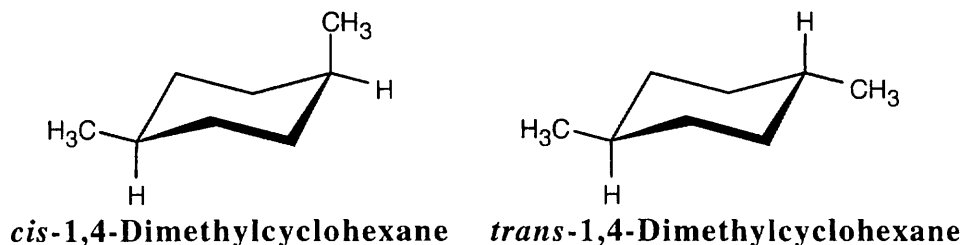


## 9.76



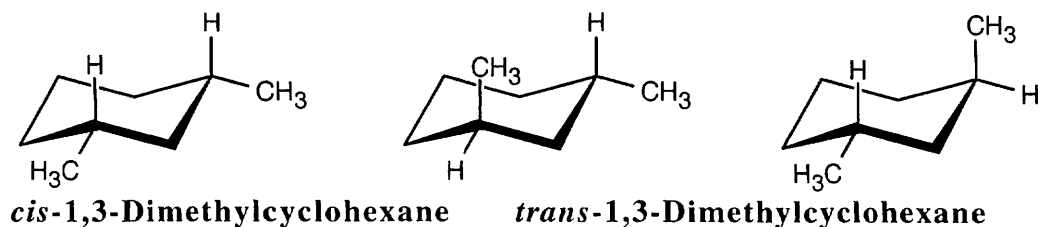
There are four stereoisomers of 2,4-dibromo-3-chloropentane. **C** and **D** are enantiomers and are optically active. **A** and **B** are optically inactive meso compounds and are diastereomers.

9.77



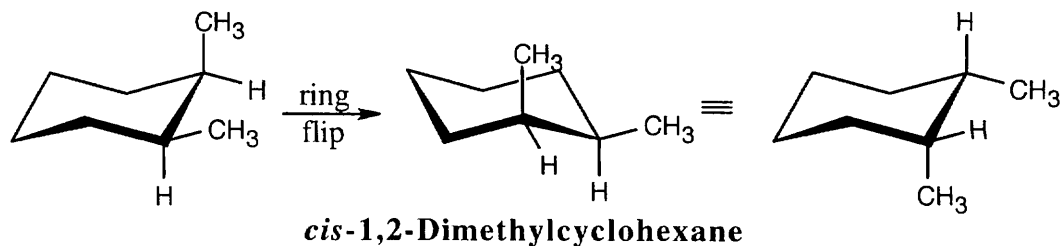
- (a) There is only one stereoisomer of each of the 1,4-dimethylcyclohexanes.  
 (b) Neither 1,4-dimethylcyclohexane is chiral.  
 (c) The two 1,4-dimethylcyclohexanes are diastereomers.

9.78



- (a) There is one stereoisomer of *cis*-1,3-dimethylcyclohexane, and there are two stereoisomers of *trans*-1,3-dimethylcyclohexane.  
 (b) *cis*-1,3-Dimethylcyclohexane is an achiral meso compound. *trans*-1,3-Dimethylcyclohexane exists as a pair of chiral enantiomers.  
 (c) The two *trans* stereoisomers are enantiomers, and are diastereomers of the *cis* stereoisomer.

9.79



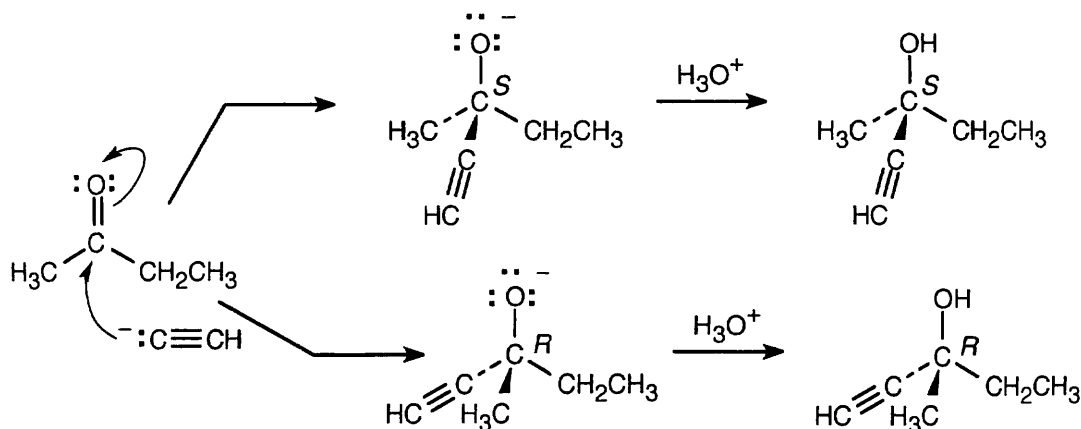
The two *cis*-1,2-dimethylcyclohexane enantiomers rapidly interconvert by a ring flip, leading to an optically inactive 1:1 mixture.

9.80



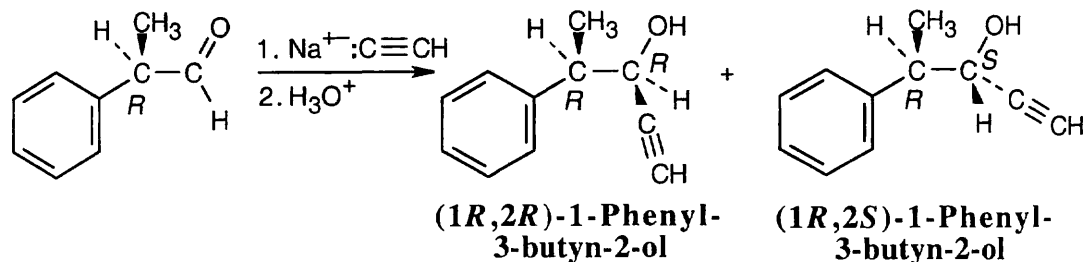
The product is (*R*)-2-butanethiol.

- 9.81 The reaction proceeds by addition of acetylide anion to the carbonyl group and occurs with equal probability from either side of the planar ketone carbon.



- (a) The product is an optically inactive racemic mixture.  
 (b) The two enantiomers are formed in a 50:50 ratio.

## 9.82



- (a) Reaction of sodium acetylide with a chiral aldehyde yields chiral products; the product mixture is optically active.  
 (b) The two products are a mixture of the (1R,2R) and (1R,2S) diastereomers of 1-phenyl-3-butyn-2-ol. The product ratio can't be predicted, but it is not 50:50.